WEST VIRGINIA
SECRETARY OF STATE
KEN HECHLER
ADMINISTRATIVE LAW DIVISION
Form #3

Do Not Mark In this Box

FILED
1990 AUG 10 [illegible] 20

NOTICE OF AGENCY APPROVAL OF A PROPOSED RULE AND FILING WITH THE LEGISLATIVE RULE-MAKING REVIEW COMMITTEE

AGENCY: WV Air Pollution Control Commission TITLE NUMBER: 45CSR24

CITE AUTHORITY Chapter 16, Article 20, Section 5

AMENDMENT TO AN EXISTING RULE: YES X NO___

IF YES, SERIES NUMBER OF RULE BEING AMENDED: 24

TITLE OF RULE BEING AMENDED: "Regulations To Prevent and Control Air Pollution From The Emission Of Volatile Organic Compounds From Petroleum Refinery Sources"

IF NO, SERIES NUMBER OF NEW RULE BEING PROPOSED: ______

TITLE OF RULE BEING PROPOSED: ______

THE ABOVE PROPOSED LEGISLATIVE RULE HAVING GONE TO A PUBLIC HEARING OR A PUBLIC COMMENT PERIOD IS HEREBY APPROVED BY THE PROMULGATING AGENCY FOR FILING WITH THE SECRETARY OF STATE AND THE LEGISLATIVE RULE MAKING REVIEW COMMITTEE FOR THEIR REVIEW.

G. DALE FARLEY, DIRECTOR

APPENDIX B

FISCAL NOTE FOR PROPOSED RULES

Rule Title: Chapter 16-20, Series 24 - "To Prevent and Control Air Pollution From The Emission Of Volatile Organic Compounds From Petroleum Refinery Sources"

Type of Rule: X Legislative ____ Interpretive ____ Procedural

Agency WVAPCC Address 1558 Washington St., E.
Charleston, WV 25311

1. Effect of Proposed Rule	ANNUAL		FISCAL YEAR		
	Increase	Decrease	Current	Next	Thereafter
Estimated Total Cost	$ -0-	$ -0-	$ -0-	$ -0-	$ -0-
Personal Services					
Current Expense					
Repairs and Alterations					
Equipment					
Other					

2. Explanation of above estimates:

The proposed amendments will have no effect on the budget due to the absence of affected facilities.

3. Objectives of these rules:

The purpose of the amendments to Regulation 24 is to address USEPA's identified deficiencies in order to provide national consistency in existing volatile organic compound regulations applicable in State Implementation Plan call areas.

4. Explanation of Overall Economic Impact of Proposed Rule.

A. Economic Impact on State Government.

There should be no economic impact on State Government.

B. Economic Impact on Political Subdivisions; Specific Industries; Specific groups of citizens.

There should be no economic impact on political subdivisions or industry. There should be no economic impact on specific groups of citizens.

C. Economic Impact on Citizens/Public at Large.

Date: August 10, 1990

Signature of Agency Head or Authorized Representative

G. DALE FARLEY, DIRECTOR

DATE:

TO: LEGISLATIVE RULE-MAKING REVIEW COMMITTEE

FROM: G. DALE FARLEY, DIRECTOR, WVAPCC

Regulation 24 - "Regulations To Prevent and Control Air Pollution
LEGISLATIVE RULE TITLE: From The Emission Of Volatile Organic Compounds From Petroleum Refinery Sources"

1. Authorizing statute(s) citation

Chapter 16, Article 20, Section 5

2. a. Date filed in State Register with Notice of Hearing:

April 6, 1990

b. What other notice, including advertising, did you give of the hearing?

Notice of hearing was provided in each of four (4) designated air quality control regions in the state. (See attached list with dates of publication).

c. Date of hearing (s): June 5, 1990

d. Attach list of persons who appeared at hearing, comments received, amendments, reasons for amendments.

Attached X No comments received ________

e. Date you filed in State Register the agency approved proposed Legislative Rule following public hearing: (be exact)

August 10, 1990

f. Name and phone number of agency person to contact for additional information:

G. Dale Farley, Director, WVAPCC
1558 Washington Street, E., Charleston, WV 25311
(304) 348-2275

3. If the statute under which you promulgated the submitted rules requires certain findings and determinations to be made as a condition precedent to their promulgation:

a. Give the date upon which you filed in the State Register a notice of the time and place of a hearing for the taking of evidence and a general description of the issues to be decided.

N/A

b. Date of hearing: N/A

c. On what date did you file in the State Register the findings and determinations required together with the reasons therefor?

N/A

d. Attach findings and determinations and reasons:

Attached N/A

August 10, 1990

ERRATA

CHANGES TO REGULATION 24
(45CSR24)

"Regulations to Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds from Petroleum Refinery Sources"

Page 4, Section 3.26.:	Changed definition of "Vapor Control System"
Page 5, Section 3.27.:	Added compounds exempted in "VOC" definition: HCFC-123, HFC-134a, HCFC-141b, HCFC-142b, and others listed by U.S. EPA
Page 6, Section 4.2.a.:	Changed "covers or seals" to "covers and seals"
Page 6, Section 4.3.b.:	Changed "unless" to "until"
Page 10, Section 8:	Changed entire section
Page 11, Section 10:	Added new section "Enforceability", and deleted proposed section "Inconsistency Between Regulations"

Renumbered sections as required.

Regulation was amended as a result of comments from industry and U.S. EPA.

[PROPOSED]
45CSR24

SUMMARY

45CSR24 was promulgated by the commission on May 8, 1979 and became effective on October 27, 1979. The regulation provides a mechanism to control emissions of volatile organic compounds from petroleum refinery sources. The regulation is being revised to address EPA's identified deficiencies and the requirement to provide a greater degree of equity and national consistency among all states and localities that received post-1987 ozone SIP calls. The areas affected were expanded to include additional counties that were identified as nonattainment of the ozone standards after 1979.

[PROPOSED]
45CSR24

TITLE 45
LEGISLATIVE RULES
WEST VIRGINIA AIR POLLUTION CONTROL COMMISSION

SERIES 24
REGULATIONS TO PREVENT AND CONTROL AIR POLLUTION FROM THE EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM PETROLEUM REFINERY SOURCES

Index.

AFFIDAVIT OF PUBLICATION

STATE OF WEST VIRGINIA,

KANAWHA COUNTY, TO-WIT:

I, Welha Caldwell OF

THE CHARLESTON GAZETTE, A DAILY DEMOCRATIC NEWSPAPER, PUBLISHED IN THE CITY OF CHARLESTON, KANAWHA COUNTY, WEST VIRGINIA, DO SOLEMNLY SWEAR THAT THE ANNEXED NOTICE OF: PUBLIC HEARINGS

WAS DULY PUBLISHED IN SAID PAPER(S) ON THE DATES LISTED BELOW, AND WAS POSTED AT THE FRONT DOOR OF THE COURT HOUSE OF SAID KANAWHA COUNTY, WEST VIRGINIA, ON THE

2ND DAY OF MAY , 1990 .

DATES PUBLISHED:

05/01/90 GAZETTE 05/08/90 GAZETTE

SUBSCRIBED AND SWORN TO BEFORE ME THIS

11TH DAY OF MAY , 1990 .

Frances A. Hartman

NOTARY PUBLIC OF KANAWHA COUNTY, WEST VIRGINIA

MY COMMISSION EXPIRES

PRINTERS FEE $ 36.16

OFFICIAL SEAL
NOTARY PUBLIC
STATE OF WEST VIRGINIA
FRANCES A. HARTMAN
1429 Longridge Road
Charleston, West Virginia 25314
My Commission Expires Dec. 19, 1999

NOTICE OF PUBLIC HEARING

On Tuesday, June 5, 1990 beginning at 9:15 a.m. the West Virginia Air Pollution Control Commission will hold public hearings on proposed amendments to the following Regulations:

Regulation 21—"To Prevent and Control Air Pollution From the Storage of Petroleum Liquids in Fixed Roof Tanks"

Regulation 23—"To Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds From Bulk Gasoline Terminals"

Regulation 24—"To Prevent and Control Air Pollution From Emission of Volatile Organic Compounds From Petroleum Refinery Sources"

.These hearings will be held in the Commission's conference room located at 1558 Washington Street, East, Charleston, Kanawha County, West Virginia.

These hearings are open to the public and written and oral testimony by all interested parties will be heard and made part of the record.

Copies of the proposed Regulations are available for public review in the office of the West Virginia Air Pollution Control Commission, 1558 Washington Street, East, Charleston, West Virginia.

All comments and inquiries relative to these proposed amendments should be directed to:

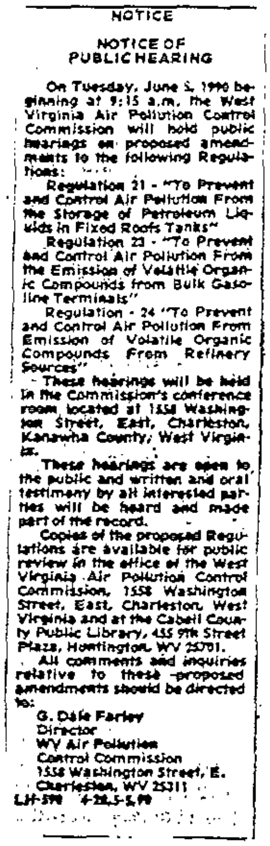
G. Dale Farley
Director
WV Air Pollution
Control Commission
1558 Wash. St., E.
Charleston, WV 25311

(810641)

COPY

AFFIDAVIT OF PUBLICATION

STATE OF WEST VIRGINIA, COUNTY OF CABELL, TO-WIT:


NOTICE

NOTICE OF PUBLIC HEARING

On Tuesday, June 5, 1990 beginning at 9:15 a.m. the West Virginia Air Pollution Control Commission will hold public hearings on proposed amendments to the following Regulations:

Regulation 21 - "To Prevent and Control Air Pollution From the Storage of Petroleum Liquids in Fixed Roofs Tanks"

Regulation 23 - "To Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds from Bulk Gasoline Terminals"

Regulation - 24 "To Prevent and Control Air Pollution From Emission of Volatile Organic Compounds From Refinery Sources"

These hearings will be held in the Commission's conference room located at 1558 Washington Street, East, Charleston, Kanawha County, West Virginia.

These hearings are open to the public and written and oral testimony by all interested parties will be heard and made part of the record.

Copies of the proposed Regulations are available for public review in the office of the West Virginia Air Pollution Control Commission, 1558 Washington Street, East, Charleston, West Virginia and at the Cabell County Public Library, 455 9th Street Plaza, Huntington, WV 25701.

All comments and inquiries relative to these proposed amendments should be directed to:

G. Dale Farley
Director
WV Air Pollution
Control Commission
1558 Washington Street, E.
Charleston, WV 25311

LH-590 4-28,5-5,90

I, Dianna Webb being first duly sworn, depose and say that I am Legal Clerk for Huntington Publishing Company, a corporation, who publishes at Huntington, Cabell County, West Virginia, the newspaper: The Herald-Dispatch, a independent newspaper, in the morning seven days each week, Monday through Sunday including New Year's Day, Memorial Day, the Fourth of July, Labor Day, Thanksgiving and Christmas; that I have been duly authorized by the Board of Directors of such corporation to execute this affidavit of publication for and on behalf of such corporation and the newspaper mentioned herein; that the legal advertisement attached in the left margin of this affidavit and made a part hereof and bearing number LH-590, was duly published in

The Herald-Dispatch

one time, once a week for 2 successive weeks, commencing with its issue of the 28th day of April, 19 90, and ending with the issue of the 5th day of May, 1990, and was posted at the East Door of Cabell Co. Courthouse on the 28th day of April, 19 90; that said legal advertisement was published on the following dates: April 28, 1990 May 5, 1990 ; that the cost of publishing said annexed advertisement as aforesaid was $38.69; that such newspaper in which such legal advertisement was published has been and is now published regularly, at least as frequently as once a week for at least fifty weeks during the calendar year as prescribed by its mailing permit, and has been so published in the municipality of Huntington, Cabell County, West Virginia, for at least one year immediately preceding the date on which the legal advertisement set forth herein was delivered to such newspaper for publication; that such newspaper is a newspaper of "general circulation" as defined in Article 3, Chapter 59, of the West Virginia Code, within the publication area or areas of the municipality of Huntington, Cabell and Wayne Counties, West Virginia, and ; that such newspaper is circulated to the general public at a definite price or consideration; that such newspaper on each date published consists of not less than four pages without a cover; and that it is a newspaper to which the general public resorts for passing events of a political, religious, commercial and social nature, and for current happenings, announcements, miscellaneous reading matters, advertisements and other notices.

Dianna Webb

Taken, subscribed and sworn to before me in my said county this 5th day of May, 19 90

My commission expires 23 March 1992

Ben H Howard

Notary Public
Cabell County,
West Virginia

10M Form A - 135 (876H)

LEGAL NOTICE

NOTICE OF PUBLIC HEARING

On Tuesday, June 5, 1990 beginning at 9:15 a.m. the West Virginia Air Pollution Control Commission will hold public hearings on proposed amendments to the following Regulations:

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Regulation 24 - "To Prevent and Control Air Pollution From Emmission of Volatile Organic Compounds From'Petroleum Refinery Sources"

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These hearings are open to the public and written and oral testimony by all interested parties will be heard and made part of the record.

Copies of the proposed Regulations are available for public review in the office of the West Virginia Air Pollution Control Commission, 1558 Washington Street, East, Charleston, West Virginia and at the Parkersburg/Wood County Public Library, 3100 Emerson Avenue, Parkersburg, WV 26104.

All comments and inquiries relative to these proposed amendments should be directed to:

G. Dale Farley
Director
WV Air Pollution Control Commission
1558 Washington Street, E.
Charleston, WV 25311

May 2,9 N

MAR C IA MOORE

being first duly sworn, says that the notice of public hearing--- JUNE 5th

hereto attached was printed in the Parkersburg News a daily newspaper published in the City of Parkersburg, Wood County, West Virginia, and posted at the front door of the Court House for two successive weeks, the first publication ~~and posting~~ thereon being on the 2nd day of MAY 1990, and subsequent publication on the 9th day of MAY 1990, the ...... day of ...... 19......, the ...... day of ...... 19......, the ...... day of ...... 19......, and the ...... day of ...... 19......

Printer's Fee $ 25.48

233 words @ 10.9375 Marcia Moore

Subscribed and sworn to before me this 9th day of MAY 1990

Notary Public for Wood County, West Virginia

My commission expires 2-20-91

Parkersburg Printing Co. - 5/71

THE WEST VIRGINIA DAILY NEWS
P.O. BOX 471
LEWISBURG WV 24901
PHONE: (304) 645-1206

NOTICE OF PUBLIC HEARING

On Tuesday, June 5, 1990 beginning at 9:15 a.m. the West Virginia Air Pollution Control Commission will hold public hearings on proposed amendments to the following Regulations:

Regulation 21 - "To Prevent and Control Air Pollution From the Storage of Petroleum liquids in Fixed Roof Tanks"

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These hearings will be held in the Commission's conference room located at 1558 Washington Street, East, Charleston, Kanawha County, West Virginia.

These hearings are open to the public and written and oral testimony by all interested parties will be heard and made part of the record.

Copies of the proposed Regulations are available for public review in the office of the West Virginia Air Pollution Control Commission, 1558 Washington Street, East, Charleston, West Virginia and at the Greenbrier County Library and Museum, 301 Courtney Drive, Lewisburg, WV 24901.

All comments and inquiries relative to these proposed amendments should be directed to:

G. Dale Farley
Director
WV Air Pollution Control Commission
1558 Washington Street E.
Charleston, WV 25311
(Apr.30, May 7c)

AFFIDAVIT OF PUBLICATION

STATE OF WEST VIRGINIA
COUNTY OF
GREENBRIER, TO WIT:

I, Louise Bowman, one of the editors of the West Virginia Daily News, a daily newspaper of general circulation published at Lewisburg, West Virginia, in the County of Greenbrier, State of West Virginia, do certify that publication of the advertisement or advertisements attached hereto was made in two issues of said newspaper, dated Apr. 30th, May 7th.

Given under my hand this, the 14th day of May 1990.

Louise Bowman
Editor or Publisher

Subscribed and sworn to before me this 14th day of May. 1990. My Commission expires Sept 11, 1990.

Judy Dowdy, Notary Public.

Publication Fee: $ 40.43

MAILING LIST FOR HEARING

Mr. Charles White
Chairman
Sub Area Planning Committee
PO Box 113
Institute, WV 25112

Dr. Paul Hill
President
National Institute for
Chemical Studies
University of Charleston
2300 MacCorkle Avenue, SE
Charleston, WV 25304

The Honorable William Croye
Mayor, City of Belle
National Institute for
Chemical Studies
Upper Kanawha Valley Committee
110 East DuPont Avenue
Belle, WV 25015

Mr. Ray de Bolt
Fire Chief
Charleston Fire Department
808 Virginia Street, West
Charleston, WV 25302

Ms. Suzzanne Tenkhoff
National Institute for
Chemical Studies
Nitro/St. Albans Committee
31 Bailes Drive
Nitro, WV 25143

Ms. Lillian Erskin
52 Bailes Drive
Nitro, WV 25143

Ms. Mildred Holt
PO Box 367
Institute, WV 25112

Ms. Joline Brady
103 Timberlake Circle
Scott Depot, WV 25560

Dr. Ernest Capstack, Jr.
91 Smithfield Street
Buckhannon, WV 26201

Mr. Robert Hieronymus
1338 Morningside Drive
Charleston, WV 25314

Mr. Bob Parsons
Jackson & Kelly
1600 Laidley Tower
Charleston, WV 25301

Mr. Eric Niiler
Charleston Gazette
1001 Virginia Street, East
Charleston, WV 25301

Mr. Norm Steenstra
Environmental Coordinator
West Virginia Citizen Action Group
1324 Virginia Street, East
Charleston, WV 25301

Ms. Becky Fleming
Charleston Daily Mail
1001 Virginia Street, East
Charleston, WV 25301

Mr. Rob Hill
ERM Midwest
5088 West Washington Street
Charleston, WV 25313

Mr. Brain Broderick
BNA PLUS
Bureau of National Affairs
1231 25th Street, NW
Washington, DC 20037

COMMISSION MEETING

REGISTER
JUNE 5, 1990

Date	Name	Address	Company Affiliation
06-05-90	Don Boyer	FAIRMONT	WAP
"	Shirley Hanson, Reporter	So. Chas, WV	Hudson Reporting
"	Ed Fosse	Chas. W.V.	Quality Works
"	Kim Fosse	Chas WV	Quality Works
"	K. B. Poland	Charleston, WV	Robinson + McElwee
"	John Cummings	Charleston, WVa	Robinson + McElwee
"	Patrick McGalley	Charleston, WV	West Virginia Manufacturers Assn
"	[illegible]	Mason	Raven-Hocking Coal
"	Al Sweeney	Gassaway, WV.	Go-Mart Inc.
"	David Wilkison	1001 Va. St. E	Associated Press

Please Print

COMMISSION MEETING

REGISTER
JUNE 5, 1990

Date	Name	Address	Company Affiliation
06-05-90	R.L. FOSTER	So. Chas	UCC
"	Doug Fry	Spencer	[illegible] Forest, Inc.
"	E.W. BRAMMER F.A. DECKER P.M. HUFFMAN	Charleston WV	Columbia Gas.
"	Kuhner	Metro News	
"	SAM HEATER	Gassaway WV	Go-MART INC
"	Bruce Morgan	1134 Market street, Wheeling	Wheeling - Pitt Steel
"	Bob Parsons	JACKSON & KELLY	CHARLESTON, W.Va.
"	Mike [illegible]	Technimedia	STeub, Ohio
"	Dick Manchetti	Squibb Manchetti &Co	Wheeling WV.
"			

Please Print

<u>COMMISSION MEETING</u>

REGISTER
JUNE 5, 1990

Date	Name	Address	Company Affiliation
06-05-90	Daniel Daniels	Charleston	WQBE News
"			
"			
"			
"			
"			
"			
"			
"			
"			

West Virginia Department of
Commerce, Labor & Environmental Resources
Air Pollution Control Commission

1558 Washington Street, East
Charleston, West Virginia 25311

Telephone: (304)348-4022
or (304) 348-3286

MEMORANDUM

To: File

From: G. Dale Farley
Secretary

Date: August 10, 1990

Subject: Regulations 21, 23 and 24

Regulations 21, 23 and 24 were brought before the Commission for final approval on August 10, 1990. The Commission voted unanimously to adopt the proposed regulations with amendments [to the proposed regulations] as shown on the Errata sheet. In addition, the Commission took comments from an interested party who had previously submitted comments, and voted to maintain the definitions of "Approved", "Commission", and "Director", notwithstanding the comments from EPA.

Further, a discussion was held regarding EPA's approval of delayed compliance programs and Orders. It was determined that no change to the proposed regulation was necessary to effectuate the Commission's intent.

WEST VIRGINIA
MANUFACTURERS ASSOCIATION

June 5, 1990

HAND DELIVERED

West Virginia Air Pollution
Control Commission
1558 Washington Street East
Charleston, West Virginia 25311

ATTENTION: Mr. G. Dale Farley, Director

Re: Comments on Rules Regarding Emissions of Volatile Organic Compounds from Storage of Petroleum in Fixed-Roof Tanks, Bulk Gasoline Terminals, and Petroleum Refinery Sources, Proposed April 10, 1990

Dear Director Farley:

Enclosed, please find for filing the comments of the West Virginia Manufacturers Association on the rules governing emissions of volatile organic compounds from storage of petroleum in fixed-roof tanks, bulk gasoline terminals, and petroleum refinery sources, proposed as amendments to Series 21, 23 and 24 on April 10, 1990 by the Air Pollution Control Commission. Thank you for your consideration of these comments, and please contact me if you have any questions.

Very truly yours,

P. M. Gallagher

Patrick M. Gallagher
President

JCC/bjf

Enclosure

COMMENTS OF THE WEST VIRGINIA MANUFACTURERS ASSOCIATION ON PROPOSED AMENDMENTS TO VOC REGULATIONS
45 CSR SERIES 21, 23, AND 24

A. INTRODUCTION

On April 13, 1990 public notice appeared in the State Register announcing the filing on April 10, 1990 of proposed amendments of the West Virginia Air Pollution Control Commission ("Commission") to the regulations regarding emissions of volatile organic compounds ("VOC") from fixed roof tanks (45 CSR 21), bulk gasoline terminals (45 CSR 23), and petroleum refinery sources (45 CSR 24) (collectively referred to as the "proposed rules" or "proposed VOC rules"). Pursuant to this notice, the West Virginia Manufacturers Association ("WVMA") files these comments concerning the proposed rules. The WVMA represents a broad cross-section of West Virginia's industrial sector. These comments on the proposed VOC rules are intended in the tradition of the active and supportive role that the WVMA has taken regarding the attainment of ambient air quality standards in West Virginia.

B. GENERAL COMMENTS

1. THE COMMISSION MUST ELIMINATE AMBIGUITIES IN THE DEFINITION OF THE "TERM VOLATILE ORGANIC COMPOUND" UNDER SECTIONS 45-21-3.25, 45-23-3.20, AND 45-24-3.27

The proposed rules would amend the definition of the term "Volatile Organic Compound" in each of the affected regulations to include any organic compound which participates in atmospheric photochemical reactions, excluding several compounds determined to have negligible effect on photochemical activity. See Sections 45-

21-3.25; 45-23-3.20; 45-24-3.27. This proposed amended definition creates a degree of uncertainty which was not present under the former definition of the term "volatile organic compound," which included any compound of carbon having a vapor pressure greater than one-tenth millimeters of mercury at standard conditions excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate.

Furthermore, it is not clear from the proposed rule what effect the Commission intended for the last sentence of the proposed definition, which states, "Where such a method <u>also inadvertently measures</u> compounds with negligible photochemical reactivity, an owner or operator may exclude these negligibly reactive compounds when determining compliance with an emissions standard." (emphasis supplied). This language implies that, in addition to those compounds listed, other compounds may also be excluded from the definition of "volatile organic compound" if shown by an approved test method to exhibit negligible photochemical reactivity. However, the language chosen by the Commission to express this highly practical exclusion is susceptible to misinterpretation as applying only to compounds which are "inadvertently measured."

The WVMA encourages the Commission in defining the term "volatile organic compounds," to retain the requirement that an organic compound must exhibit a vapor pressure of greater the one-tenth millimeters of mercury at standard conditions, excluding carbon monoxide, carbon dioxide, carbon acid, metallic carbides or carbonates, and ammonium carbonate. This requirement would provide an objective standard upon which manufactures could readily determine whether a given compound's participation in atmospheric photochemical reactions is "negligible." In addition, the last sentence of the definition of the term "volatile organic compound" should be changed to state that "other organic compounds may be excluded when determining compliance with an emission standard if shown to exhibit negligible photochemical reactivity as measured by an approved test method." In this way, the definition would clearly reflect the Commission's intent that, in addition to the organic compounds specifically listed as negligible, other compounds might also be excluded from regulation as VOCs if shown to also exhibit negligible participation in atmospheric photochemical reactions.

2. THE TERM "VAPOR CONTROL SYSTEM" SHOULD BE DEFINED CONSISTENTLY IN SECTIONS 45-21-3.26, 45-23-3.19 AND 45-24-3.26, AND SHOULD BE MODIFIED TO REFLECT THE TECHNOLOGICAL IMPOSSIBILITY OF PREVENTING 100% OF VOC EMISSIONS.

The term "vapor control system" is defined in the proposed VOC rules for bulk gasoline terminals (Section 45-23-3.19) and petroleum refinery sources (Section 45-24-3.26) as "a system that prevents release to the atmosphere of volatile organic compounds emitted during the operation of any transfer, storage, or process equipment." The proposed VOC rule for fixed roof storage tanks (Section 45-21-3.26), however, defines the same term as "a device or method that collects volatile organic compound emissions from the storage vessel (fixed roof tank) and prevents their release to the atmosphere. This includes, but is not limited to, vapor/liquid absorption, and thermal oxidation." In the interest of regulatory consistency, and because the Commission has indicated no reason why the meaning of the term "vapor control system" should vary as applied among fixed roof storage tank, bulk gasoline terminal and petroleum refinery sources, the WVMA requests that the following definition of the term "vapor control system" be adopted by the Commission for each of the above-mentioned regulatory provisions:

> "Vapor Control System" means a device or method that collects volatile organic compound emissions from any transfer, storage or process equipment, and limits their release to the atmosphere. This includes, but is not limited to, vapor/liquid absorption, vapor compression, vapor cooling, vapor/solid absorption, and thermal oxidation.

This definition is based upon the more objective, unambiguous language of the "vapor control system" definition found in the proposed VOC rule regarding fixed-roof storage tanks (Section 45-21-3.26). However, the specific reference to "fixed-roof storage tanks" in Section 45-21-3.26 would be deleted in favor of the language above, in order that the definition would be equally applicable to fixed-roof storage tanks, bulk gasoline terminals, or petroleum refinery sources.

Furthermore, in describing the technological capabilities of a "vapor control system," the definition advanced by the WVMA would substitute the phrase "<u>limits</u> their release to the atmosphere" for "prevents their release to the atmosphere." This change is requested in recognition of the fact that even the most advanced forms of vapor control technologies may be incapable of removing 100% of VOC emissions. Use of the word "limits" or "limitation" is thus consistent with the Commission's intent that "vapor control systems" be utilized to control or limit the emission of VOC's to the extent which is technologically possible. See Sections 45-21-1.1, 45-23-1.1 and 45-24.1. It is also consistent with the definition of "vapor recovery system" found in the U.S. EPA's regulations at 40 CFR §501 in connection with the regulation of bulk gasoline terminals ("any equipment used for containing total organic compounds vapors displaced during the loading of gasoline tank trucks") (emphasis supplied). Conversely, use of the word "prevents" or "prevention" would suggest that vapor control systems would be expected to completely eliminate emissions of VOC. Such a standard would be impossible to meet.

3. THE COMMISSION SHOULD NOT DELETE PROVISIONS PRESENTLY CONTAINED IN SECTIONS 45-21-4.4, 45-23-4.4 AND 45-24-4.4 WHICH PROVIDE FOR PETITIONS BY OWNERS AND OPERATORS OF COVERED SOURCES FOR THE GRANTING OF EXEMPTIONS ON A CASE-BY-CASE BASIS.

Presently, the regulations covering VOC emissions from fixed-roof storage tanks (Section 45-21-4.4) bulk gasoline terminals (Section 45-23-4.4), and petroleum refinery sources (Section 45-24-4.4) specifically recognize the need for case-by-case consideration of whether individual sources should be exempt from all or part of the regulatory provisions on VOC emissions applicable to such source. These regulations allow owners and operators of individual sources to petition the Commission for exemption from applicable VOC emission standards. The Commission is then empowered to grant such petitions upon a sufficient showing that applicable VOC emission standards are technologically infeasible as applied to the specific fixed-roof tank, bulk gasoline terminal, or petroleum refinery sources. These petitions are required to include detailed analysis of proposed alternative VOC emission controls, plans for reduction of VOC emissions from related sources not covered under the VOC rules, and schedules for implementation of these proposed controls. The present VOC rules also allow the Commission to revise or terminate exemptions granted pursuant to such petitions at any time a given exemption is deemed unwarranted.

The WVMA considers the present regulatory provisions for exemption from the VOC emissions standards as both consistent with the legislative purpose of W. Va. Code §16-20-5, and essential to a flexible and balanced regulatory approach in West Virginia. The fact that such petitions are considered by the Commission on a case-by-case basis, along with the other procedural requirements of the present provisions provide sufficient protection of ambient air quality to comply with federal requirements of the state implementation plan ("SIP"). The WVMA urges the Commission to leave these provisions for case-by-case exemption from VOC standards in place until all other alternatives for reduction of VOC emissions have been exhausted.

4. THE PROPOSED PROVISIONS OF SECTIONS 45-21-4.4, 45-23-4.4, AND 45-24-4.4 REQUIRING THAT, ONCE REGULATED, A SOURCE REMAINS SUBJECT TO VOC RULES DESPITE LATER FALLING WITHIN AN EXEMPTION LEVEL, SHOULD BE ELIMINATED.

The WVMA strongly urges the Commission to delete the "once covered, always covered" provision of the proposed VOC rules, where it is stated:

> If a source becomes subject to any requirement in this regulation because it exceeds an exemption level, the source shall continue to be subject to all applicable requirements, regardless of whether the source falls below the exemption level in the future.

(Sections 45-21-4.4, 45-23-4.4, and 45-24-4.4).

The WVMA objects to this proposed provision on the basis that it overreaches the statutory authority of the Commission by regulating various transfer, storage, and process equipment without regard to whether such sources pose any significant threat to ambient air concentrations. In addition, implementation of this rule would cause the Commission to divert its limited resources to the regulation of a number of sources which pose little or no threat to ambient concentrations.

5. STORAGE TANKS WITH DOUBLE SEAL INTERNAL FLOATING ROOFS SHOULD NOT BE SUBJECTED TO THE SAME MAINTENANCE, INSPECTION, REPORTING AND TESTING REQUIREMENTS AS STORAGE TANKS WITH SINGLE SEAL INTERNAL FLOATING ROOFS.

As is the case under the present regulations regarding storage tanks with internal floating roofs, the proposed rules for Series 21 do not distinguish between single seal and double seal internal floating roofs. Thus, under the proposed rule, the maintenance requirements of Section 45-21-4.2 and 4.3, the inspection requirements of Section 45-21-7.1, the reporting requirements of Section 45-21-7.2, and the testing requirements of Section 45-21-7.3 are presumably the same for double seal internal floatation roof tanks as for single seal internal floatation roof tanks.

The proposed rule thus fails to take account of the significant safety and maintenance benefits associated with double seal internal floatation roof tanks or the difficultly of inspecting the secondary (inside) seal without emptying the tank, thus taking it out of service. This is in stark contrast to U.S. EPA regulations on the maintenance, inspection, reporting, and testing requirements of double seal internal floatation roof tanks, found at 40 CFR §60.113b(a)(3). For example, the Federal regulations require that primary outside double seal tanks put into service or modified after July 23, 1984 be visually inspected every five years, or when emptied, as opposed to the annual inspection required for single seal tanks. See 40 CFR §§60.113b(a)(3)(i); 60.113b(a)(2). Furthermore, the secondary seal of a double-seal tank need only be inspected every 10 years or when emptied, unless the secondary seal is otherwise found to contain holes or leaks. See 40 CFR §60.113(b)(a)(4). Indeed, it should be noted that, unlike the federal regulations, the rules proposed by the Commission for Series 21 fail to differentiate storage tanks on the basis of when a given tank was modified or placed into service.

See 40 CFR §§60.111(a); 60.111(b).

For these reasons, the WVMA urges the Commission to exempt double seal internal floatation tanks from the maintenance, inspection, reporting, and testing requirements of Sections 45-21-4.2 and 45-21-7.1 et. seq. of the proposed rule, or to propose alternative rules more appropriate to such tanks, such as those in similar federal rules.

6. THE DEFINITION OF THE TERM "GASOLINE" UNDER THE PROPOSED RULE FOR BULK GASOLINE TERMINALS SHOULD BE CLARIFIED TO EXCLUDE LIGHTER GRADES OF PETROLEUM PRODUCTS SUCH AS DRY GAS, PROPYLENE, AND BUTANES.

The term "gasoline" is defined in Section 45-23-3.12 of the proposed regulations as "a petroleum distillate having a Reid vapor pressure of 27.6 kPa (four (4) pounds / square inch) or greater which is used as a fuel for internal combustion engines." This definition of "gasoline" could be misconstrued as extending to the storage of lighter grade petroleum products, including dry gas, propane, propylene, and butanes. This result is inconsistent with the U.S. EPA's standards of performance for new stationary sources for bulk gasoline terminals, which apply specifically to "the total of all the loading racks at a bulk gasoline terminal which deliver liquid product into gasoline tank trucks." 40 CFR §60.500(a). This result also ignores the stated scope of Series 23 of the Commission's regulations, which states that "It is the intent of the Commission that all persons engaged in the operating of bulk gasoline terminals and the appurtenant equipment necessary to load tank trucks or trailer compartments control the emission of volatile organic compounds through the application of reasonably available control technology." (Section 45-23-1.1).

For these reasons, and because of the insignificant contribution to total VOC emissions which are posed by the loading of these lighter grades of petroleum products into tank trucks, the WVMA encourages the Commission to amend the proposed definition of the term "gasoline" in Section 45-23-3.12 to make it clear that lighter grades of petroleum products, including dry gas, propane, propylene, and butanes, are excluded from the definition of "gasoline."

7. THE PROPOSED RULE CONCERNING BULK GASOLINE TERMINALS SHOULD BE CLARIFIED TO ALLOW THE DISCHARGE OF GASOLINE INTO SEWERS CONTAINING OIL/WATER SEPARATORS

Section 45-23-4.3 prohibits all discharges of gasoline into sewers. This provision must be clarified by prohibiting the discharge of gasoline into sewers except where the sewer is connected to an oil/water separator or other waste water treatment unit. In this way, the rule would recognize the widely accepted and environmentally sound practice of mitigating the escape of gasoline to the air after accidental spills by washing the spilled gasoline into sewers equipped with treatment units. Indeed, the Commission has recognized the need for discharges into sewers with oil/water separators in the context of petroleum refineries. See Sections 43-24-3.28 and 45-24-4.2.

C. CONCLUSION

The WVMA appreciates the opportunity to comment on these regulations, and trusts that our comments will be given due and deliberate consideration.

Submitted June 5, 1990

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION III
841 Chestnut Building
Philadelphia, Pennsylvania 19107

JUN 4 1990

Mr. G. Dale Farley, Director
West Virginia Air Pollution Control
Commission
1558 Washington Street, East
Charleston, West Virginia 25311

Dear Mr. Farley:

In response to your request for EPA review of the draft VOC regulations being corrected pursuant to the November 1, 1989 SIP call, we have prepared the following comments. Please enter these comments as part of the public hearing record.

FIXED ROOF TANKS

§45-21-1 GENERAL

1.1 For clarity the Scope should also include the applicability level. The affected facilities are fixed roof storage tanks with capacities greater than 150,000 liters containing petroleum liquids with a true vapor pressure greater than 10.5 kPa.

1.4 This regulation should become effective upon promulgation.

§45-21-3 DEFINITION

3.25 The definition of VOC should be amended to include the following compounds exempted by EPA on January 18, 1989 (54 FR 1987):

(1) Dichlorotrifluoroethane (HCFC-123)
(2) Tetrafluoroethane (HFC-134a)
(3) Dichlorofluoroethane (HCFC-141b)
(4) Chlorodifluoroethane (HCFC-142b)

The fourth sentence should also be amended to read as follows: For purposes of determining compliance with emissions limits, VOC will be measured by the <u>EPA</u> approved test methods.

§45-21-4 CONTROL AND PREVENTION OF EMISSIONS

4.1b) West Virginia Air Pollution Control Commission (WV APCC) should amend this sub-section to read, "The source has been equipped with an approved vapor control system capable of achieving 85% emissions reduction."

4.2b)(2) WV APCC should add the word "support" following roof leg~~s~~, to keep this sub-section consistent with the entire regulation.

§45-21-7 INSPECTION, REPORTS, AND TESTING

7.1b) WV APCC should add the phrase "or once per year" at the end of this sub-section.

7.4 Any revisions to this sub-section (i.e., test precedures and reporting instructions) should be submitted to EPA as a SIP revision.

§45-21-8 COMPLIANCE PROGRAMS

This section is not acceptable to EPA, because it would not be federally enforceable. Refer to enclosure 1, Compliance Schedules for Volatile Organic Compounds (VOC's), which states that sources have one year to comply, from the date of the regulation change.

§45-21-11 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

BULK GASOLINE TERMINALS

WV APCC needs to develop regulations to require that all tank trucks loading and unloading at bulk gasoline terminals use vapor recovery systems, and be certified leak-tight by bulk terminals.

These regulations should be developed pursuant to the CTG entitled, "Control of Volatile Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems." (EPA-450/2-78-051).

§45-23-1 GENERAL

1.4 This regulation should become effective upon promulgation.

§45-23-3 DEFINITION

3.20 The definition of VOC should be amended to include the following compounds exempted by EPA on January 18, 1989 (54 FR 1987):
(1) Dichlorotrifluoroethane (HCFC-123)
(2) Tetrafluoroethane (HFC-134a)
(3) Dichlorofluoroethane (HCFC-141b)
(4) Chlorodifluoroethane (HCFC-142b)

The fourth sentence should also be amended to read as follows: For purposes of determining compliance with emissions limits, VOC will be measured by the <u>EPA</u> approved test methods.

§45-23-4 CONTROL AND PREVENTION OF EMISSIONS

4.2(a)(1) As specified in the CTG entitled "Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals" (EPA-450/2-77-026), WV APCC should amend this sub-section to read, "an approved adsorption, absorption, compression or condensation system which processes and recovers vapors and gases from the equipment being controlled <u>capable of achieving 90% emissions reduction</u>."

§45-23-7 REPORTS, AND TESTING

7.3 (a) WV APCC should amend line two of this sub-section to read, " ... sampled and analyzed in an <u>EPA</u> approved manner such that the ...."

7.3 (b) WV APCC should amend line three of this sub-section to read, "... shall be computed using accepted engineering practices and in <u>EPA</u> approved manner ..."

7.3 (c) WV APCC should amend line three of this sub-section to read, "... <u>EPA</u> approved manner ."

§45-23-8 COMPLIANCE PROGRAMS

See comments under §45-21-8.

§45-23-11 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

PETROLEUM REFINERY SOURCES

§45-24-1 GENERAL

1.4 This regulation should become effective upon promulgation.

§45-24-3 DEFINITION

3.27 The definition of VOC should be amended to include the following compounds exempted by EPA on January 18, 1989 (54 FR 1987):

(1) Dichlorotrifluoroethane (HCFC-123)
(2) Tetrafluoroethane (HFC-134a)
(3) Dichlorofluoroethane (HCFC-141b)
(4) Chlorodifluoroethane (HCFC-142b)

The fourth sentence should also be amended to read, "For purposes of determining compliance with emissions limits, VOC will be measured by the EPA approved test methods."

§45-24-4 CONTROL AND PREVENTION OF EMISSIONS

4.2(a) WV APCC should amend this sub-section to read, "Provide approved covers and seals on all separators and forebays, and,"

4.3(b) WV APCC should amend this sub-section to read as follows: "Preventing emissions of volatile organic compounds from a process unit or vessel [unless] until ..."

§45-24-7 REPORTS, AND TESTING

7.1 WV APCC should amend the third line of this section to read, " .....to conduct or have conducted EPA approved tests to determine the compliance of such ..."

§45-24-8 COMPLIANCE PROGRAMS

See comments under §45-21-8. In addition, WV APCC needs to add specific requirements as suggested in the control technique guideline entitled "Control of Refinery Vacuum Producing Systems, Wastewater Separators and Process Unit Turnarounds" (EPA-450/2-77-025). This provision should specify the timetable for compliance, to include the dates for ordering, receiving, installation, and start-up of necessary equipment.

§45-24-10 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

We appreciate the opportunity to review and comment on these draft regulations. Should you have any questions regarding our comments, please feel free to call me at (215) 597-9075 or your staff may contact Ms. Jacqueline Lewis at (215) 597-6863.

Sincerely,

Marcia L. Spink, Chief
Air Programs Branch

Enclosure

ENCLOSURE

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

MAR 16 1989

MEMORANDUM

SUBJECT: Compliance Schedules for Volatile Organic Compounds (VOC's)

FROM: John Calcagni, Director
Air Quality Management Division

John Seitz, Director
Stationary Source Compliance Division

TO: David Kee, Director
Air and Radiation Division, Region V

We have reviewed your memorandum dated December 7, 1988 regarding two issues on compliance schedules for VOC's. The first issue pertains to U.S. Environmental Protection Agency's (EPA's) continuity policy, which requires that each source comply with an existing State implementation plan (SIP) until the new or revised SIP is met. As you stated in your memorandum, this policy has been (and continues to be) a key feature of EPA's implementation of Part D of the Clean Air Act. This memorandum reaffirms EPA's intention of supporting and maintaining this policy, particularly in light of the post-1987 SIP calls and correction of VOC deficiencies and deviations.

The second issue pertains to a source's need and/or request for additional time to comply with the revised VOC regulations. You proposed two approaches for extending compliance schedules for corrected VOC rules.

The first approach would not grant any additional compliance time <u>except</u> through the delayed compliance order (DCO) process. (Under the DCO process, a source may request up to an additional 3 years to comply with a VOC regulation.) We recommend this approach (i.e., immediately effective rules with case-by-case DCO's) when the changes are trivial or simply clarify previous interpretations and do not impose significant new, additional burdens on sources that were otherwise in compliance with the approved SIP. (Sources not in compliance with existing requirements should not be allowed additional compliance time, and instead should be handled through a traditional compliance approach.) In addition, when a rule change affects only part of a source category or the State cannot document how the change will affect sources, the rule should be immediately effective (and the DCO process is appropriate).

However, this first approach (no additional compliance time) may be unduly restrictive in circumstances where previously exempted sources are newly regulated, or where sources that previously complied with the approved SIP now require major process changes and/or major capital expenditures to comply. In these instances, we recommend the second approach of setting a "presumptive norm" compliance schedule of 1 year or less (from the effective date of the revised rule). However, under this second approach, the State is obligated to clearly demonstrate that these circumstances exist for all sources eligible for this "presumptive norm." The "presumptive norm" compliance time frame would not necessarily apply to an entire source category. In this case, the State's regulation allowing the "presumptive norm" would need to clearly specify that portion of the source category affected. Conversely, the regulation would need to clearly specify that the other sources in the category have an immediately effective compliance date (i.e., the DCO is the only route available for an extension).

Under the "presumptive norm" approach, we also agree with your suggestion that any source requesting additional time beyond the 1 year would be required to apply for a DCO, rather than submitting a rule revision. If a DCO becomes necessary, we would encourage the Regional Offices to limit compliance date extensions to the minimum time necessary to comply with the modified regulations, not to exceed 3 years from the date of rule adoption. Further, the DCO should be limited only to changes made necessary by the rule change. Noncompliance incidental to the rule change should not be included in the DCO; instead, these cases should be handled through normal compliance mechanisms. In any case, EPA retains the responsibility to ensure that any compliance schedule, whether it is contained in the SIP submittal or is the result of a DCO, meets the Clean Air Act's requirements of expeditiousness.

While EPA's policy on grandfathering provisions would apply in these compliance cases (memorandum from Gerald A. Emison, Office of Air Quality Planning and Standards, to Air Division Directors, "Grandfathering of Requirements for Pending SIP Revisions," June 27, 1988), we are not aware of any SIP submittals that would be grandfathered by this policy. Please advise us if this is not the case.

If you have any questions or comments, please call John Silvasi at FTS 629-5666 or David Cole at FTS 629-5497.

Attachment

cc: R. Ossias, OGC
Air Director, Regions I-X
Air Branch Chief, Regions I-X
Regional Division Directors
Regional Air Branch Chiefs (Programs and Compliance)
VOC Regulatory Contacts
VOC Compliance Contacts

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION III
841 Chestnut Building
Philadelphia, Pennsylvania 19107

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Mr. Dale Farley, Director
West Virginia Air Pollution Control Commission
1558 Washington Street, East
Charleston, West Virginia 25311

Dear Mr. Farley:

On November 8, 1989, Edwin B. Erickson, EPA Region III Regional Administrator, notified Governor Caperton that the State Implementation Plan (SIP) was substantially inadequate to achieve the National Ambient Air Quality Standards (NAAQS) for certain areas within the State of West Virginia. Additional air quality data that have since been obtained for 1988 have shown that Greenbrier County and the Charleston Metropolitan Statistical Area (MSA) are now showing ozone nonattainment. The Charleston, West Virginia MSA consists of Kanawha and Putnam Counties.

The letter to Governor Caperton requested that West Virginia respond to EPA's letter in two phases. The second phase of the response will follow the issuance of EPA's final program requirements for ozone and CO nonattainment areas, and therefore will not be addressed in this letter. The first phase response, however, is expected in the near future. This phase involves:

(1) correcting deficiencies and inconsistencies in existing regulations;

(2) developing a base year emission inventory for Greenbrier County and Charleston MSA; and

(3) if the Clean Air Act Amendments and/or EPA policy requires it, commit to and develop a schedule for conducting an ambient sampling program for nonmethane organic compounds (NMOC).

<u>Correcting Existing Deficiencies and Inconsistencies</u>

On November 24, 1987, EPA proposed its post-1987 ozone and CO policy. Appendix D of the proposed policy contained a listing of

SIP deficiencies and inconsistencies that should be addressed and corrected when States respond to notifications of SIP deficiencies. On May 24, 1988, EPA prepared a supplement to Appendix D entitled, Issues Relating To VOC Regulations, Cutpoints, Deficiencies, and Deviations), to provide additional clarification of those deficiencies described in Appendix D (Enclosure 1). This document addresses existing reasonable available control technology regulations for volatile organic compounds (VOC's) that have not been adopted and/or that have been implemented on a nationally inconsistent basis.

This clarification does not expand or modify existing regulatory requirements, but merely enhances Appendix D by providing more specific and detailed guidance. This document addresses many of the Appendix D problems found during EPA's review of State regulations following the April 1987 letter from the EPA Administrator to the Governors. Corrections of the deficiencies described in the document will provide for a greater degree of equity and national consistency among all States and localities that develop and implement revised plans to deal with the continuing ozone problem.

EPA has reviewed the West Virginia regulations identified in Enclosure 2 and has included guidance on how those regulations can be changed to meet the required Reasonably Available Control Technology (RACT) level of control. While we believe that we have identified, in Enclosure 2, all known deficiencies and inconsistencies in your existing VOC regulations, we request that you independently ascertain that your SIP is consistent with the May 24, 1988 guidance, the Control Techniques Guideline (CTG) documents, and Enclosure 2.

Emission Inventory

Guidance concerning methodologies for preparing VOC emission inventories, "Procedures for the Preparation of Emission Inventories for Precursors of Ozone", Volume I, EPA-450/4-88-021, December 1988, and guidance for preparation of the Mobile Source Inventory "Procedures For Emission Inventory Preparation", Volume IV, Mobile Sources EPA-450/4-81-026d (revised), July 1989, have previously been sent to you.

Workplan

To assure timely action on the first phase requirements, we are asking you to develop a work plan describing both interim and final milestones for completing these various tasks, and to submit that plan to the Regional Office within 60 days of receiving this letter. This work plan should show expeditious completion of Phase I activities. Generally, EPA presumes expeditions to mean one (1) year from the date the plan is submitted. The work plan should provide a timetable for at least the following activities:

Regulatory Actions

Completion of technical analysis (as appropriate);
Preparation of draft rule/regulations;
Notification of public hearing;
Hearing date;
Adoption date;
Date of submission to EPA.

Emission Inventory

Submittal of format/sample calculations;
Data collection;
Submittal of draft inventory.

When preparing your work plan please account for EPA's need to review your drafts and for the time needed for you to incorporate EPA's comments.

I realize that resource constraints have made it difficult to comply with the 1988 ozone SIP call. When you develop your work plan as described above, you should indicate your progress in satisfying the previous SIP call requirements. This new SIP call should not interfere with the progress of the 1988 SIP call. The 1988 SIP call commitments must be met.

We hope that EPA and West Virginia will work closely in the coming months in order to fully respond to both this and last year's SIP calls in a more timely manner. We look forward to your response by January 31, 1990. Please feel free to contact me or Marcia L. Spink, Chief, Air Programs Branch, at (215) 597-9075, if you have any questions.

Sincerely

Thomas J. Maslany, Director
Air, Toxics & Radiation
Management Division

2 Enclosures

Enclosure 2

WEST VIRGINIA REGULATION DEVIATION AND DEFICIENCIES

I. Regulation XXI - Storage of Petroleum Liquids in Fixed Roof Tanks

A. Definitions

1. Section 3.15 - The definition of "hydrocarbon" may be eliminated since the term "volatile organic compound" will be used exclusively to refer to those organic compounds which contribute to ozone formation.

2. Section 3.17 - The definition of "organic material" may be eliminated for the same reason already stated above.

3. Section 3.27 - The definition of "volatile organic compound" (VOC) should be changed, consistent with EPA guidance. The most current definition of VOC is:

"Any organic compound which participates in atmospheric photochemical reaction. This includes any organic compound other than the following compounds: methane, ethane, methyl chloroform (1,1,1-trichloroethane), CFC-113 (trichlorotrifluoroethane), methylene chloride, CFC-11 (trichlorofluoromethane), CFC-12 (dichlorodifluoromethane), CFC-22 (chlorodifluoromethane), FC-23 (trifluoromethane), CFC-114 (dichlorotetrafluoroethane), CFC-115 (chloropentafluoroethane). These compounds have been determined to have negligible photochemical reactivity. For purposes of determining compliance with emission limits, VOC will be measured by the approved test methods. Where such a method also inadvertently measures compounds with negligible photochemical reactivity, an owner or operator may exclude these negligibly reactive compounds when determining compliance with an emissions standards."

B. Section 4 - Control and Prohibition of Emissions

1. Section 4.01(c) - EPA cannot generically approve any alternative control system into a State regulation which is not explicitly described in the regulation.

<u>Action</u>:

Before inclusion of this section into West Virginia's SIP, West Virginia must clearly specify that any such alternative compliance plans must be submitted to EPA for approval. Alternatively, West Virginia may delete this provision from its regulations. Deletion of the provision does not prohibit any source from soliciting approval for alternative compliance plans.

2. Section 4.03 - The reference to "Alternative Control System" should be deleted or modified to reflect an EPA approved alternative control system.

3. Section 4.04 - This section provides for alternative compliance plans to be approved by the State. As stated above, EPA cannot allow such generic authority.

Action:

Before inclusion of this section into West Virginia's SIP, West Virginia must clearly specify that any such alternative compliance plans must be submitted to EPA for approval. Alternatively, West Virginia may delete this provision from its regulations. Deletion of the provision does not prohibit any source from soliciting approval for alternative compliance plans.

II. Regulation XXIII - Bulk Gasoline Terminals

A. Definitions

1. Section 3.13 - Definition of hydrocarbon - See I.A.1 above

2. Section 3.14 - Definition of Organic material - See I.A.2 above

3. Section 3.22 - The definition of volatile organic compound should be changed to that described above in I.A.3.

B. Section 4 - Control and Prohibition of Emissions

1. Section 4.02(3) - The reference to an alternative control system approved by the Commission should either be deleted or modified to state that the alternative control system must be approved by the Commission and EPA.

2. Section 4.04 - See comments above in I.B.1 and I.B.3

Action:

Before inclusion of this section into West Virginia's SIP, West Virginia must clearly specify that any such alternative compliance plans must be submitted to EPA for approval. Alternatively, West Virginia may delete this provision from its regulations. Deletion of the provision does not prohibit any source from soliciting State and EPA approval for alternative compliance plans.

3. Issue: Compliance test methods and procedures should be specified in regulations.

Action:

Before inclusion of this regulation into West Virginia's SIP, West Virginia must add test methods and recordkeeping procedures so that compliance with the standard can be determined. West Virginia should consult EPA Document 450/2-77-026 "Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals" to find the appropriate compliance test methods and procedures for the State regulations.

III. Regulation XXIV - Petroleum Refinery Sources

A. Definitions

1. Section 3.16 - Definition of hydrocarbon - see I.A.1 above

2. Section 3.17 - Definition of organic material - see I.A.2 above

3. Section 3.29 - Definition of VOC - see I.A.3 above

B. Section 4 - Control and Prevention of Emissions

1. Section 4.01(b)(3) - Alternative control systems - EPA cannot approve of such generic authority. See comments for I.B.1 above.

2. Section 4.02(b) - Alternative control system. See comments for I.B.1 above.

3. Section 4.04 - Alternative compliance plans - See comments for I.B.1 above.

IV. For all the above regulations, records should be required to be kept by the source for a two (2) year period. In addition to this requirement and in lieu of specific recordkeeping requirements for each source category, West Virginia may choose to place a generic recordkeeping requirement applicable to all regulations stating that records must be kept such that compliance with the applicable standard may be determined. In addition, sources which now exceed or have ever exceeded the exemption level described in the specific regulation, are required to be subject to the regulation from that time forward. This is described as the concept of "once-in-always-in".

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WEST VIRGINIA
AIR POLLUTION
CONTROL COMMISSION

WEST VIRGINIA AIR POLLUTION CONTROL COMMISSION

PUBLIC HEARING

IN RE: PROPOSED AMENDMENTS TO REGULATION 21
PROPOSED AMENDMENTS TO REGULATION 23
PROPOSED AMENDMENTS TO REGULATION 24

TRANSCRIPT OF PROCEEDINGS HAD IN THE CONFERENCE ROOM AT THE OFFICES OF THE WEST VIRGINIA AIR POLLUTION CONTROL COMMISSION AT 1558 WASHINGTON STREET, EAST, CHARLESTON, KANAWHA COUNTY, WEST VIRGINIA, ON THE 5TH DAY OF JUNE, 1990, AT 9:15 A.M., PURSUANT TO NOTICE DULY GIVEN.

HUDSON REPORTING
402 POPLAR FORK ROAD
SCOTT DEPOT, WV 25560
(304) 757-8192

APPEARANCES

BEFORE:	CREDE D. DOUGLASS, JR., CHAIRMAN
	L. NEWTON THOMAS, JR., VICE-CHAIRMAN
	CLEVE BENEDICT, COMMISSIONER
	JOSEPH SCHOCK, COMMISSIONER
	SAMUEL KUSIC, COMMISSIONER
	DALE FARLEY, DIRECTOR
	LARRY G. KOPELMAN, SPECIAL ASSISTANT ATTORNEY GENERAL

INDEX

PROPOSED AMENDMENTS:

SPEAKER:

MR. DOUGLASS: I'D LIKE TO CALL THIS MEETING BEFORE THE AIR POLLUTION CONTROL COMMISSION TO ORDER. WE'RE HAVING PUBLIC HEARINGS TODAY AND WE HAVE A COURT REPORTER ON HAND, SHIRLEY HANSON OF HUDSON REPORTING. ANYONE WISHING A COPY OF THE HEARING SHOULD MAKE THEIR OWN ARRANGEMENTS WITH THE COURT REPORTER.

THE COMMISSION PRESENT TODAY IS L. NEWTON THOMAS, SAMUEL KUSIC, JOSEPH SCHOCK, CLEVE BENEDICT, AND CHAIRMAN CREDE DOUGLASS.

THE FIRST ITEM ON THE AGENDA IS PROPOSED AMENDMENTS TO REG 21, "TO PREVENT AND CONTROL AIR POLLUTION FROM THE STORAGE OF PETROLEUM LIQUIDS IN FIXED ROOF TANKS".

DO WE HAVE ANYONE WHO WISHES TO BE HEARD?

MR. FARLEY: JUST BRIEFLY, TO OPEN ON THIS, THOSE FIRST THREE REGULATIONS THAT WE HAVE ON THE AGENDA TODAY FOR AMENDMENT COULD PROBABLY BE HEARD, FROM A PRACTICAL STANDPOINT, TOGETHER. I WOULD IMAGINE THAT'S THE WAY WE WOULD GET COMMENTS, BUT WE COULD SEE HOW THAT WOULD GO AS FAR AS ANY PUBLIC COMMENTS. THESE REGULATIONS ARE BEING AMENDED BASED UPON AN ANALYSIS OF THE REGULATIONS DONE BY E.P.A. EARLIER. THIS IS PURSUANT TO A WORK PLAN WE FILED IN EARLY FEBRUARY OF THIS YEAR WITH E.P.A. TO DO VARIOUS THINGS TO SATISFY NON-

ATTAINMENT PROBLEMS. WITH THAT BEING SAID, I'LL LET JOHN BENEDICT MAKE A FEW COMMENTS ABOUT THE REGULATIONS IN THAT HIS GROUP DID THE ANALYSIS ON THEM.

MR. JOHN BENEDICT: MY NAME IS JOHN BENEDICT AND I AM THE CHIEF OF THE PLANNING DIVISION FOR THE AGENCY.

THE FIRST REGULATION, REGULATION 21, DEALS WITH CONTROLLING VOLATILE ORGANIC COMPOUND EMISSIONS FROM THE STORAGE OF PETROLEUM LIQUIDS IN FIXED-ROOF TANKS. BASICALLY, THIS ONLY COVERS TANKS OF ABOUT 39,000 GALLONS OR MORE CAPACITY AND WHICH STORE FLUIDS WITH 1.52 P.S.I.A. TOTAL VAPOR PRESSURES.

GENERALLY, WHAT WE'RE CONCERNED WITH IS THE STORAGE OF GASOLINE IN FIXED-ROOF TANKS. AND, AS DALE SAID, THE REVISIONS WERE TO ADDRESS E.P.A.'S DEFICIENCIES AND E.P.A.'S REQUIREMENTS TO PROVIDE A GREATER DEGREE OF EQUITY AND NATIONAL CONSISTENCY ON ALL THE REGULATIONS IN ALL STATES.

WE'VE ADDED -- ORIGINALLY, THE REGULATION, IT WAS A 1979 VERSION AND IT ONLY AFFECTED KANAWHA, PUTNAM AND JUST A PORTION OF FAYETTE COUNTY THAT CONSIDERED AIR QUALITY CONTROL WAS POOR -- WE'VE ADDED FOUR COUNTIES, CABELL, WAYNE, WOOD, AND GREENBRIER, WHICH HAVE RECENTLY BEEN IDENTIFIED AS NON-ATTAINMENT FOR OZONE.

RUPERT BURFORD IS SITTING IN THE BACK. HE'S ON OUR PLANNING STAFF RIGHT NOW. HE DID AN ANALYSIS AND REVIEWED THE INVENTORIES OF ALL THESE REGIONS TO DETERMINE HOW THIS PARTICULAR REG WOULD AFFECT THESE VARIOUS SOURCES. BASICALLY, IT DOESN'T AFFECT ANY SOURCE OTHER THAN MAYBE THE REQUIREMENT TO KEEP RECORDS OF THEIR THROUGHPUTS AND TESTING FOR A TWO-YEAR PERIOD OF TIME, AND WE MAY REQUIRE TESTING AT SOME POINT.

MOST FACILITIES HAVE ALREADY GONE TO FLOATING ROOFS FOR THEIR GASOLINE STORAGE JUST TO SAVE THE VAPORS THAT WOULD BE LOST BY LOADING THROUGH THE TANK AND OUTLOADING TO THE TANK. SO, GENERALLY, THIS REGULATION IS BEING UPDATED BUT IT REALLY HAS NO EFFECT ON ANY SOURCE WITHIN THE STATE OTHER THAN THE TESTING RECORD REQUIREMENTS.

MR. DOUGLASS: ANY QUESTIONS? DO YOU HAVE ANYTHING ON NUMBER 2 OR NUMBER 3?

MR. JOHN BENEDICT: LET ME SKIP TO REGULATION 24, CONTROLLING VOLATILE ORGANIC COMPOUND EMISSIONS FROM PETROLEUM REFINERIES. WE ORIGINALLY ENACTED OR PROMULGATED THIS REGULATION TO CONTROL THE PENNZOIL FALLING ROCK FACILITY UP ELK RIVER. IT HAS SINCE BEEN CLOSED. SO, REVIEWING ALL THE AFFECTED AREAS, THOSE ADDITIONAL COUNTIES, TO OUR KNOWLEDGE, THERE ARE NO REFINERIES THAT THIS REGULATION WOULD COVER IN ANY OF THE AFFECTED AREAS. AND THE COMMISSION MAY CONSIDER AT

SOME POINT EITHER GETTING RID OF THIS REGULATION OR RETAINING THIS REGULATION.

WE DO HAVE REFINERIES IN AREAS THAT AREN'T IN THE AFFECTED AREAS AND AT SOME POINT IN TIME THIS COMMISSION MAY HAVE TO IMPLEMENT A REGULATION CONTROLLING EMISSIONS FROM THOSE PARTICULAR REFINERIES SHOULD WE FIND OURSELVES IN AN OZONE NON-ATTAINMENT SITUATION IN THOSE AREAS OR THE CLEAN AIR ACT, DEPENDING ON WHAT VERSION COMES OUT THAT MAY REQUIRE THE CONTROL OF THESE TYPE SOURCES.

MR. DOUGLASS: DO WE HAVE ANY COMMENTS FROM THE PUBLIC?

MR. GALLAGHER: YES.

MR. DOUGLASS: WILL YOU COME FORWARD AND BE SWORN IN?

(WITNESS SWORN)

THEREUPON CAME

PATRICK GALLAGHER

WHO, HAVING BEEN FIRST DULY SWORN ACCORDING TO LAW, TESTIFIED AS FOLLOWS:

MR. GALLAGHER: MY NAME IS PATRICT GALLAGHER AND I'M PRESIDENT OF THE WEST VIRGINIA MANUFACTURERS ASSOCIATION. WVMA REPRESENTS A 250-MEMBER COMPANY. FOR YOUR INFORMATION, I HAVE SEVERAL WRITTEN COMMENTS WHICH I'LL LEAVE WITH THE

COMMISSION UPON CONCLUSION OF MY VERY BRIEF REMARKS.

THE WVMA REPRESENTS A BROAD CROSS-SECTION OF WEST VIRGINIA'S INDUSTRIAL SECTOR. OUR COMMENTS ON THE PROPOSED VOLATILE ORGANIC COMPOUND RULES ARE FULLY IN THE POSITION OF THE ACTIVE AND SUPPORTIVE ROLE THAT THE WVMA HAS TAKEN REGARDING THE ATTAINMENT OF AMBIENT AIR-QUALITY STANDARDS IN WEST VIRGINIA.

FIRST OF ALL, THE WVMA BELIEVES THAT THERE IS A NEED TO ELIMINATE AMBIGUITIES IN THE DEFINITION OF THE TERM "VOLATILE ORGANIC COMPOUND". THE PROPOSED DEFINITION CREATES A DEGREE OF UNCERTAINTY WHICH WAS NOT PRESENT UNDER THE FORMER DEFINITION. WE BELIEVE YOU SHOULD RETAIN THE EXISTING DEFINITION WHICH INCLUDES THE REQUIREMENT THAT AN ORGANIC COMPOUND MUST EXHIBIT A VAPOR PRESSURE GREATER THAN ONE-TENTH MILLIMETER OF MERCURY AND THAT THE TERM BE MADE TO INCLUDE THAT OTHER ORGANIC COMPOUNDS WHICH EXHIBIT NEGLIGIBLE PHOTOCHEMICAL REACTIVITY BY AN APPROVED TEST METHOD MAY BE EXCLUDED FROM THE DEFINITION.

TWO. THE TERM "VAPOR CONTROL SYSTEM" SHOULD BE MODIFIED TO BE CONSISTENT IN ALL SECTIONS OF THE REGULATION AND TO REFLECT THE TECHNOLOGICAL IMPOSSIBILITY OF PREVENTING 100 PER CENT OF VOC EMISSIONS.

THREE. THE COMMISSION SHOULD NOT DELETE PROVISIONS WHICH PROVIDE OWNERS AND OPERATORS OF COVERED SOURCES A MEANS FOR PETITIONING FOR EXEMPTIONS ON A CASE-BY-CASE BASIS.

FOUR. THE WVMA FURTHER BELIEVES THAT, WHEN AN OWNER-OPERATOR DECREASES HIS EMISSIONS BELOW AN EXEMPTION LEVEL, THEY SHOULD NOT CONTINUE TO BE REGULATED. IMPLEMENTAITON OF THE PROPOSED RULE WOULD CAUSE THE COMMISSION TO DIVERT ITS ALREADY LIMITED RESOURCES TO THE REGULATION OF A NUMBER OF SMALL SOURCES WHICH POSE LITTLE OR NO THREAT TO THE AMBIENT CONCENTRATIONS.

FIVE. THE ASSOCIATION ALSO BELIEVES STORAGE TANKS HAVING DOUBLE-SEAL INTERNAL FLOATING ROOFS SHOULD NOT BE SUBJECTED TO THE SAME MAINTENANCE, INSPECTION, REPORTING AND TESTING REQUIREMENTS AS THOSE HAVING SINGLE-SEAL INTERNAL FLOATING ROOFS. WE URGE THE COMMISSION TO ADOPT RULES MORE APPROPRIATE TO THESE TANKS SUCH AS THOSE IN SIMILAR FEDERAL RULES.

SIX. WE REQUEST THE COMMISSION TO CONSIDER CLARIFYING THE DEFINITION OF THE TERM "GASOLINE" TO EXCLUDE LIGHTER GRADES OF PETROLEUM PRODUCTS SUCH AS DRY GAS, PROPYLENE, AND BUTANES. VOC EMISSIONS FROM LOADING THESE LIGHTER GRADES OF PETROLEUM PRODUCTS WOULD BE INSIGNIFICANT COMPARED TO REGULAR GASOLINE.

FINALLY, FOR SAFETY REASONS, WE BELIEVE SPILLED GASOLINE AT BULK GASOLINE STORAGE TERMINALS SHOULD BE ALLOWED TO BE FLUSHED INTO SEWER SYSTEMS CONTAINING OIL AND WATER SEPARATORS. THE COMMISSION RECOGNIZES SUCH PRACTICES FOR PETROLEUM REFINERIES.

THE WVMA APPRECIATES THE OPPORTUNITY TO COMMENT ON THESE REGULATIONS. AS I NOTED EARLIER, I WILL LEAVE WITH EACH OF YOU A MORE DETAILED WRITTEN COMMENT ON EACH OF THE ITEMS PREVIOUSLY MENTIONED. THANK YOU.

MR. DOUGLASS: THANK YOU.

(WITNESS EXCUSED)

MR. DOUGLASS: DO WE HAVE ANYONE ELSE WHO WANTS TO SPEAK TO THE COMMISSION?

(NO RESPONSE)

MR. FARLEY: JOHN, DO YOU THINK YOU NEED TO MAKE ANY COMMENTS ABOUT REG 23?

MR. JOHN BENEDICT: YES.

MR. FARLEY: YOU MIGHT WANT TO MAKE ANOTHER COMMENT OR TWO ABOUT THAT PARTICULAR REGULATION.

MR. JOHN BENEDICT: SHOULD I ATTEMPT TO ADDRESS SOME OF HIS CONCERNS?

MR. KOPELMAN: HE'S ASKING YOU IF YOU ALL WOULD LIKE MAYBE A REBUTTAL TO THE CONCERNS FROM THE WEST VIRGINIA

MANUFACTURERS ASSOCIATION? GO AHEAD.

MR. JOHN BENEDICT: I THINK WE'LL HAVE TO LOOK A LITTLE CLOSER AT THE DEFINITION OF VOC. WE WENT BY WHAT E.P.A. SUGGESTED ON VOC WHICH DOES EXCLUDE SOME OF THE THINGS THAT WERE DISCUSSED. IT EXCLUDES METHANE, EXANE, METHYLENE CHLORIDE, A LOT OF THE CFC COMPOUNDS. IT ALSO MENTIONS, AND THIS IS ON PAGE FOUR OF THAT REG 21 WHICH -- THESE DEFINITIONS ARE CONSISTENT IN THE REGULATION. AND IT ALSO SAYS, "FOR THE PURPOSE OF DETERMINING COMPLIANCE WITH EMISSION LIMITS, VOC'S WILL BE MEASURED BY THE APPROVED TEST METHODS WHERE SUCH A METHOD ALSO INADVERTENTLY MEASURES COMPOUNDS WITH NEGLIGIBLE CHEMICAL REACTIVITY AND OTHER OPERATORS MAY EXCLUDE THESE NEGLIGIBLE REACTIVE COMPOUNDS WHEN DETERMINING COMPLIANCE." SO, I THINK THAT MAY ADDRESS SOME OF HIS CONCERNS.

AS FAR AS THE ALTERNATIVE CONTROL SYSTEM, E.P.A., IN ORDER TO MAKE -- PART OF ITS SIP REQUIREMENT, E.P.A. HAS TO APPROVE ANYTHING THE COMMISSION APPROVES BEFORE THE REGULATIONS BECOME SIP-APPROVABLE. SOME OF E.P.A.'S COMMENTS WERE THAT IT GAVE TOO MUCH DISCRETION TO THE COMMISSION TO ALLOW A FACILITY TO HAVE AN ALTERNATIVE-CONTROLLED SYSTEM. AND, ULTIMATELY, E.P.A. WOULD HAVE TO APPROVE WHATEVER THE DECISION THE COMMISSION MADE ALLOWING SOMEBODY TO DO THAT. I GUESS, IN OUR VIEW, AND LARRY MAY CORRECT ME, WE CAN ALWAYS

ENTER INTO A CONSENT ORDER IF SOMEBODY WISHES NOT TO MEET CERTAIN PROVISIONS OF THE REGULATION AND HAS AN ALTERNATIVE-CONTROLLED PROGRAM. WE'VE DONE THAT REGULARLY. SO, BASICALLY, WE DID DELETE A LOT OF LANGUAGE WITHIN THE REGULATION ALLOWING ALTERNATIVE-CONTROL SYSTEMS, BUT WE'VE ALWAYS HAD THE OPTION OF A CONSENT ORDER. WE HAVE TO LOOK AT THE DOUBLE-SEAL VERSUS --

MR. KOPELMAN: JOHN, CAN I INTERRUPT YOU THERE?

MR. JOHN BENEDICT: YES.

MR. KOPELMAN: IF WE DID A CONSENT ORDER, DOES THAT HAVE TO BE SUBMITTED TO E.P.A. AS A SIP CHANGE?

MR. JOHN BENEDICT: YES.

MR. KOPELMAN: EACH CHANGE WOULD HAVE TO BE SUBMITTED?

MR. JOHN BENEDICT: YES. AT THE OUTSET WE HAVE TO LOOK A LITTLE CLOSER INTO THE DOUBLE-SEAL VERSUS THE SINGLE-SEAL ISSUE. GASOLINE, THE LIGHTER GRADES, AGAIN, WE HAVE TO LOOK A LITTLE CLOSER. DISTILLED GAS, THAT'S SOMETHING WE NEVER CONSIDERED, AND I DON'T KNOW HOW IMPORTANT OR RELEVANT THAT IS, BUT WE WILL GET BACK TO THE COMMISSION AND ADDRESS THOSE QUESTIONS.

ONE OTHER REGULATION IS REG 23 WHICH COVERS THE EMISSIONS OF VOC OR VOLATILE ORGANIC COMPOUND EMISSIONS FROM

BULK GASOLINE TERMINALS. A TERMINAL IS CONSIDERED ANYTHING-- A TERMINAL THAT PRODUCES GREATER THATN 20,000 OR HAS A FLOW-THROUGH OF 20,000 GALLONS PER DAY OF GASOLINE. BULK STORAGE FACILITIES MAY BE LESS THAN THAT AND AT SOME POINT IN TIME WE WILL BRING BEFORE THE COMMISSION REGULATIONS CONTROLLING BULK STORAGE TANKS ALSO.

RECENT ANALYSIS OF THE FACILITIES IN THE AFFECTED AREA ONLY SHOWS THIS WOULD AFFECT THE PENNZOIL FACILITY UP ELK RIVER. BASICALLY, THIS REGULATION REQUIRES SOME TYPE OF VAPOR RECOVERY SYSTEM ON THE LOADING OF GASOLINE FROM BULK-STORAGE TANKS INTO TRUCKS. THE PENNZOIL FACILITY -- THIS REGULATION WAS FIRST ADOPTED IN 1979. AT THAT TIME PENNZOIL ASKED FOR AN EXEMPTION FROM THE COMMISSION. THEY CONTENDED THEY WERE GOING TO SHUT DOWN THE ELK RIVER REFINERY AND, THUS, THEY WERE GOING TO HAVE MUCH MORE REDUCTION IN VOC EMISSIONS AND, ESSENTIALLY, THEY WERE ASKING FOR A TRADE-OFF -- DON'T LET US CONTROL OUR FACILITY HERE AND WE'RE TRADING OFF THESE EMISSIONS BY SHUTTING DOWN THE ELK RIVER REFINERY. SINCE THAT TIME WE'VE HAD EXCEEDANCE OF THE OZONE STANDARD WITH THAT FACILITY UNDER CONTROL.

THEY HAVE ONE LOADING RACK AND THEY HAVE THREE POSITIONS. IN OTHER WORDS, THEY LOAD OUT THREE GRADES OF GASOLINE THROUGH THAT LOADING RACK. LAST YEAR THEY LOADED A

LITTLE OVER 18,000,000 GALLONS OF GASOLINE AT THE LOADING RACK. MY CALCULATION OF THE LOSSES IS ROUGHLY 17,000 GALLONS OF GASOLINE WAS LOST TO THE ATMOSPHERE LAST YEAR THROUGH THE LOADING OF THAT 18,000,000 GALLONS OF GASOLINE. THEY CAN SAVE A LITTLE OVER 16,000 GALLONS BY REPLACING -- BY INSTALLING A VAPOR RECOVERY SYSTEM WHICH COULD BE ANYWHERE FROM 90 TO 95 PER CENT EFFICIENCY.

PENNZOIL CONTENDS IN THEIR 1983 LETTER REQUESTING THAT EXEMPTION THAT, TO RETROFIT THAT FACILITY, MAKE MODIFICATIONS TO THE TRUCKS, IT WOULD COST THEM $750,000. OUR REVIEW OF LITERATURE, E.P.A.'S LITERATURE, AND UPDATING THAT TO 1990 DOLLARS, THESE GUIDANCE DOCUMENTS THAT RESULTED IN THE DEVELOPMENT OF THESE REGULATIONS WERE 1979 VERSIONS, WE ESTIMATE ROUGHLY ANYWHERE FROM $300,000 TO $350,000 THAT IT WOULD COST THEM TO RETROFIT THAT FACILITY. BUT, AGAIN, THEY WOULD SAVE A LITTLE OVER 16,000 GALLONS A YEAR.

THE OTHER FACILITY THAT COULD BE AFFECTED IS THE EXXON TERMINAL IN PARKERSBURG. AND MY UNDERSTANDING, FROM DISCUSSIONS WITH A MR. LOWE IN HOUSTON, IS THAT THAT FACILITY WILL BE CLOSED. NOW, WHETHER IT WILL BE SOLD OR NOT, I'M NOT SURE. IF IT IS SOLD, WE WOULD REQUIRE CONTROLS ON THAT PARTICULAR FACILITY.

MR. DOUGLASS: ANY QUESTIONS? ANY OTHER COMMENTS?

MR. CLEVE BENEDICT: JOHN, I DON'T UNDERSTAND THE SIGNIFICANCE OF ONE PART OF MR. GALLAGHER'S COMMENTS. WHAT IS HE SUGGESTING? THAT WE REMOVE THE TERMINOLOGY COMPOUND OF CARBON HAVING A VAPOR PRESSURE GREATER THAN ONE-TENTH MILLIMETERS OF MERCURY? THAT WE REMOVE THAT VAPORIZATION TEST? OR MAYBE MR. GALLAGHER WOULD LIKE TO HAVE THAT VAPORIZATION TEST REMAIN. I DON'T UNDERSTAND THE SIGNIFICANCE OF THE DIFFERENCE.

MR. JOHN BENEDICT: TO BE HONEST, I DON'T KNOW EITHER. I WOULD LIKE TO HEAR A LITTLE BIT MORE FROM HIM AND WHAT HE HAD IN MIND. IN LOOKING AT OUR REGISTRATION FORMS, OUR INVENTORY REGISTRATION FORMS, MOST FACILITIES, RECOGNIZING THEY ARE LOSING QUITE A BIT OF GASOLINE THROUGH THE STORAGE TANKS OR LOADING OF GASOLINE, HAVE ALREADY GONE VOLUNTARILY TO INTERNAL FLOATING ROOFS OR THEY'VE STORED IN WHAT THEY CALL EXTERNAL FLOATING ROOFS.

GENERALLY, AS FAR AS WE'RE CONCERNED, THIS ONLY APPLIES TO GASOLINE. MOST OF THE HEAVIER OILS, THE DIESEL FUELS AND THAT SORT OF THING, FALL BELOW THE VAPOR PRESSURE CUTOFF AND THERE'S VERY LITTLE VOLATILIZATION OF THOSE COMPOUNDS INTO THE ATMOSPHERE. THEY HAVE SINCE -- TERMINALS

HAVE SWITCHED THEIR STORAGE OF DIESEL INTO THE FIXED-ROOF TANKS AND THEIR GASOLINE INTO THE FLOATING ROOFS OR EXTERNAL FLOATING-ROOF TANKS TO SAVE THE LOSS OF GASOLINE. AND THAT WAS DONE -- MOST OF THEM DID THAT LONG AGO.

MR. CLEVE BENEDICT: SO, IN YOUR VIEW, THIS WORDING IS JUST AN UNNECESSARY REQUIREMENT THEN. THE DEFINITION, IT DOESN'T MEET ANY PRACTICAL FIELD APPLICATION.

MR. JOHN BENEDICT: I WOULD LIKE TO GET WITH MR. GALLAGHER AND SEE WHAT HIS CONCERNS ARE. THERE MAY BE SOMETHING WE'RE UNAWARE OF. MOST PEOPLE KNOW MORE ABOUT THAT INDUSTRY THAN WE DO.

I WILL MENTION THAT THERE ARE TWENTY-NINE CTG PUBLICATIONS. CTG PUBLICATIONS ARE E.P.A. PUBLICATIONS THAT ARE CONTROL TECHNIQUES GUIDANCE PUBLICATIONS, AND, GENERALLY, THEY COVER A SPECIFIC TYPE OF SOURCE AND THEY LIST WHAT THE COST WOULD BE TO CONTROL THOSE SOURCES AND THE VARIOUS OPTIONS THAT WOULD BE USED TO CONTROL THOSE SOURCES. E.P.A. IS GOING TO BE REQUIRING THIS AGENCY OR THIS COMMISSION TO IMPLEMENT MOST OF THESE REGULATIONS IF WE HAVE THOSE SOURCES WITHIN THIS STATE. SO WE WILL BE COMING BEFORE YOU A NUMBER OF TIMES AND IT MAY BE AS MANY AS AN ADDITIONAL TWENTY-SIX CTG REGULATIONS.

MR. DOUGLASS: ALL RIGHT. I BELIEVE THAT CONCLUDES THE DISCUSSION ON THESE REGULATIONS.

(WHEREUPON, THE HEARING IN THE ABOVE-ENTITLED MATTER WAS CONCLUDED.)

STATE OF WEST VIRGINIA

COUNTY OF KANAWHA, TO-WIT:

I, SHIRLEY T. HANSON, BEING A MEMBER IN GOOD STANDING OF AND HOLDING THE CERTIFICATE OF MERIT AWARDED BY THE NATIONAL STENOMASK VERBATIM REPORTERS ASSOCIATION, INC., A NOTARY PUBLIC WITHIN AND FOR THE COUNTY AND STATE AFORESAID, DULY COMMISSIONED AND QUALIFIED, DO HEREBY CERTIFY THAT THE FOREGOING IS, TO THE BEST OF MY SKILL AND ABILITY, A TRUE, ACCURATE AND COMPLETE TRANSCRIPT OF ALL THE PROCEEDINGS HAD AS SET FORTH IN THE CAPTION HEREOF DURING SAID PUBLIC HEARING.

GIVEN UNDER MY HAND THIS 13th DAY OF June, 1990.

Shirley T. Hanson

SHIRLEY T. HANSON, CVR-CM

MY COMMISSION EXPIRES JULY 5, 1999.

West Virginia

DEPARTMENT OF COMMERCE,
LABOR & ENVIRONMENTAL RESOURCES
OFFICE OF THE SECRETARY

State Capitol
Charleston, West Virginia 25305
304/348-3255

FILED
1990 APR -6 AM 9:28
[illegible]

April 2, 1990

Mr. Dale Farley
Secretary
West Virginia Air Pollution
Control Commission
1558 Washington Street, East
Charleston, WV 25311

Dear Mr. Farley:

Pursuant to the workplan that I previously filed with U. S. EPA - Region III to address nonattainment of the National Ambient Air Quality Standard for ozone, I hereby authorize the Air Pollution Control Commission to proceed with hearings and to propose amendments to the following legislative rules:

Regulation 21 (45CSR21) - "To Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds From the Storage of Petroleum Liquids in Fixed Roof Tanks"

Regulation 23 (45CSR23) - "To Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds From Bulk Gasoline Terminals"

Regulation 24 (45CSR24) - "To Prevent and Control Air Pollution From the Emission of Volatile Organic Compounds From Petroleum Refinery Sources".

Sincerely yours,

Leonard A. Harvey
Secretary

LAH/tlm

90 JUL -9 [illegible]
AIR POLLUTION
CONTROL COMMISSION

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION III
841 Chestnut Building
Philadelphia, Pennsylvania 19107

JUL 6 1990

Mr. G. Dale Farley, Director
West Virginia Air Pollution Control
 Commission
1558 Washington Street, East
Charleston, West Virginia 25311

Dear Mr. Farley:

As requested in your letter of June 19, 1990, we have reviewed West Virginia's second draft of the volatile organic compound (VOC) regulatory corrections. We have also reviewed the public hearing comments submitted by the West Virginia Manufacturers Association (WVMA). Our comments on both documents follow:

FIXED ROOF TANKS

§45-21-1 GENERAL

1.1 WVAPCC has resolved this issue, by incorporating EPA's comment, clarifying the applicability of this subsection.

1.4 WVAPCC has indicated that this regulation will become effective, upon approval of the Commission.

§45-21-3 DEFINITIONS

3.2 The definition of "approved" is acceptable to EPA.

3.3 This definition should be amended to read, "Commission means the West Virginia Air Pollution Control Commission, and, where applicable, the U.S. EPA (see §45-21-12)."

3.10 This definition should be amended to read, " Director means the director of the West Virginia Air Pollution Control Commission, and, where applicable, the U.S. EPA (see §45-21-12)."

3.25 The definition of VOC is acceptable, since the definition of approved has been amended.

3.26 The definition of "vapor control system" is acceptable.

§45-21-4 CONTROL AND PROHIBITION OF EMISSIONS

4.1b) West Virginia Air Pollution Control Commission (WV APCC) has amended this sub-section to read, "The source has been equipped with an approved vapor control system capable of achieving 85% emissions reduction." Therefore the issue has been resolved.

4.2b)(2) WV APCC added the word "support" following roof legs, keeping the sub-section consistent with the entire regulation. This issue has been resolved.

§45-21-7 INSPECTION, REPORTS, AND TESTING

7.1a) EPA recommends that this sub-section read, "routine visual inspections are conducted through roof hatches once per month; and,". However, the current draft language in this sub-section is acceptable to EPA.

7.1b) Please note this language was inadvertently incorrect in the EPA comments on the first draft. This sub-section should read, " a complete inspection of cover and seal is conducted,once per year, or whenever the tank is emptied for nonoperational reasons;

7.1b)(2) This sub-section should be deleted, since the above language will address inspection requirements.

§45-21-8 COMPLIANCE PROGRAMS

This section should be amended to read, "For sources previously not subject to the requirements of 45CSR21 (1979) or, for sources that previously complied with the requirements of 45CSR21 (1979), but as a result of amendments to this regulation (1991) are required to make major process changes and/or major capital expenditures, as determined by the commission, an acceptable program to comply with this regulation shall be developed and submitted to the commission by the owner and/or operator of such source within sixty (60) days of the effective date of this regulation. The program shall include the dates for ordering, receiving, installations, and start-up of necessary equipment. All such programs shall be approved by the commission. No such compliance program shall exceed one (1) year from the effective date of this regulation unless the owner and/or operator can demonstrate to the commission that compliance within such time limit is technically or economically infeasible. If the owner and/or operator can make such a demonstration, the commission may issue an order for additional time for compliance up to three (3) years from the effective date of this regulation. All such orders shall be issued only after notice to the public. All such orders shall contain a schedule and timetable for compliance, including increments of progress which will require compliance with the applicable requirements as expeditiously as practicable, and shall further require that the source comply with all the requirements of these regulations insofar as the source is able to do so. All such orders shall further require the source to include such measures as the commission determines are necessary to avoid an imminent and substantial endangerment to the public health. In the case of any major stationary source, no such order issued by the commission shall take effect until the Administrator of U.S. EPA determines that such order was issued in accordance with these requirements, or within the applicable provisions of the federal Clean Air Act. In the case of any source other than a major stationary source, any such order issued by the commission shall cease to be effective upon a determination by the Administrator of U.S. EPA that it was not issued in accordance with these requirements or with the applicable provisions of the federal Clean Air Act."

§45-21-11 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

§45-21-12 ENFORCEABILITY

This section should be amended to read, "For the purpose of federal enforceability of the provisions of this regulation, references to the commission and/or director, where applicable, shall also include the requirement that the Administrator of the U.S. EPA shall also approve the decisions of the commission and/or director."

BULK GASOLINE TERMINALS

§45-23-1 GENERAL

1.4 Refer to comment under §45-21-1, 1.4.

§45-23-3 DEFINITION

3.2 See comments under §45-21-3, 3.2.

3.4 See comments under §45-21-3, 3.3.

3.9 See comments under §45-21-3, 3.10.

3.12 The definition of "gasoline" is acceptable.

3.19 See comments under §45-21-3, 3.26

3.20 See comments under §45-21-3, 3.25.

§45-23-4 CONTROL AND PREVENTION OF EMISSIONS

4.2(a)(1) Issue resolved, since the WVAPCC has amended this sub-section to require 90 percent emissions reduction.

§45-23-7 REPORTS, AND TESTING

7.3 (a) Issue resolved, since the definition of approved has been amended.

7.3 (b) There is a typographical error in this sub-section. The second sentence should read, "... organic compound emissions from their point _of_ origination to the control equipment..."

7.3 (c) Issue resolved, since the definition of approved has been amended.

§45-23-8 COMPLIANCE PROGRAMS

See comments under §45-21-8.

§45-23-11 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

§45-23-12 ENFORCEABILITY

See comments under §45-21-12.

PETROLEUM REFINERY SOURCES

§45-24-1 GENERAL

1.4 See comments under §45-21-1.

§45-24-3 DEFINITION

3.3 See comments under §45-21-3, 3.2.

3.4 See comments under §45-21-3, 3.3.

3.10 See comments under §45-21-3, 3.10.

3.26 See comments under §45-21-3, 3.26.

3.27 See comments under §45-21-3, 3.25.

§45-24-4 CONTROL AND PREVENTION OF EMISSIONS

4.2(a) Issue resolved, since WVAPCC has amended this subsection to reflect EPA's comment.

4.3(b) Issue resolved, since WVAPCC has amended this subsection to reflect EPA's comment.

§45-24-7 REPORTS, AND TESTING

7.1 Issue resolved, since the definition of approved has been amended.

§45-24-8 COMPLIANCE PROGRAMS

See comments under §45-21-8.

§45-24-10 INCONSISTENCY BETWEEN REGULATIONS

EPA cannot approve this section, and recommends that this section be deleted.

§45-24-11 ENFORCEABILITY

See comments under §45-21-12.

EPA'S RESPONSE TO WVMA COMMENTS

WVMA COMMENT:

The Commission must eliminate ambiguities in the definition of the term "volatile organic compound" under sections 45-21-3.25, 45-23-3.20, and 45-24-3.27.

EPA'S RESPONSE:

West Virginia Manufacturers Association (WVMA) proposed definition of volatile organic compound (VOC) is inconsistent with EPA policy. References to vapor pressure cut-offs, i.e. 0.1 mm Hg must be excluded from the definition. Refer to enclosure 1 for further information.

WVMA COMMENT:

The Silicones Health Council proposed definition of volatile organic compound should be considered.

EPA'S RESPONSE:

WVMA's proposed definition of VOC as stated by the Silicones Health Council would be acceptable if sub-section iii were excluded.

WVMA COMMENT:

The term "vapor control system" should be defined consistently in sections 45-21-3.16, 45-23-3.19 and 45-24-3.26, and should be modified to reflect the technological impossibility of preventing 100% of VOC emissions.

EPA'S RESPONSE:

The definition of vapor control system (VCS) is acceptable to EPA.

WVMA COMMENT:

The Commission should not delete provisions presently contained in sections 45-21-4.4, 45-23-4.4 AND 45-24-4.4 which provide for petitions by owners and operators of covered sources for the granting of exemptions on a case-by-case basis.

EPA'S RESPONSE:

EPA cannot generically approve any alternative control system into a State regulation which is not explicitly described in the regulation.

Before inclusion of this section into West Virginia's SIP, West Virginia must clearly specify that any such alternative compliance plans must be submitted to EPA for approval. Alternatively, West Virginia may delete this provision from its regulations. Deletion of the provision does not prohibit any source from soliciting approval for alternative compliance plans.

WVMA COMMENT:

The proposed provisions of section 45-21-4.4, 45-23-4.4 and 45-24-4.4 requiring that, once regulated, a source remains subject to VOC rules despite later falling within an exemption level, should be eliminated.

EPA'S RESPONSE:

EPA policy requires all sources which now exceed or ever exceed the exemption level, to be subject to the applicable regulation from that time forward. Refer to enclosure 2 which is an excerpt from Appendix D of the November 24, 1987 Federal Register notice.

WVMA COMMENT:

Storage tanks with double seal internal floating roofs should not be subjected to the same requirements as storage tanks with single seal internal floating roofs.

EPA'S RESPONSE:

The Federal regulations cited by the WVMA regarding single seals verses double seals reflect the New Source Performance Standards (NSPS) for Volatile Organic Liquids Storage Vessels (Including Petroleum Liquid Storage Vessels) for which Construction, or Modification Commenced after July 23, 1984 and Storage Vessels for Petroleum Liquids for which Construction, Reconstruction, or Modification, Commended After June 11, 1973, and Prior to May 19, 1978. West Virginia's proposed regulations are being developed to provide for implementation of reasonably available control technology (RACT) for these source categories as required by the Clean Air Act. RACT requirements are established to ensure continued progress towards attainment of an ambient based air quality standard (in this case ozone). NSPS requirements are in many cases less stringent than RACT standards. In order for the Fixed Roof Petroleum Tanks to be controlled to RACT levels, WVAPCC proposed regulations must be consistent with the Control Technique Guideline for this source category.

WVMA COMMENT:

The definition of the term "gasoline" under the proposed rule for bulk gasoline terminals should be clarified to exclude lighter grades of petroleum products such as dry gas, propylene, and butanes.

EPA'S RESPONSE:
The definition of "gasoline" is acceptable to EPA.

WVMA COMMENT:
The proposed rule concerning bulk gasoline terminals should be clarified to allow the discharge of gasoline into sewers containing oil/water separators.

EPA'S RESPONSE:
EPA guidelines require this prohibition, in order for this proposed regulation to be approved by EPA as a SIP revision.

We appreciate the opportunity to review and comment on these draft regulations. As required by our SIP call of November 1989, and EPA's efforts to "level the playing field", these comments reflect the necessary changes that need to be made in order to make these VOC regulations federally approvable. Should you have any questions regarding our comments, please feel free to call me at (215) 597-9075 or your staff may contact Ms. Jacqueline Lewis at (215) 597-6863.

Sincerely,

Marcia L. Spink

Marcia L. Spink, Chief
Air Programs Branch

Enclosures

ENCLOSURE 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

MEMORANDUM

SUBJECT: Definition of VOC

FROM: G. T. Helms, Chief
Control Programs Operations Branch (MD-15)

TO: Chief, Air Branch, Regions I-X

Attached is a copy of a letter addressed to the State of Illinois Environmental Protection Agency, dated February 27, 1987, concerning the definition of "volatile organic compounds (VOC)."

As stated in the letter, "No VOC rules will be approved by USEPA unless VOC is substantively defined as all organic compounds except those that USEPA has listed as negligibly photochemically reactive in its Federal Register notices." This is USEPA's current policy.

In light of the post-1987 ozone policy and in order to ensure national consistency in the definition of VOC, State regulations with definitions that include a vapor pressure cutoff such as 0.1 mm Hg or 0.0019 PSIA that effectively exempts some photochemically reactive compounds from control must be revisited and revised as necessary.

The definition of VOC as cited in the letter or the definition cited in 40 CFR 60, Subpart A, 60.2, would be approved by USEPA; however, the recommended definition for VOC is as follows:

> Volatile Organic Compound (VOC) - Any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method or by procedures specified under 40 CFR Part 60. A reference method, an equivalent method, or an alternative method, however, may also measure nonreactive organic compounds. In such cases, an owner or operator may exclude the nonreactive organic compounds when determining compliance with a standard.

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Should you have any questions, please contact me (FTS 629-5526).

Attachment

cc: Ron Campbell
Gerald Emison
Jack Farmer
John Rasnic
B. J. Steigerwald
Peter Wyckoff
VOC Regulatory Contact, Regions I-X
VOC Enforcement Contact, Regions I-X

CTG RACT REGULATION CUTOFFS/EXEMPTIONS

- Recommended cutoffs contained in CTG's, model regulations, or EPA policy memorandums (See Attachment 1)

- For additional CTG categories size cutoffs, see SELECTED COATINGS CTG CATEGORY RECOMMENDED EXEMPTION LEVEL, page 16.

- Calculating regulation size cutoffs for CTG sources

  - Base tpy cutoff on theoretical potential to emit (design capacity [or maximum production] and 8760 hr/yr) before add-on controls. Care should be taken to make enforceable any regulations specified on an "actual" emissions basis.

  - Cutoff total determined from the sum of individual emission sources within same CTG category (Exception: petroleum marketing--storage tanks, terminals and loading racks must be combined)

  - Apply RACT if plantwide emissions > cutoff limit

  - If caught with emissions > cutoff limit in the future, then State must apply RACT ("once in, always in")

  - CTG area sources have no cutoff (e.g., cold cleaner degreasers and tank trucks)

- SIP call requires States to assess their existing VOC regulations and address cutoffs in EPA guidance. Exemptions can be granted only by way of the 5% rule (see Attachment 2)

- In cases where past guidance recommends high cutoff (e.g., 100 tpy), SIP call should also recommend that State investigate small exemption levels to prepare for additional emission reductions under full response to SIP call

REVIEW OF THE UCR PROTOCOL FOR DETERMINATION OF OH RATE CONSTANTS WITH VOCS AND ITS APPLICABILITY TO PREDICT PHOTOCHEMICAL OZONE PRODUCTION

by

Joseph J. Bufalini
Robert R. Arnts

Atmospheric Sciences Research Laboratory
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Research Triangle Park, North Carolina 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The experimental protocol for determining the rate constants for reactions of hydroxyl radicals (OH) with volatile organic chemicals (VOCs) as developed by the University of California-Riverside group is evaluated. Limits of detection and precision are discussed. This protocol is to be used as a measure of the ozone forming potential of a VOC; a compound with a high OH rate constant also very often produces high levels of ozone. Adaptations of the protocol for compounds containing halogen atoms are suggested. The protocol may not be applicable for compounds that do not produce RO_2 and HO_2 radicals such as carbon disulfide. Also, compounds that are free radical scavengers such as phenol, benzaldehyde and amines may not give high levels of ozone even though they may have a high rate of reaction with OH radicals. The long chained paraffins also present problems with the protocol since the RO_2 radicals produced after reacting with OH radicals in air do not oxidize NO to NO_2 but instead combine with the NO to form nitrates. When this occurs, it is recommended that the protocol be complemented with smog chamber experiments in order to establish the reactivities of VOCs.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF FIGURES

LIST OF TABLES

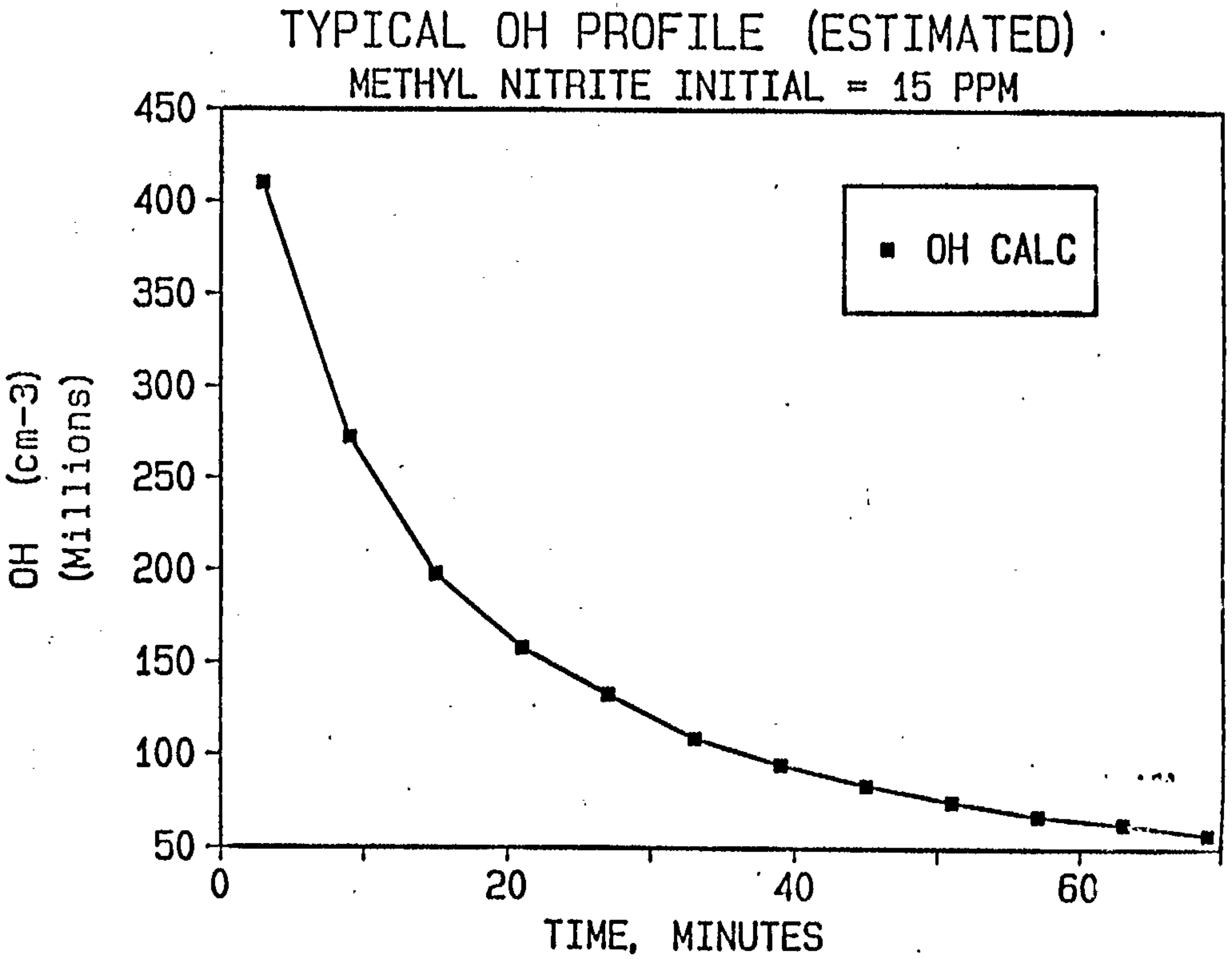

FIGURE 3. TYPICAL OH CONCENTRATION PROFILE RESULTING FROM THE PHOTODISSOCIATION OF METHYL NITRITE

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EPA/600/3-85/05E

EXPERIMENTAL PROTOCOL FOR DETERMINING HYDROXYL RADICAL REACTION RATE CONSTANTS FOR ORGANIC COMPOUNDS

Estimation of Atmospheric Reactivity

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Research and Development

October 1987

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PROJECT REPORT

REVIEW OF THE UCR PROTOCOL FOR DETERMINATION OF OH RATE CONSTANTS WITH VOCS AND ITS APPLICABILITY TO PREDICT PHOTOCHEMICAL OZONE PRODUCTION

A Review of UCR Protocol for Determination of OH Rate Constants with VOCs and Its Applicability to Predict Photochemical Ozone Production

Introduction

An experimental protocol for determining the rate constants for the reactions of hydroxyl radicals (OH) with volatile organic chemicals (VOCs) has been recently developed by the University of California-Riverside (1). This protocol provides a basis for determining the photochemical reactivity of organics in the atmosphere since it has been shown that the rate of reaction of an organic with OH radicals could be used as a measure of an organic compound's ability to produce ozone under polluted stagnant conditions (2). The reason for this is that the rate of reaction of an organic compound with OH radicals is normally the rate determining step. This is demonstrated in the following sequence of reactions:

(1) $RH + OH \rightarrow H_2O + R\cdot$

(2) $R\cdot + O_2 \rightarrow RO_2\cdot$

(3) $RO_2\cdot + NO \rightarrow RO\cdot + NO_2$

(4) $NO_2 + h\nu \rightarrow O + NO$

(5) $O + O_2 \xrightarrow{M} O_3$

Reactions (2) thru (5) are very fast and under sunlight conditions the rate at which ozone is produced (reaction (5)) is dependent primarily upon reaction (1). If reaction (1) is very fast, then ozone will also be produced quickly. However, not all organic compounds will undergo the sequence of reactions shown above. Therefore, not all organics will produce ozone since its formation is dependent upon the free radical chain process shown above. Also, some organics produce free radical scavengers which will interrupt the chain and the compound will produce little or no ozone. The protocol is based upon simultaneously monitoring the disappearance rates of a test compound (T) and a reference compound (R) whose OH reaction rate constant is already known.

$$(6) \quad T + OH \xrightarrow{k_6} \text{products}$$

$$(7) \quad R + OH \xrightarrow{k_7} \text{products}$$

$$(8) \quad T + h\nu \xrightarrow{k_p} \text{products}$$

$$(9) \quad T + \text{walls} \xrightarrow{k_w} \text{loss to walls}$$

where the loss of T is defined by

$$\text{I.} \quad \frac{d(T)}{dt} = k_6\,(OH)\,(T) + k'\,(T)$$

and the loss of R is defined by

$$\text{II.} \quad \frac{d(R)}{dt} = k_7\,(OH)\,(R)$$

where k_6 and k_7 are the OH rate constants for the test compound T and reference compound R respectively. The $k' = (k_p + k_w)$ is the first order photodissociation constant and/or wall loss of the test compound. The integration and combination of the I and II results in:

$$\text{III.} \quad \frac{1}{t-t_o} \ln \frac{T_o}{T_t} = \frac{k_6}{k_7} \cdot \frac{1}{(t-t_o)} \ln \frac{R_o}{R_t} + k'$$

Hence a plot of $(t-t_o)^{-1} \ln (T_o/T_t)$ versus $(t-t_o)^{-1} \ln (R_o/R_t)$ yields a straight line with a slope of k_6/k_7 and an intercept of k'. The rate constant of the test compound, k_6, is equal to the slope X k_7. If k' = 0 then Atkinson et al. (3) recommend evaluating k_6 by eliminating the time dependence from III which reduces to:

$$\text{IV.} \quad \ln \frac{T_o}{T_t} = \frac{k_6}{k_7} \ln \frac{R_o}{R_t}$$

and again solving for k_6 by calculating the product of the slope and k_7. They note that use of regression analysis with equation III to solve for the slope (k_6/k_7) and the intercept (k') places the most weight on those data points collected in the earliest part of the irradiation where the least amount of test compound has reacted. Their results and those of Edney et al. (4) using the same technique produced better regression coefficients with Equation IV than those using Equation III.

The experimental details can be found elsewhere (1). However we will summarize the basic procedures. Equation III (or IV) requires that the loss of reference compound and test compound be measured in the presence of OH as a function of time. The reference compound should be chosen with the following criteria: (1) should have an accurately known room temperature rate constant which is approximately equal to the anticipated rate of the test compound; (2) should not photolyze (at wavelengths > 290 nm) or air oxidize; (3) should be sufficiently volatile to remain in the gas phase and not be adsorbed on the walls; (4) be accurately measured by an available analytical technique; and (5) not react with the test compound, ozone, nitrogen dioxide, nitric acid, and nitrate radical. (Reactions with O_3 and NO_3 can be prevented and are discussed below.)

Similarly the test compound must satisfy certain criteria in order to be a candidate for this protocol: (1) An accurate analytical method must be available for making repeated measurements over a two hour period, and (2) the rates of loss by photolysis and wall losses are not much higher than the loss due to OH reaction $[(k_{OH-T})\,(OH) > k_{photolysis}]$. NOTE: for compounds which have a very high photolysis rate an alternate procedure for generation of OH in the dark is available (5).

The OH is generated by the photolysis of methyl nitrite in the presence of excess nitric oxide:

(10) $CH_3ONO + h\nu \rightarrow CH_3O + NO$

(11) $CH_3O + O_2 \rightarrow HCHO + HO_2$

(12) $HO_2 + NO \rightarrow NO_2 + OH$

The nitric oxide is added in excess in order to drive reaction (12) to completion and to prevent ozone formation since the NO_2 produced from reaction (12) will also photodissociate.

(13) $NO_2 + h\nu \rightarrow NO + O$

(14) $O + O_2 \xrightarrow{M} O_3$

(15) $O_3 + NO \rightarrow NO_2 + O_2$

The NO also prevents NO_3 formation which can in some cases react with the test compound.

Experimentally, a 100 liter light shielded Teflon bag is charged with 2 ppm each of test and reference compound, 5 ppm of nitric oxide and 10-15 ppm of methyl nitrite in zero air. The bag (two simultaneously in our experiments) is placed in the irradiation chamber. Before the bag cover is removed and the lamps switched on the reference and test compound are monitored for up to one hour. This is used to establish analytical precision and evaluate possible wall losses (k_w). The irradiation is then begun and the reference and test compounds monitored for up to one hour of irradiation. Pitts et al. recommend increasing the ratio of reference to test compound when the test compound is halogenated (1). They have found that the halogen may be released after OH attack and subsequently contribute competing non-OH removal processes. This gave a rate constant for the test compound that varied with different concentrations of reference and test compounds. By increasing the ratio of reference to test, the reference organic will scavenge the free halogen and the rate constant measured will reach a stable value.

In this report we will examine whether the UCR protocol is a valid technique for measuring OH rate constants, what precautions must be exercised to produce valid results, and the influence of error propagation on the rate constant and its application to compounds to which the protocol may not be applicable.

Comparability of OH Protocol to Other Methods

Since its development the University of California-Riverside (UCR) group has used this protocol to measure OH rate constants for a number of volatile and semi-volatile organics for which absolute rate constants have been reported. Comparison of UCR results with rates determined by absolute rate methods at room temperature and atmospheric pressure shows they produce equivalent results within their respective experimental errors (3, 6-9). The compounds tested represent a wide range of characteristics. They include alkanes, mono and di-alkenes, aromatics, chlorinated aromatics, alkynes, and a few miscellaneous chlorinated compounds (trichloroethylene, allyl chloride, benzyl chloride, and vinylidene chloride) (10). In addition we have recently determined the OH rate constant for five compounds: acetylene, 1,2-dichloroethane, 1,2-dibromoethane, p-dichlorobenzene, and carbon disulfide. The detailed results of that study are reported elsewhere (11). These compounds were studied primarily because EPA's Office of Air Quality Planning and Standards (OAQPS) needs to know if they are more, less, or of equivalent reactivity with OH compared to ethane. Ethane is being proposed by OAQPS as the reactivity reference compound because its reactivity, at concentrations normally found in the atmosphere, is not sufficient to produce ozone above the National Ambient Air Quality Standard (NAAQS). Modeling and smog chamber experiments have shown that ethane under usually observed ambient levels cannot produce enough ozone to exceed the standard even upon prolonged irradiations that may be encountered during multi-day stagnant conditions. Compounds of equivalent or less reactivity than ethane are not subject to regulation for control of photochemical ozone. All of these compounds have reported OH rate constants close to that of ethane. We found that acetylene, carbon disulfide, and p-dichlorobenzene have faster rates than ethane. Ethylene dichloride and ethylene dibromide were found to have rates which are statistically indistinguishable from ethane. The sixth compound studied, nitrobenzene, was not amenable to determination by the UCR protocol. The reasons for this were that the rate constant was low and the precision of the measurements were not very good. Its rate was less than 1.2 X 10^{-13} cm^3 $molec^{-1}$ s^{-1}. The rate we determined for acetylene (7.8 ± 21%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} is in excellent agreement with the recently recommended rate of (7.8 ± 25%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} at atmospheric pressure and room temperature (12). The rates we determined for ethylene dichloride and ethylene dibromide are (2.8 ± 21%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} and (2.4 ± 20%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1}. Atkinson (12) found only one report of these rate constants. They are (2.20 ± 27%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} and (2.50 ± 22%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} for CH_2ClCH_2Cl and CH_2BrCH_2Br respectively (12). The rate determined for p-dichlorobenzene was (4.3 ±20%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} which compares favorably with the single reported value of (3.2 ± 6%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} (12). The rate constant obtained for carbon disulfide is (29 ± 21%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1}. This is in good agreement with recently reported room temperature atmospheric pressure (in the presence of oxygen) rate constants of (27 ±22%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} and (20 ± 50%) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} (13-14).

In summary, it appears that the UCR protocol can be used to generate room temperature OH rate constants for a wide range of compounds. The results obtained in general produce results equivalent to those obtained by absolute methods (such as flash photolysis - resonance fluorescence and discharge flow-laser magnetic resonance). The method has been used by five different laboratories (University of California, Riverside (UCR), Atmospheric Sciences Research Laboratory (ASRL), Northrop Services Incorporated (NSI), Research Triangle Institute (RTI), and University of North Carolina (UNC) with good success and therefore does not appear to be a difficult technique to use.

As a result of the application of the UCR protocol in the studies mentioned above, we will present some additional recommendations for the use of this protocol and re-emphasize some important points stated in the original protocol.

Limit of Detection of the OH Rate Constant and Precision

As mentioned earlier UCR recommends using equation IV (the time excluded method) for calculating the OH rate constant when possible (if it can be demonstrated by using equation III that photolysis and wall reactions are not important). In such cases UCR, NSI, RTI, and UNC obtained better regression coefficients using equation IV (4). We obtained better correlations using equation III with those compounds for which photolysis and wall loss was unimportant (acetylene, ethylene dibromide, ethylene dichloride, and the 16:1 ethane/p-dichlorobenzene irradiations). Figures 1 and 2 show the data of one acetylene irradiation plotted by both equation III and IV respectively. The respective correlation coefficients are 0.960 and 0.830. Figure 3 illustrates the estimated OH concentration-time profile for this experiment. As can be seen the OH is decreasing exponentially with time. This also means that the test and reference organics are likewise exhibiting the most rapid decrease early in the irradiation. Thus, it is critical for calculating by equation III that samples withdrawn from the reaction vessel (bag) for analysis be accurately assigned their proper time (from the start of the irradiation). Our gas chromatographic analytical system was automatically controlled to withdraw samples from the bags and inject at 3 minute intervals (± 1 S). The UCR, NSI, RTI, and UNC experimental apparatus do not appear to be as precisely controlled. Most withdrew samples manually for analysis. Under such conditions it is difficult to achieve accurate measurements early in the irradiation where the concentrations are changing most rapidly. Thus, their use of the time excluded calculation (equation IV) obviates the need to know the irradiation time associated with a given analyses. Therefore, we recommend that data collected using the UCR protocol be analyzed by both equation III and IV (where applicable) to determine best fit.

The UCR protocol states that the procedure can be used to determine OH rates greater than 3 X 10^{-13} cm^3 $molec^{-1}$ s^{-1}. This limit is defined by the analytical precision of the method used to measure the test and reference compounds. If the protocol is applied to a test compound for which no statistically significant loss is measured over the irradiation period, an upper limit for the rate constant can be calculated based on the loss of the reference compound and the analytical precision of the test compound. An example of this is our experiments with nitrobenzene. Our analytical precision for nitrobenzene and ethane was ± 2.0% and ± 0.39% respectively. Over a 70 minute irradiation we observed 2.66% loss of ethane but no significant loss of nitrobenzene. If one assumes that a decrease in concentration of nitrobenzene equivalent to 3 times the analytical precision would be recognized as a significant loss, then an upper limit for the rate can be calculated from equation III.

$$\frac{1}{70\text{ min}} \ln \frac{2\text{ ppm}}{2\text{ ppm}-(0.0266)(2\text{ ppm})} = \frac{1}{70} \frac{k_6}{k_7} \ln \frac{2\text{ ppm}}{2\text{ ppm}-(3 \text{ X } 0.02)(2\text{ ppm})}$$

Solving for k_6 where $k_7 = 2.74 \text{ X } 10^{-13}$ cm^3 molec^{-1} s^{-1} an upper limit of 1.2 X 10^{-13} cm^3 molec^{-1} s^{-1} is obtained. The only reported rate for nitrobenzene is 1.3 X 10^{-13} cm^3 molec^{-1} s^{-1} (12).

Error analysis is not addressed in the UCR protocol. Some discussion is warranted since the primary use of this procedure is to determine whether a given VOC is sufficiently reactive to be considered for emission control. Thus, the question may be asked: Is compound A more reactive than compound B or vice versa? If compound A and B are reacted together using the UCR protocol, then the question can be answered by the determination of the slope as defined by equations III or IV. Regression analysis can be used to determine the ratio k_{A-OH}/k_{B-OH} along with a statistical measure of its random variation i.e. standard error. Thus, if the error bar (standard error, 95% confidence interval, etc.) does not include 1.0 then compound A can be significantly ranked faster or slower than B. If the error bar includes 1.0 then they must be classified equivalent. This procedure can be very accurate since the selected reference compound may be a benchmark compound such as ethane which defines a classification point. The method is not subject to concentration calibration errors since absolute concentrations are not required; only relative loss of compounds are measured. Determination of absolute concentrations, either OH or reactant, is usually the largest source of systematic error in absolute rate determination methods i.e. flash photolysis-resonance fluorescence.

If the protocol is used to calculate an absolute rate constant, then the error of the reference compound rate constant must be included. In general the error of the reference compound rate constant will contribute most to overall estimated error. The overall rate of k_6 and its relative standard deviation (rsd) is calculated by:

$$k_6 = (k_7)(\text{slope}) = [(\text{rsd})^2_{k_7} + (\text{rsd})^2_{\text{slope}}]^{1/2}$$

Thus, if a precisely defined rate for k_6 is needed, the reference compound selected must have a rate with a commensurate small error bar.

Special precautions for halogenated organics

Our last recommendation concerns the application of the protocol to halogenated compounds. Pitts et al. (1) caution that use of the protocol with halogenated compounds may result in the release of halogen atoms from the molecule after attack by OH. Free halogen can then attack the reference and/or the test compound causing non-OH loss of either or both compounds. Preferential attack of either may cause the plots of equation III to become non-linear as the irradiation progresses. If the free halogen attacks both test and reference compounds indiscriminately, then no apparent effect may be seen in plots of equation III. However, if the ratio of reference to test compound is increased from 1:1 to where the reference is in excess (i.e. 16:1) then the free halogen will preferentially react with the reference. This has the dual effect of (1) scavenging the free halogen from reacting with the test compound and (2) increasing the reference to free halogen ratio such that the loss of reference due to halogen attack is negligible compared to loss due to OH attack. NSI has studied a group of chlorinated compounds using the UCR protocol and has developed a procedure to extract a chlorine corrected OH rate constant (10). The procedure requires that irradiations be conducted over a range of reference to test compound ratios such that the ratio reflects a high excess of reference to test compound. The data is plotted by setting $y = \ln([R]_o/[R]_t)/\ln([T]_o/[T]_t)$ and $x = [T]_o/[R]_o$ where

$$\text{V.} \quad \frac{\ln([R]_o/[R]_t)}{\ln([T]_o/[T]_t)} = \alpha \frac{[T]_o}{[R]_o} + \frac{k_7}{k_6}$$

and α is the branching ratio, the halogen (X) released resulting from OH attack on the test compound.

$$(16) \quad OH + T \rightarrow \text{products} + \alpha X$$

The slope then is equal to α and the intercept is equal to k_7/k_6. This method was used to evaluate our data for 1,2-dichloroethane, 1,2-dibromoethane, and p-dichlorobenzene. The branching ratios obtained along with their associated 95% confidence intervals are: (1) ethylene dichloride $\alpha = 0.05 \pm 0.10$, (2) ethylene dibromide $\alpha = 0.86 \pm 0.97$ and (3) p-dichlorobenzene $\alpha = 0.20 \pm 0.16$. Since the error bars include $\alpha = 0$ for ethylene dichloride and ethylene dibromide, more experiments would have to be performed to ascertain the possible release of free halogen. There seems to be some indication that p-dichlorobenzene may be releasing some chlorine but further experiments would be required to confirm this effect. Nevertheless, computation of k_6/k_7 for ethylene dichloride and ethylene dibromide by equation III and V indicates that neither compound is more reactive than ethane; p-dichlorobenzene is according to calculation by equation III and V significantly faster reacting than ethane despite the uncertainty in the role of free chlorine.

Special Cases: The OH rate constant as a misleading indicator of VOC reactivity

As outlined earlier the accuracy with which the OH-organic rate constant may be used to indicate the role the VOC will play in ozone formation is dependent on a number of factors. The key assumption is that attack of the organic by OH will lead to the formation of free radicals (RO_2, HO_2) which will oxidize NO to NO_2 with the subsequent formation of ozone. If after attack by OH, free radicals are not formed or the organic reacts with the OH reaction product (as a free radical scavenger such as aniline) then the organic will produce less ozone than expected. Also, the OH rate constant may over-predict the ozone potential of the VOC if the OH reaction product is removed by heterogeneous processes i.e. condensation to form aerosol.

The OH rate constant may under-predict the ozone potential of a VOC if the OH reaction produces more radicals than would be predicted from the initial OH attack. An example of this is the production of photolabile compounds as a result of the initial OH-organic reaction. Subsequent photolysis of these products could produce more radicals leading to faster NO-NO_2 conversions with subsequent faster ozone formation rates. An example of this is acetylene which produces glyoxal upon reaction with OH radicals.

Lastly, to evaluate the overall ozone potential of a VOC, the rate of reaction of the VOC with O_3, NO_3, and by photolysis should be examined. Reaction by these routes in addition to OH reaction can lead to radical formation (or chain termination). Thus these processes could add to or subtract from the OH rate categorization procedure. Note: an indicator of the importance of photolysis as a tropospheric sink may be revealed by a positive y intercept (equation III) when using the OH protocol. Also if the VOC absorbs radiation at wavelengths greater than 290 nm then the possible role of photolysis should be evaluated. The photolysis rate may be further evaluated by another procedure (15).

Ultimately the use of the OH rate constant as a predictor for ozone potential is a crude though fundamental first step in ranking a VOC. To accurately assess whether an incremental change in emissions of a given VOC will result in a 'significant' change in ambient ozone concentration requires an understanding of not only the OH rate constant but a thorough understanding of the products generated by the oxidation and/or photolysis of that VOC. Also the chemistry of that VOC must be assessed in conjunction with the composition and chemistry of the airshed to which the VOC is emitted.

In the following section we present some examples of compounds which may be misclassified by sole reliance on their OH rate constant. They serve to point out the importance of understanding the OH oxidation products and their chemistry.

Carbon Disulfide

The OH rate constant for carbon disulfide was recently measured with this protocol and found to be $(2.7 \pm 0.6) \times 10^{-12}$ cc molec^{-1} s^{-1} (14). This makes CS_2 more reactive than ethane by a factor of approximately 10.

However, it does not necessarily follow that CS_2 will generate any ozone when irradiated in the presence of NO_x. The reason for this is that XO_2 (HO_2, RO_2 or other XO_2 radicals) must be produced to oxidize NO to NO_2. The reaction pathway for CS_2 is not clear. It has been shown that the OH reaction with CS_2 increases with increasing pressure and increases with decreasing temperature. Also the CS_2-OH reaction rate increases with increasing pressure of oxygen. Presumably the following set of reactions occur:

(17) $OH + CS_2 \overset{M}{\rightleftarrows} CS_2 OH$

(18) $CS_2OH + O_2 \rightarrow CS_2(OH)O_2\cdot$

The peroxide radical from reaction (18) has not been identified but its decomposition products COS and SO_2 have been. We can therefore postulate that the following is occurring.

(19) $CS_2(OH)O_2 \rightarrow HO_2 + CS_2O$

(20) $CS_2O + O_2 \rightarrow SO_2 + COS$

This mechanism is compatible with the data of Sickles and Wright (16) who observed ozone formation when CS_2 was irradiated in the presence of NO_x. However, additional work is needed with this compound since the peroxyl product from reaction (18) is speculative as is the formation of HO_2 from reaction (19). The ozone levels observed by Sickles and Wright could be a result of chamber artifacts or contamination. If additional smog chamber work indicates that ozone is produced from a CS_2/NO_x system, then the above mechanism is probably correct and CS_2 must be classified as a reactive VOC.

Phenol, Benzaldehyde and Amines

It has been shown that some organic compounds can act as smog inhibitors when added to a reactive system. In the photooxidation of propene in the presence of NO_x, the addition of phenol, benzaldehyde and aniline greatly reduced the rate of NO conversion to NO_2 and thus prevented significant ozone buildup (17). When benzaldehyde was added to a VOC/NO_x system, almost all smog manifestations decreased (less PAN, HCHO, ozone, HC reacted). However, eye irritation increased (18). All of these compounds have high OH rate constants; phenol - 28.3×10^{-12}, benzaldehyde - 11.9×10^{-12} and aniline - 1.19×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (12).

These compounds presumably inhibit free radical formation. In the case of phenol, the OH attack on the phenol molecule either occurs at the OH substituent or on the ring. If the former happens, the phenol doesn't promote free radical reaction but produces a nitrophenol. When the aromatic ring is fractionated, apparently some free radicals are produced but not enough to sustain the formation of RO_2 type radicals necessary for NO oxidation.

The photooxidation of benzaldehyde starts with the removal of the aldehydic hydrogen since this is the weakest bond. Once this happens, a rapid reaction with molecular oxygen occurs to produce a benzoyl peroxy radical,

(21) $\phi CO\cdot + O_2 \rightarrow \phi CO_3\cdot$

The radical will then react with NO_2 to produce peroxybenzoyl nitrate, ϕCO_2NO_3 (PbzN) or will oxidize NO to NO_2 to produce a benzoyloxy radical ($\phi CO_2\cdot$). This radical apparently decarboxylates to produce a phenyl radical which results in the production of o-nitrophenol after combining with NO_2 in air. Thus, benzaldehyde acts as a sink for NO_x and causes the chain length for the photooxidation reactions not to be very long and little ozone is produced. However PBzN is a strong eye irritant and probable phytotoxicant which in itself is not desirable in ambient air. Also preliminary Ames test data show PBzN has an approximately 10 fold greater mutagenic activity than PAN.

Carter and Atkinson (19) have recently determined the incremental reactivity (the effect on ozone production caused by the addition of the organic to a hydrocarbon surrogate-NO_x-air mixture designed to represent the current composition of urban air) of benzaldehyde and found this reactivity to be negative with all emission and VOC/NO_x ratio scenarios including a multi-day modeling scenario.

The photooxidation of amines proceeds thru the abstraction of a hydrogen both from the C-H and N-H bonds. The fate of the RNH radical is not known. For the dimethyl amine, nitrosamine, nitramine and methyl-methylene amine are produced.

It unclear whether these compounds will produce ozone upon prolonged irradiation. Diethyl hydroxyl amine (DEHA) for example has been proposed as a smog inhibitor (20). Heicklen has shown that the addition of DEHA to a photochemically reactive system can effectively control the photooxidation products. Product formation especially photochemically produced ozone can be inhibited as long as DEHA is present. This approach seems to work for first day irradiations as long as the DEHA persists. However, upon prolonged irradiation, both ozone and PAN are produced as products from DEHA. Also, the addition of DEHA to a reactive system produces mutagenic products (21). In the case of DEHA, one of the degradation products is acetaldehyde which is a good precursor for peroxyacetyl nitrate (PAN), a moderately strong mutagen (22).

Long Chained Paraffins

Long chained paraffins such as those used for printing oils ($>C_{15}$) react quickly with OH radicals ($k_{OH} = 1.3 \times 10^{-11}$ cc molec^{-1} sec^{-1}. However, the results of the environmental chamber experiments performed by Battelle are ambiguous (23). Some of their data suggest that the printing oils produce more ozone than ethane while some others produce less ozone than ethane. Thus, these long chain paraffins appear to be of borderline reactivity. Since those compounds have a high k_{OH} value, why do they not produce high levels of ozone? The probable reason is due to the following set of reactions:

(22) $n\text{-}C_{15}H_{32} + OH \xrightarrow{O_2} C_{15}H_{31}O_2\cdot$

(23) $C_{15}H_{31}O_2\cdot + NO \rightarrow a\, C_{15}H_{31}ONO_2 + (1-a)C_{15}H_{31}O\cdot + (1-a)NO_2$

(24) $C_{15}H_{31}O\cdot \xrightarrow{O_2} HOC_{15}H_{30}O_2\cdot$

(25) $HO\,C_{15}H_{30}O_2 + NO \rightarrow a'HOC_{15}H_{30}ONO_2 + (1-a')C_{15}H_{30}O\cdot + (1-a')NO_2$

(26) $HO\,C_{15}H_{30}O\cdot \xrightarrow{O_2}$ bifunctional group products + HO_2

The major differences between the higher molecular weight paraffins and the lower paraffins is the formation of stable nitrates. Rather than oxidizing the nitric oxide to NO_2 (as with reaction 3), the peroxy radicals rearrange to produce alkyl nitrates. This is an extremely important factor since the formation of a nitrate serves both as a free radical removal process as well as a NO_x removal process. Carter and Atkinson (19) estimate that as much as 43% of the radicals form nitrates.

Multi-day Effects

The UCR protocol was designed to measure the k_{OH} rate constant of a VOC. A VOC's reactivity in terms of ozone formed per amount of VOC reacted, however, as previously noted, will depend upon the chemical structure. The VOC/NO_x ratio and length of irradiation is also important. Reactive olefins such as trans-2-butene or the terpenes will at high VOC/NO_x ratios (>20/1) produce very little ozone. At high ratios, ozone is produced very quickly but the ozone quickly reacts with the olefins and little or no ozone remains. Since NO_x is also depleted through nitric acid and some peroxy acyl nitrate formation, there is insufficient NO_x to sustain ozone formation and subsequent buildup. Unless additional NO_x is added to the system, further exposure to irradiation (sunlight) similar to multi-day exposures will not produce additional ozone.

The slow reacting organics such as propane and butane show the opposite effect. In low VOC/NO_x ratios (<4/1) little or no ozone is produced on the first day of irradiation. The reason for this is that at low ratios, there are insufficient HO_2 and RO_2 radicals to convert all of the NO to NO_2. As long as NO is present, little ozone can be produced. However, as irradiation proceeds with the air-mass moving downwind, the VOC/NO_x ratio begins to increase due to the shorter lifetime of NO_x relative to the VOC. When this happens, usually late in the day, the solar intensity is decreasing and little ozone can be produced. On the second day conditions are more favorable for ozone formation. Sufficient HO_2 and RO_2 radicals are produced to sustain NO oxidation and ozone buildup will occur. Similarly, compounds that are free radical scavengers such as diethyl hydroxyl amine will also give rise to ozone upon prolonged irradiation encountered in multi-day exposures.

The favorable aspect of these observations is that ozone formation is curtailed until late in the afternoon or the next day. If curtailed, only the downwind area will be exposed to the ozone. This may not be a problem in some geographical areas. If ozone is delayed the second day, sufficient dilution will occur to reduce and spread the ozone over a larger area. If the dilution is sufficiently great, little ozone is observed on subsequent multi-day irradiations.

Concluding Comments and Recommendations

It is apparent that there are a significant number of compounds that are not amenable to this protocol. However, it is also apparent that these exceptions are usually compounds containing heteroatoms or are very high molecular weight compounds. We recommend that if there are any doubts concerning the reactivity of a specific compound either because of its structure or because it contains dissimilar atoms, then smog chamber experiments should be performed. These experiments involve a comparison of the photooxidation of a known concentration of ethane with NO_x in one chamber with the photooxidation of the test compound and NO_x in another chamber. By comparing the amount of ozone produced in both chambers, repeating the experiments with the compounds and chamber exchanged, the reactivity of the compound under consideration will be established.

This approach was recently tested with acetylene (24). Acetylene was found to have an OH reaction rate constant approximately three times that of ethane. We were uncertain that the reactivity of acetylene was greater than that of ethane because the mechanism for the photooxidation of acetylene is considerably different than that of ethane. The side by side experiments conclusively proved that acetylene produced more ozone upon photooxidation than ethane.

It should also be noted that reactivities measured with the k_{OH} protocol are on a molar basis. The rate constant is in cc molecule^{-1}s^{-1} i.e., the size of the molecule is not considered. Ordinarily, this does not present any problems since one is usually concerned with mechanistic relationships. However, the size of the molecules may become important when control strategies are considered. For example, 1 ppm of a C_{15} compound (such as the printing ink oils) contain many more atoms than a C_3 compound such as propane. Therefore, on a molar basis the C_{15} organic will be much more reactive (if we assume that the k_{OH} values are the same). However, on a weight basis, the C_{15} would be considered less reactive since many of the carbons, as noted earlier, will be involved in nitrate formation. When carrying out an assessment of reactivities for the purpose of regulatory action, reactivities in terms of mass emitted must be considered.

EXPERIMENTAL PROTOCOL FOR DETERMINING HYDROXYL RADICAL REACTION RATE CONSTANTS FOR ORGANIC COMPOUNDS

Estimation of Atmospheric Reactivity

by

James N. Pitts, Jr., Arthur M. Winer, Sara M. Aschmann
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Cooperative Agreement

CR-810214

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NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under cooperative agreement CR-810214 to the Statewide Air Pollution Research Center, University of California, Riverside. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

An experimental protocol for the determination at room temperature of rate constants for the reactions of hydroxyl radicals with organic chemicals in the gas phase is described in detail. This protocol provides a basis for evaluating the reactivity of organic substances which are emitted into the environment and which are consumed primarily by reaction with hydroxyl radicals.

The experimental technique is based upon monitoring the disappearance rates of the test compound and of a reference organic in irradiated methyl nitrite-NO-organic-air mixtures. Irradiations, employing blacklamps emitting in the actinic region, are carried out in ~75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite, zero to ~15 ppm; NO, ~5 ppm; test compound, ~1 ppm; reference organic, ~1 ppm. The test compound and reference organic are monitored by gas chromatography or other appropriate techniques and NO, NO_x, and O_3 by chemiluminescence instruments. Using this technique, OH radical rate constants $\geq 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} can be measured.

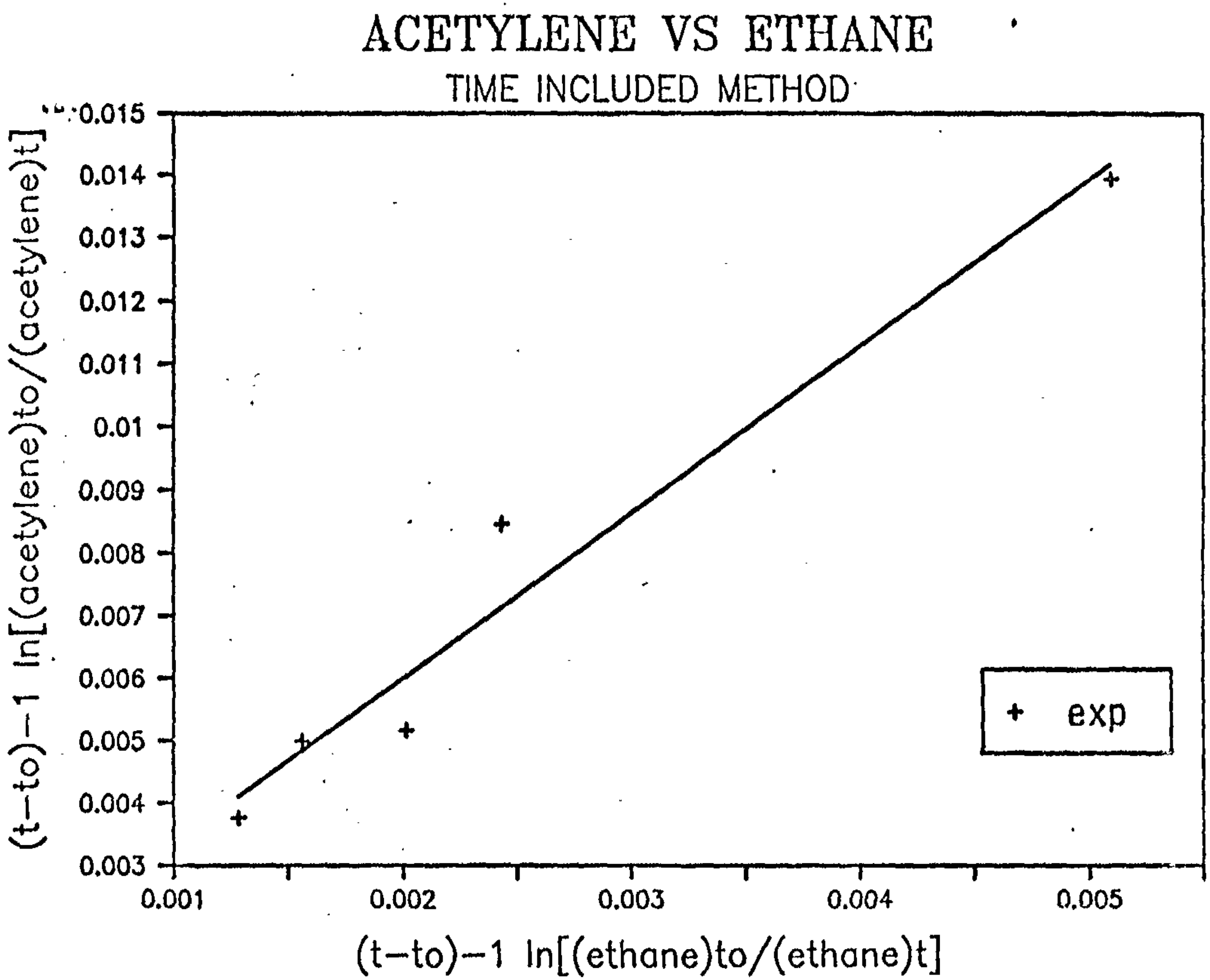

FIGURE 1. ACETYLENE DATA USING THE TIME DEPENDENT EQUATION III

②

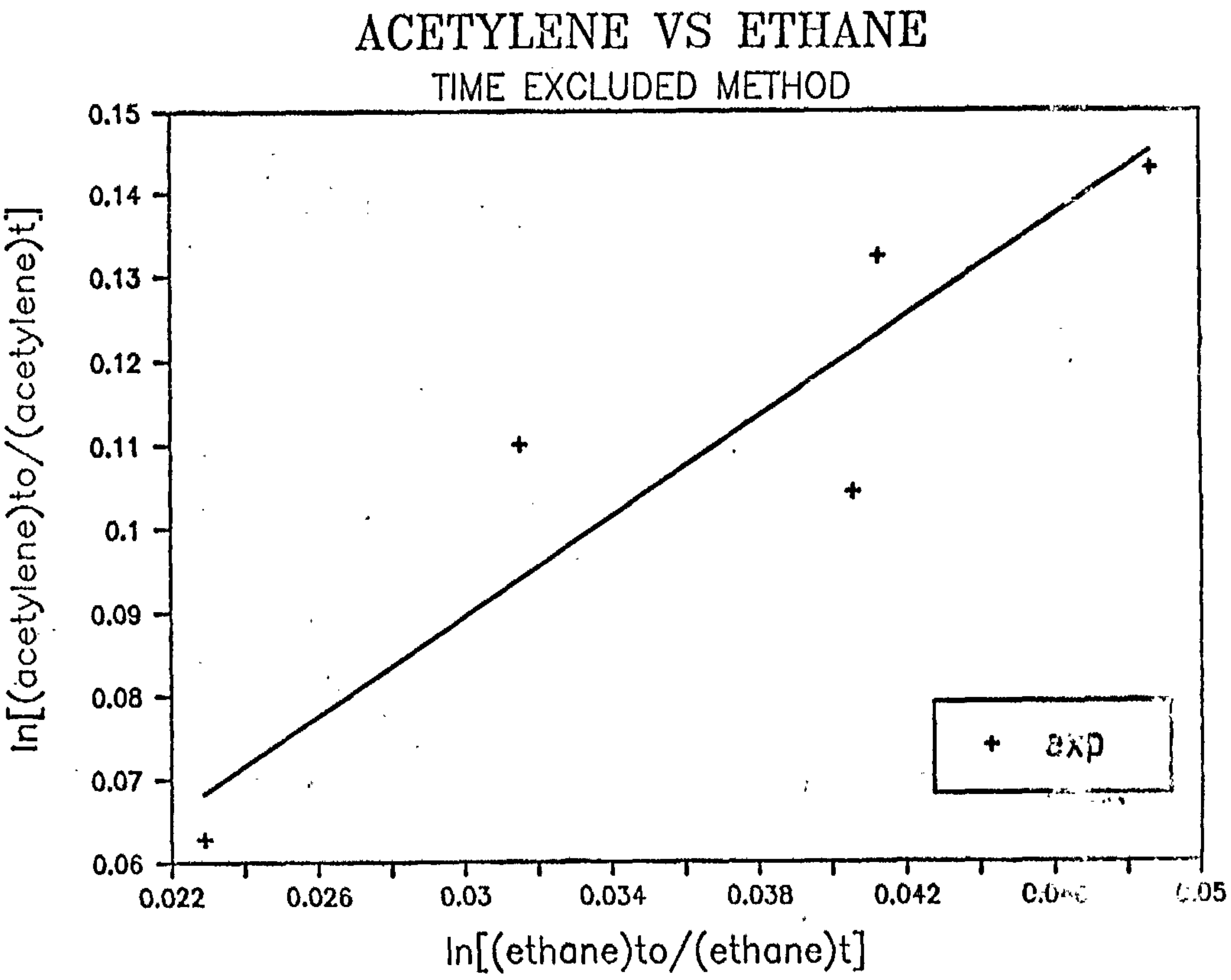

FIGURE 2. ACETYLENE DATA USING THE TIME INDEPENDENT EQUATION IV

**WEST VIRGINIA
MANUFACTURERS ASSOCIATION**

SUITE 505
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CHARLESTON, WV 25301
TELEPHONE (304) 342-2123

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AIR POLLUTION
CONTROL COMMISSION

June 18, 1990

Mr. G. Dale Farley
Director
West Virginia Air Pollution
Control Commission
1558 Washington Street, E.
Charleston, West Virginia 25311

Re: Amendments to Regulations on Volatile Organic Compounds.

Dear Director Farley:

As a follow-up to the recent hearing and filing of comments on the proposed amendments to rules governing the emissions of volatile organic compounds, we have come into the possession of some information from the State of California which we find to be interesting and helpful in dealing with the universe of VOCs to be regulated.

On behalf of the Manufacturers, we are therefore submitting these additional comments for your consideration. Enclosed you will find correspondence and documents with the California Air Resources Board dealing with the definition of "volatile organic compound". This definition proposed for use in California allows for flexibility in the regulation of VOCs by tying the State definition to the EPA listings for negligibly reactive compounds. Adopting a similar regulation would help to clarify this term and to exclude chemicals of low reactivity from regulation.

We urge your review and consideration of this approach for defining volatile organic compounds in each of the three regulations now under consideration by you.

Very truly yours,

Patrick M. Gallagher
President

Enclosures

cc: Mr. Robert L. Foster

DOW CORNING

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CONTROL COMMISSION

June 1, 1990

Ms. Peggy Vanicek
Manager, Solvents Control Section
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Ms. Vanicek:

The Silicones Health Council is an Association comprised of domestic and foreign silicone producer companies. Attached is a proposed definition of VOLATILE ORGANIC COMPOUND which the Council wishes to offer as a more flexible, yet meaningful, approach in regulating VOC's. The rationale supporting this proposed definition is also enclosed.

Your review and consideration of this proposal would be most appreciated. If further elaboration of this submittal is desired, please feel free to contact me.

Sincerely yours,

James W. Pollack

James W. Pollack, P.E.
Chairman
Environmental Affairs Committee
Silicones Health Council

JWPI/1-33

DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640 TELEPHONE 517 496-4000

Proposed Definition of Volatile Organic Compound

DEFINITION

Volatile Organic Compound means any compound containing at least one atom of carbon, excluding:

i) carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, methane, 1,1,1-trichloromethane [methyl chloroform], methylene chloride, trifluoromethane [FC-23], trichlorotrifluoromethane [CFC-113], dichlorodifluoromethane [CFC-12], trichlorofluoromethane [CFC-11], chlorodifluoromethane [CFC-22], dichlorotetrafluoroethane [CFC-114], chloropentafluoroethane [CFC-115], dichlorotrifluoroethane [HCFC-123], tetrafluoroethane [HFC-134a], dichlorofluoroethane [HCFC-141b], chlorodifluoroethane [HCFC-142b];

ii) any other negligibly reactive compounds listed by the Environmental Protection Agency pursuant to its Recommended Policy on the Control of Volatile Organic Compounds; and

iii) any other compounds less photochemically reactive than ethane. Photochemical reactivity shall be measured by the compound's hydroxyl radical (OH) reaction rate constant (kOH).

RATIONALE

The above definition for volatile organic compound (VOC) allows for flexibility in the regulation of VOC's. The Federal list of exemptions has expanded twice since its inception in 1977, the most recent expansion occurring just last year. By tying the California definition of VOC to the EPA listing, California will automatically keep current with developments in this area. Once a compound has been included in the EPA list of exempted compounds, the State of California may not take credit for controlling releases of the compound as part of the State's ozone SIP control strategy.

The South Coast Air Quality Management District Rules and Regulations contain an incomplete definition. The date of the rules and regulations is January, 1990, but the definition of reactive organic gases does not exclude the four compounds added to the Federal exemption list in 1989. In contrast, regulations proposed by the Bay Area Air Quality Management District in April, 1990, do not include the new additions to the list. This discrepancy demonstrates the need to link the State definition of VOC to the Federal definition of VOC.

EPA first announced its Recommended Policy on Control of Volatile Organic Compounds on July 8, 1977. See 42 Fed. Reg. 35314. EPA identified four negligibly reactive compounds in that initial notice: methane, ethane, methyl chloroform, and Freon 113. Ethane is the most reactive of these compounds. the EPA has since agreed that compounds found to be less reactive than ethane may be "considered for addition to the current list of negligibly reactive VOC's". 54 Fed. Reg. 1987, 1988 (1989) (adding specified halocarbons to the list of negligibly reactive compounds). The above definition allows for the exemption of a chemical less photochemically reactive than ethane without requiring an actual EPA listing of the chemical.

In January, 1990, the United States District Court for the Northern District of California ordered the CARB to adopt measures to reduce VOC emissions from consumer solvents by 4.0 tons per day. It would be inappropriate to seek to comply with the Court's order by reducing emissions of negligibly reactive compounds. Unless a definition of VOC similar to above definition is adopted, the CARB regulations may require reductions in emissions of compounds that the EPA has determined do not contribute to significant ozone buildup.

Faced with the immediate need to reduce ozone and smog formation, the substitution of less reactive compounds for higher reactive compounds should be encouraged. To this end, it is important to exclude chemicals of low reactivity from SIP regulation. An overly inclusive regulation will frustrate environmentally beneficial product reformulations, and may lead to more costly product reformulations or reduce product use and in some cases product bans without any environmental benefit.

Submitted by:

Silicones Health Council
1330 Connecticut Ave., N.W. #300
Washington, D.C. 20036-1702

Attn: William Smock
Executive Director

202/659-0060

SECTION I

INTRODUCTION AND BACKGROUND

Volatile organic compounds, when emitted into the atmosphere in the presence of oxides of nitrogen (NO_x), can react in sunlight to contribute to the photochemical formation of ozone and other photochemical oxidants, a major air quality problem in many areas of the United States. Organic compounds are known to differ to the extent in which they contribute to ozone formation, or increase the rate of its formation. In particular, certain organics react to form ozone extremely rapidly when irradiated in the presence of NO_x, while others are essentially inert in the lower troposphere or react too slowly to affect ozone formation in the area in which they are emitted. These differences, which are referred to as the "reactivity" of the compound, need to be taken into account in assessing the impacts of emissions of different organic compounds on photochemical ozone formation.

The reactivity of organic compounds with respect to ozone formation has been defined and measured in a number of ways. These include:

- The amount of ozone produced when the organic compound is irradiated in environmental chambers in the presence of NO_x.
- The rate of NO oxidation observed in such environmental chamber irradiations [NO oxidation in organic-NO_x-air irradiations is directly related to ozone formation, as discussed in detail elsewhere (Bufalini et al. 1976, Finlayson-Pitts and Pitts 1977, Atkinson and Lloyd 1984)].
- The rate of removal of the organic compound in environmental chamber irradiations.
- The rate at which the organic compound reacts with hydroxyl radicals.

The first three of these approaches to defining and measuring reactivity involve the use of environmental chamber irradiations, which have served as the basis of most past studies of ozone forming reactivity. However, environmental chamber irradiations are subject to a number of problems, for example "dirty chamber" effects, and this experimental technique has been shown to be particularly unsatisfactory in determining the ozone-forming reactivities of slowly reacting compounds

(Bufalini et al. 1977). Since an important question concerning the reactivity of organic compounds involves differentiating between organic compounds considered to be unreactive and those which are reactive, this is a serious limitation.

Some of the problems with defining and measuring reactivity using smog chamber experiments can be circumvented by defining reactivity in terms of the rates at which the organic compounds react with the hydroxyl (OH) radical. This involves, in general, far fewer experimental problems, since for most compounds these rate constants can be measured to a fair degree of accuracy by a number of techniques, some of which are suitable for slowly reacting compounds (Atkinson et al. 1979, Atkinson 1985). This definition of reactivity assumes that reaction with the hydroxyl radical is the major atmospheric loss process for the organic compound being tested, and that the rate at which the compound reacts in the atmosphere is the most important factor in influencing its overall reactivity. As discussed below in section I.A, these assumptions are not always correct. Thus some organic compounds are consumed to a significant extent in the atmosphere by other reaction pathways, and in certain cases factors other than the initial OH radical reaction rates can have a significant influence on their overall reactivity. However, for a majority of the organics which are currently emitted in significant quantities into the atmosphere and whose atmospheric reactions have been studied, reaction with OH radicals is indeed the major removal process (Atkinson et al. 1979, Atkinson 1985). Furthermore after reaction with OH radicals, these compounds generally tend to form intermediates which cause ozone formation in the presence of NO_x and sunlight (Bufalini et al. 1976, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson et al. 1979, Atkinson and Lloyd 1984).

In this document, a procedure is described for measurement of the room temperature rate constants for the reaction of organic compounds with OH radicals, in order to assess their atmospheric reactivity. This procedure is based on the relative rate technique previously developed and tested by Pitts et al. (1982), and is among the simplest of the techniques which can be accurately applied for this purpose. An overview of this procedure is given in section I.B below. However, this procedure has a number of limitations, both with respect to the concept of defining ozone-forming reactivity solely in terms of hydroxyl radical rate constants, and with respect to experimental problems with the technique when applied to measuring OH radical rate constants for certain classes of organic compounds. The potential experimental limitations are discussed in section I.C. Despite these limitations, however, the procedure described in this document can be usefully employed as a preliminary screening method for assessing the ozone-forming reactivity for many classes of organic compounds.

A. Factors Affecting Reactivity

The extent to which an organic compound contributes to ozone formation is influenced by a number of factors, and in principle all of these should be taken into account in assessing its reactivity. These factors are:

- How rapidly the organic compound reacts in the atmosphere.
- The amount of ozone formed (or NO oxidized) when a given amount of the organic compound reacts.
- The extent to which the reactions of the organic compound enhance or suppress radical levels, which affects the rates of reaction of all organic compounds present in that particular air mass.
- The extent to which the reactions of the organic compound contribute to the consumption of NO_x; this in turn affects ozone formation since this is only significant when NO_x is present.

The chemical loss rate of an organic compound under atmospheric conditions is an important factor with regards to its ozone forming potential. This is especially so for the slower reacting organic compounds, since if they do not react they can have no effect on ozone formation. Thus the reaction rate under atmospheric conditions is an important factor with regard to whether or not an organic compound can be considered to be reactive or unreactive with respect to O_3 formation. As indicated above, the experimental protocol described in this document is concerned with measuring this aspect of reactivity.

However, once a compound emitted into the atmosphere has undergone reaction, mechanistic factors, in particular those listed above, determine the specific influence of the organic compound on ozone formation. An important factor is whether the reactions of the compound suppress or enhance radical levels. Since the formation of photochemical smog is primarily a radical chain process, radical inhibitors or initiators have an important effect on the overall reactions in the system, including the rates at which other organic compounds react to cause ozone formation. Certain compounds, such as toluene and the xylenes (Atkinson et al. 1980, Killus and Whitten 1982), and furan and pyrrole (Carter et al. 1984a) tend to be more reactive in NO_x-air irradiations than expected from their OH radical rate constants. This is attributed to the formation of radical initiators in their atmospheric photooxidation reactions pathway. Certain chlorinated compounds, such as tetrachloroethene, also tend to be more reactive than expected, due to radical initiation via the formation of chlorine atoms.

A number of other organic compounds which have been studied have been shown to have significant radical (as well as NO_x) sinks, and thus act as inhibitors for ozone formation. Examples of such compounds are benzaldehyde (Atkinson et al. 1980), the cresols (Atkinson et al. 1980), amines (Lindley et al. 1979), and the higher alkanes (Atkinson and Lloyd 1984). For these compounds, ozone formation in their NO_x-air photooxidation is markedly less than expected based solely on their rates of reaction with the OH radical. Furthermore, addition of these compounds to photochemical smog systems can cause a reduction, rather than an enhancement, of ozone formation, leading to the concept of "negative" reactivity. This possibility of negative reactivity is not taken into account when reactivity is defined solely in terms of OH radical reaction rates. However, for compounds which are not radical inhibitors the rates at which they react can serve as a semi-quantitative estimate of their ozone-forming reactivity.

The protocol described in this document is based on the assumption that organic compounds are consumed in the atmosphere primarily by reaction with the hydroxyl radical. However, certain organic compounds can react in the atmosphere in a number of other ways, and environmental chamber and laboratory studies have shown examples for which one or more of the following removal processes are of significance:

- Reaction with ozone.
- Direct photolysis.
- Reaction with the nitrate (NO_3) radical.
- Reaction with nitric acid (HNO_3).

For example, reaction with ozone is an important atmospheric sink for the alkenes and other unsaturated compounds, and may be the dominant removal process for the hydrazines (Tuazon et al. 1981, Atkinson and Carter 1984). Direct photolysis can be an important removal process for carbonyl compounds and is the dominant atmospheric sink for most nitrites and nitroso compounds. Reaction with the NO_3 radical has been shown to be a dominant sink for the reactions of phenolic compounds in atmospheres polluted with both ozone and NO_x (Carter et al. 1981, Atkinson et al. 1984), and has been more recently shown to be an important atmospheric sink for a number of other compounds, examples being furan, thiophene, and pyrrole (Atkinson et al. 1985), the monoterpenes, and dimethyl sulfide (Winer et al. 1984). For basic compounds such as the amines and pyridine, reaction with nitric acid is possibly an important removal process in polluted atmospheres, where significant quantities of nitric acid may be present.

However, as indicated above, for most organic compounds reaction with the hydroxyl radical is the dominant homogeneous atmospheric removal process. Thus, for example, reaction with hydroxyl radicals is the major atmospheric removal process for the alkanes, aromatic hydrocarbons, simple saturated alcohols and ethers, saturated halogenated organics and many other classes of compounds (Atkinson 1985). These constitute a majority of the organic compounds which are emitted in significant quantities into the atmosphere and whose atmospheric reaction rates are known or can be estimated. For compounds such as these, the application of this protocol can give a reasonably reliable indication of atmospheric removal rates, and a basis for estimating their reactivity with respect to ozone formation.

B. Overall Approach Employed

As indicated above, the experimental procedure described in this document consists of measuring the relative rate constants for the reaction of volatile organic compounds with the hydroxyl radical. This procedure also yields information regarding the photolysis rate constants for these organic compounds, though a protocol specifically designed for that purpose is described in detail elsewhere (Carter et al. 1984b). The specific experimental procedure for determining OH radical rate constants is based on measuring the relative rates of disappearance of the test compound and a reference organic in irradiated methyl nitrite (CH_3ONO)-NO-organic-air mixtures. If both the test and reference organics are consumed primarily by reaction with OH radicals, then the data can be analyzed to yield the ratio of OH radical rate constants for those two compounds. Using the known rate constant for the reaction of OH radicals with the reference organic, the rate constant for the test compound can then be determined.

The photolysis of CH_3ONO in air is a convenient method to generate high concentrations of OH radicals by the following reactions:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In the presence of added organics, the OH radicals react with these organics:

$$OH + \text{test compound} \rightarrow \text{products} \qquad (1)$$

$$OH + \text{reference organic} \rightarrow \text{products} \qquad (2)$$

In addition, the test compound may also photolyze, react with ozone and/or react with the NO_3 radical:

$$\text{test compound} + h\nu \rightarrow \text{products} \qquad (3)$$

$$\text{test compound} + O_3 \rightarrow \text{products} \qquad (4)$$

$$\text{test compound} + NO_3 \rightarrow \text{products} \qquad (5)$$

Excess NO is included in the reaction mixture in order to minimize the importance of reactions (4) and (5), since O_3 and NO_3 both react rapidly with NO:

$$OH + CH_2O \rightarrow H_2O + CHO$$

$$OH + NO_2 \rightarrow HNO_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$CHO + O_2 \rightarrow HO_2 + CO$$

$$NO + NO_3 \rightarrow 2\ NO_2$$

If the organics are lost only by reaction with OH radicals and, for the test compound, photolysis, then

$$-d[\text{test compound}]/dt = k_1[OH][\text{test compound}] + k_3\ [\text{test compound}] \qquad (I)$$

$$-d[\text{reference organic}]/dt = k_2[OH]\ [\text{reference organic}] \qquad (II)$$

where k_1 and k_2 are the OH radical rate constants for reactions (1) and (2), respectively, and k_3 is the photolysis rate constant. Hence

$$d\ln[\text{test compound}]/dt = k_1[OH] + k_3 \qquad (III)$$

and

$$d\ln[\text{reference organic}]/dt = k_2[OH] \qquad (IV)$$

Elimination of the OH radical concentration and integration leads to

$$\frac{1}{(t-t_o)} \ln \left\{ \frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t} \right\} = k_3 + \frac{k_1}{k_2(t-t_o)} \ln \left\{ \frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t} \right\} \qquad (V)$$

where $[\text{test compound}]_{t_o}$ and $[\text{reference organic}]_{t_o}$ are the concentrations of the test compound and the reference organic, respectively, at time t_o, and $[\text{test compound}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time t. Note that equation (V) is valid even if the OH radical concentration varies with time.

Hence a plot of $(t-t_o)^{-1}\ \ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $(t-t_o)^{-1}\ \ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 and intercept k_3. Knowing k_2, the rate constant k_1 may then be derived. If the test compound does not photolyze (i.e., $k_3 = 0$), then equation (V) can be simplified to yield:

$$\ln\left\{\frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}\right\} \qquad (VI)$$

and a plot of ln ([test compound]$_{t_o}$/[test compound]$_t$) against ln ([reference organic]$_{t_o}$/[reference organic]$_t$) should yield a straight line of slope k_1/k_2 with a zero intercept.

The concentrations of the test compound and the reference organic are monitored before and during irradiation of the CH_3ONO-NO-test compound-reference organic-air mixtures by gas chromatography or by other suitable analytical techniques. Hence the lower limit to k_1 that can be determined is set by the precision of the analyses, but is expected to be of the order of $\leq 3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1} under optimum conditions.

C. Limitations of the Experimental Technique

The general technique outlined above and described in detail in the following sections has been developed to provide rate constant ratios for the reactions of OH radicals with a wide variety of organic compounds, with an experimental precision in many cases exceeding that possible with current absolute techniques (see Atkinson 1985 for examples and a discussion of the current rate constant measurement techniques). However, there are certain classes of compounds for which this technique probably cannot be successfully applied, at least not without significant modifications. Examples of such classes are as follow:

- Compounds which react with OH radicals with rate constants lower than $\sim 3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. This is not a serious limitation for the purpose of estimating their ozone-forming reactivity since compounds which react slower than this are considered to be unreactive. (An OH radical rate constant of 3×10^{-13} cm^3 molecule^{-1} sec^{-1} corresponds to an atmospheric lifetime of >80 days, assuming a global 24-hour annual average OH radical concentration of $\sim 5 \times 10^5$ cm^{-3}.)

- Compounds for which no reliable and precise technique exists for measurement of their concentration in air. The measurement technique should be sensitive enough to monitor the organic compound at part-per-million (ppm) levels. This protocol presumes that such a suitable analytical technique for the test compound and the appropriate reference organic exists and is available at the laboratory carrying out this protocol. However, since this technique is based on the measurement of relative decay rates, it is not necessary to be able to measure the absolute concentrations. Thus, this protocol can be applied even if no reliable technique exists for the measurement of absolute concentrations of the test organic.

- Compounds which have insufficient volatility to be introduced into the gas phase at high enough concentrations to be measured. It should be noted, however, that extremely non-volatile compounds can be considered to be unreactive, and this protocol thus need not be applied to such compounds.

- Compounds which tend to be absorbed onto the walls of the reaction vessel. This is evidenced by (a) the levels of the compound monitored in the gas phase in the reactor being less than those expected from the quantity injected, (b) by the measured concentrations of the compound decreasing with time in the reaction chamber prior to the irradiation, or (c) by the gas phase concentration of the organic compound increasing after the lights are turned on. Tests for determining whether or not any of these occur must be carried out prior to conducting this protocol. Moderate wall adsorption problems may not be too severe a limitation providing that the organic compound reacts sufficiently rapidly that the the rate of its consumption due to chemical reaction when the lights are on is more rapid than the rate of wall adsorption/desorption. However, the kinetic data obtained will necessarily be more uncertain.

- Compounds which photolyze so rapidly that their photolysis is a more important loss process in CH_3ONO-air photolysis systems than is their reaction with OH radicals. This will be the case for compounds whose photolysis rates in sunlight or blacklight irradiation are comparable to or exceed that of methyl nitrite and can be readily checked by carrying out the experimental protocol as described below. For such compounds, an alternate procedure based on using the hydrazine + ozone reaction as a dark OH radical source can be applied — provided that they do not react with hydrazine or ozone (Tuazon et al. 1983). However, if a compound photolyzes this rapidly, then photolysis will be its dominant atmospheric removal pathway and its OH radical rate constant will not be an important factor in determining its reactivity.

- Compounds whose photooxidation mechanism involves the release of chlorine (or possibly fluorine) atoms, since these may contribute to the consumption of the test compound and the reference organic. If this is suspected to be the case, ethane, propane or some other suitable compound whose Cl atom/OH radical rate constant ratio is significantly higher than that for the reference organic can be included in the reaction mixture at sufficiently high levels that the majority of the chlorine atoms reacts with it. (Chlorine atoms are a more reactive and thus less discriminating species than OH radicals in terms of reacting with most organics, and thus the Cl atom/OH rate constant ratio will be relatively higher for less reactive compounds.) The modifications to the protocol for such cases is beyond the scope of this document.

- Compounds which react with nitric acid vapor. Nitric acid is formed as a product in irradiated CH_3ONO-NO systems from the reaction with OH radicals with NO_2, and may thus contribute to the consumption of the test organic if the test organic reacts with HNO_3. Tests can be carried out to determine whether this is the case, especially if the compound is known to be basic in nature.

In general, if the results of this protocol appear to be anomalous, as indicated, for example, by non-linear plots of equation (V), then the possibility of these or other experimental problems should be investigated. In some cases, such problems may be anticipated based on our knowledge of the chemistry of the class of compounds being investigated. In these cases, appropriate tests should be carried out to assure the validity of the protocol.

SECTION II

GENERAL EQUIPMENT AND MATERIALS REQUIRED

To determine rate constants for the reaction of OH radicals with organic compounds using the method outlined above, the following major pieces of equipment are needed:

- A gas chromatograph or other analytical equipment required for precision gas phase analyses of the test and reference organics.
- An ozone monitor equipped with a filter to remove particulates.
- An NO-NO_x monitor.
- A Teflon bag or chamber in which the reaction can be carried out.
- An arrangement of fluorescent lamps.
- A greaseless high vacuum rack.

The specific requirements and recommendations for these items of equipment are discussed below.

A. Methods for the Analyses of the Test and Reference Organics

While it can be seen [equations (V) and (VI)] that only relative measurements of the test and reference organic concentration are necessary, it is recommended that quantitative analyses be carried out. For the development of this experimental protocol, gas chromatography was used to analyze the test and reference organics. However, any analysis technique that is specific for the test and reference organics, can monitor these compounds at the concentrations necessary for this protocol, i.e., ~0.1-1 part-per-million (ppm), and which samples over a time period short compared to the irradiation times can in principle be used. (For example, mass spectrometry, combined gas chromatography-mass spectrometry or in-situ spectroscopic techniques can also be employed). Since sampling for the test and reference organics must be carried out simultaneously for this protocol, the same technique of choice should be used for both species. It is taken for granted that quantitative analyses of the test compound by such techniques will have been developed at the laboratory conducting this protocol. Hence, this aspect of the protocol is considered beyond the scope of this document.

For the reference organics which are recommended for use here (see Section III), the gas chromatographic columns and conditions used in the development of this protocol were as follows (Pitts et al. 1979):

n-Butane, cyclohexane, isoprene and 2-methyl-2-butene (and other C_4 through C_{10} n-alkanes) were analyzed using a 20-ft x 1/8-in. stainless steel column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb G, operated at 333 K. The N_2 carrier gas flow was 50 cm^3 min^{-1}, and a 3.0 cm^3 gas sample loop was used.

Propene, n-butane (and other $>C_3$ alkanes and alkenes) were analyzed using a 36-ft x 1/8-in. stainless steel column of 10% 2,4-dimethylsulfolane on C-22 firebrick (100/120 mesh) operated at 273 K. The N_2 carrier gas flow was 80 cm^3 min^{-1} and a 2.0 cm^3 gas sampling loop was used.

For all of these analytical systems, no preconcentration was necessary and flame ionization detection was employed in all uses.

B. Ozone Monitor

It is necessary to monitor ozone when carrying out this protocol in order to assure that it is not being formed at sufficiently high concentrations to contribute to the consumption of organics which might react with ozone or NO_3 radicals. A chemiluminescence ozone analyzer is recommended for this protocol since the ozone analyzers utilizing ultraviolet absorption tend to respond not only to ozone but also to some chemicals which absorb radiation at 253.7 nm [e.g., the cresols (Atkinson et al. 1980)]. This may include some of the OH radical reaction products. The ozone analyzer used will have an optimum sampling rate specified by the manufacturer; any sampling rate less than ~2 liters min^{-1} is acceptable. The ozone analyzer should be calibrated according to the manufacturer's specifications.

C. $NO-NO_x$ Monitor

A chemiluminescence $NO-NO_x$ monitor (using the ozone-nitric oxide reaction) is recommended for this protocol. The monitor should be calibrated according to the manufacturer's specifications. It should be noted that the NO_2 and NO_x readings on such monitors are subject to positive interferences by organic nitrates and other nitrogenous species (Winer et al. 1974), including methyl nitrite and the methyl nitrate formed as a product in the methyl nitrite-NO irradiation system. Thus these readings can only be taken to be upper limits to the true NO_2 or NO_x levels. This will be particularly true if the test organic or reference compound are nitrogenous compounds, or if they tend to form, as is the case for the higher alkanes, organic nitrates in their NO_x-air photooxidation reactions. Fortunately, accurate NO_2 measurements are not required for this protocol. The NO data are unaffected by this interference.

D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly

1. Reaction Chamber

A simple, yet totally adequate, reaction chamber consists of an ~75-liter FEP Teflon cylindrical reaction bag (FEP Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.), formed from three pieces of 2 mil FEP Teflon. A diagram showing the construction of such a reactor is shown in Figure 1. The two end pieces are ~45 cm in diameter with an ~45 cm wide, ~140 cm long piece forming the cylinder. Teflon is the preferred material for construction of the reaction chamber because of its general inertness to ozone and its lack of hydrocarbon offgassing.

2. Injection and Sampling Port

Prior to heat sealing the Teflon chamber sides, a port for injection of the reactants and for sampling must be fitted. This sampling and injection port should be constructed of TFE Teflon nuts and bolts with the appropriate Swagelok stainless steel fittings. (Swagelok is a registered trade name of Crawford Fitting Company.)

Figure 2 shows the design of the sampling and injection port used in this protocol. The port consists of a 2-3" long hollow bolt of Teflon (A), machined on the exterior surface with threads. The interior hold (B) is 1/4" in diameter and an ~8" long 1/4" o.d. Teflon tube is inserted as shown. Two Teflon nuts (D) then screw over the bolt (A), one on the inside of the bag, the other on the outside. Large Teflon washers (E) are placed between the Teflon bag and the nuts (D), thus enabling the nuts to be tightened without twisting or stretching the Teflon bag. The 1/4" o.d. Teflon tube is connected outside the reaction bag to a glass-Teflon stopcock.

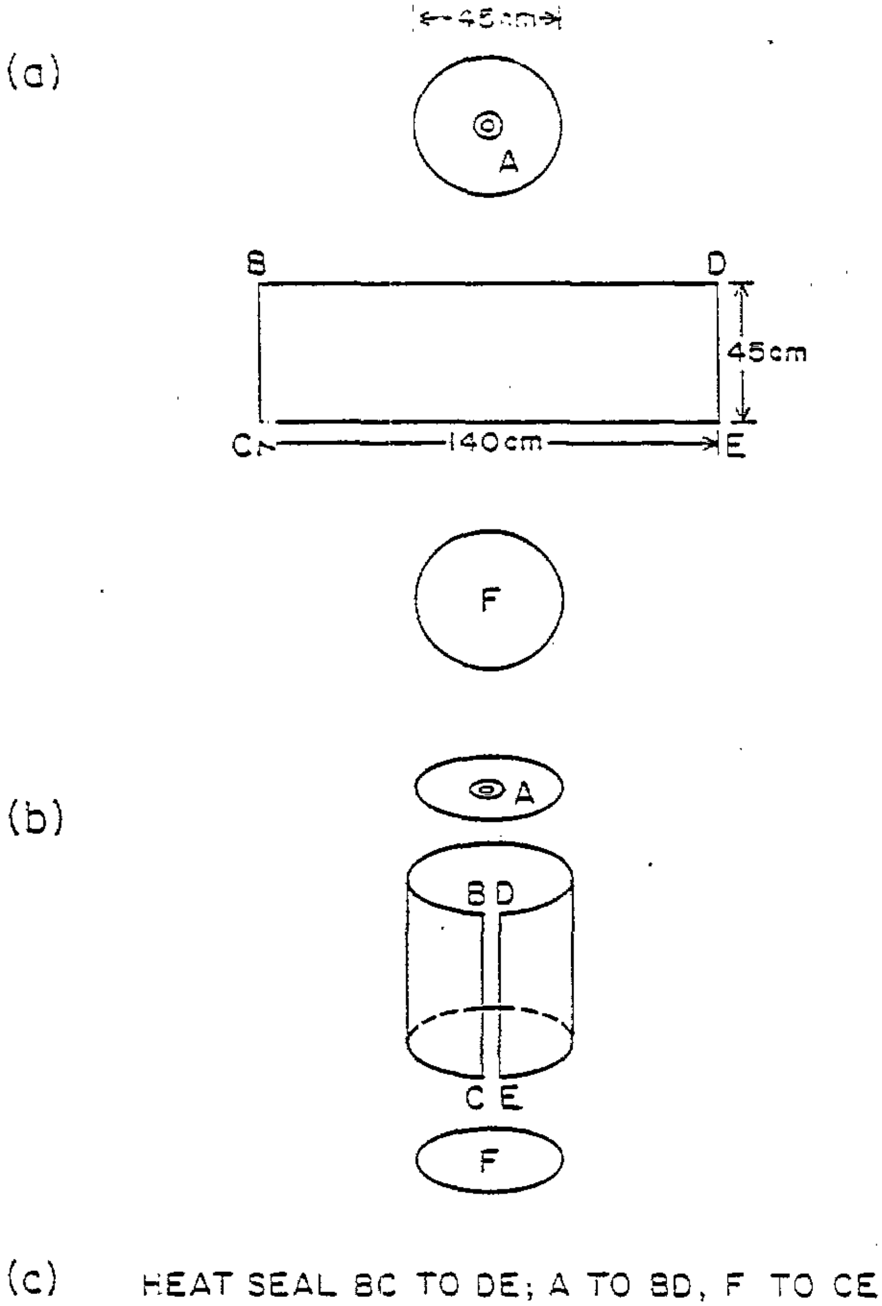
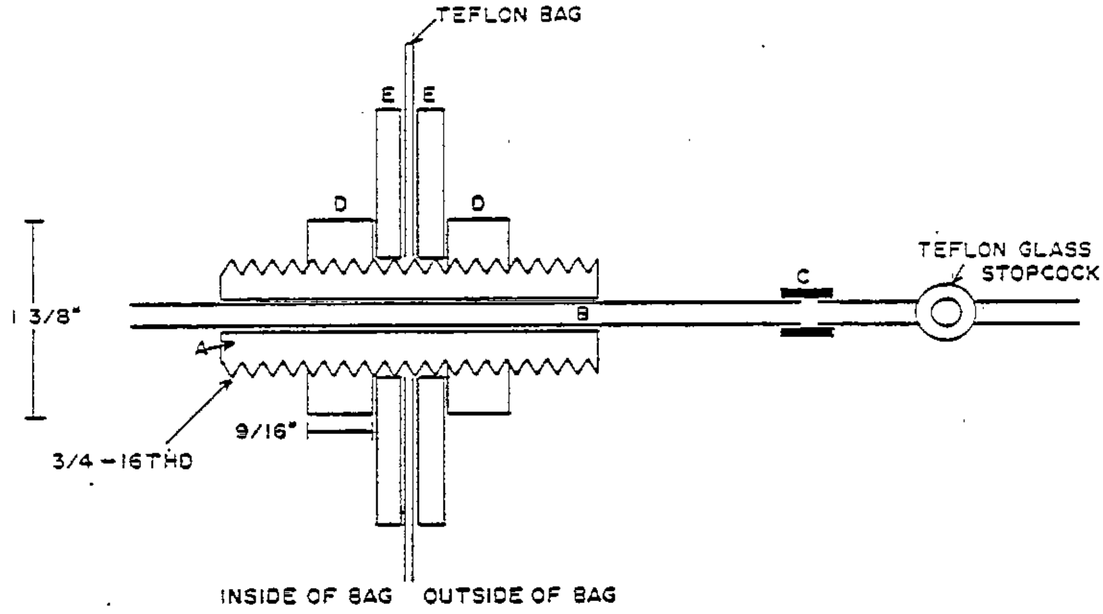


Figure 1. Construction of the Teflon Reaction Bag



A HOLLOW TEFLON BOLT
B 1/4" O.D. TEFLON TUBE INSERTED THROUGH 1/4" DIAMETER HOLE
C TYGON TUBING
D TEFLON NUTS
E TEFLON WASHERS

Figure 2. Injection and Sampling Port

3. Heat Sealing

The Teflon port is first assembled on one of the ends of the chamber by tightening the Teflon nuts, as detailed above and as shown in Figures 1 and 2. The hole in the Teflon sheet through which the Teflon bolt (A) fits can be conveniently made using a cork borer. The sides of the resulting cylindrical bag are sealed together with a 500 watt thermal impulse heat-sealer. It will probably be necessary to carry out preliminary testing of this heat-sealing technique using scrap pieces of Teflon to obtain a heat setting that yields a strong seal.

E. Reaction Bag Cover

An opaque cover is necessary in order to avoid illumination of the reaction chamber and hence possible photolysis of the methyl nitrite or the test compound being studied before the timed experiment begins. A large opaque plastic sheet functions well.

F. Seal Reinforcement and Leak Testing

The heat-sealed sides can be further protected from leaks by covering the heat-sealed seams with green Mylar tape. After the bag is constructed it should be tested for obvious leakage by filling with pure air (ultra-high purity) to capacity (not excessively so as to split the seams) and then allowing the inflated bag, with the stopcock closed, to sit for one or two hours. After this period of time, the amount of deflation can be visually estimated. A certain amount of air will have permeated through the Teflon, but the bag should still be largely filled, and no obvious leaks should result from applying a small amount of pressure to the bag. The seams should be carefully examined for splits or tears, and, if any are found, they should be resealed (probably at a lower heat setting) and more Mylar tape applied to reinforce the seams.

G. Fluorescent Lamp Assembly

The fluorescent lamp assembly used in the development of this protocol is shown schematically in Figure 3. It consists of a circular array of 24 15-watt blacklights (GE F15T8-BL15) mounted in a cylindrical frame constructed of aluminum. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on the same

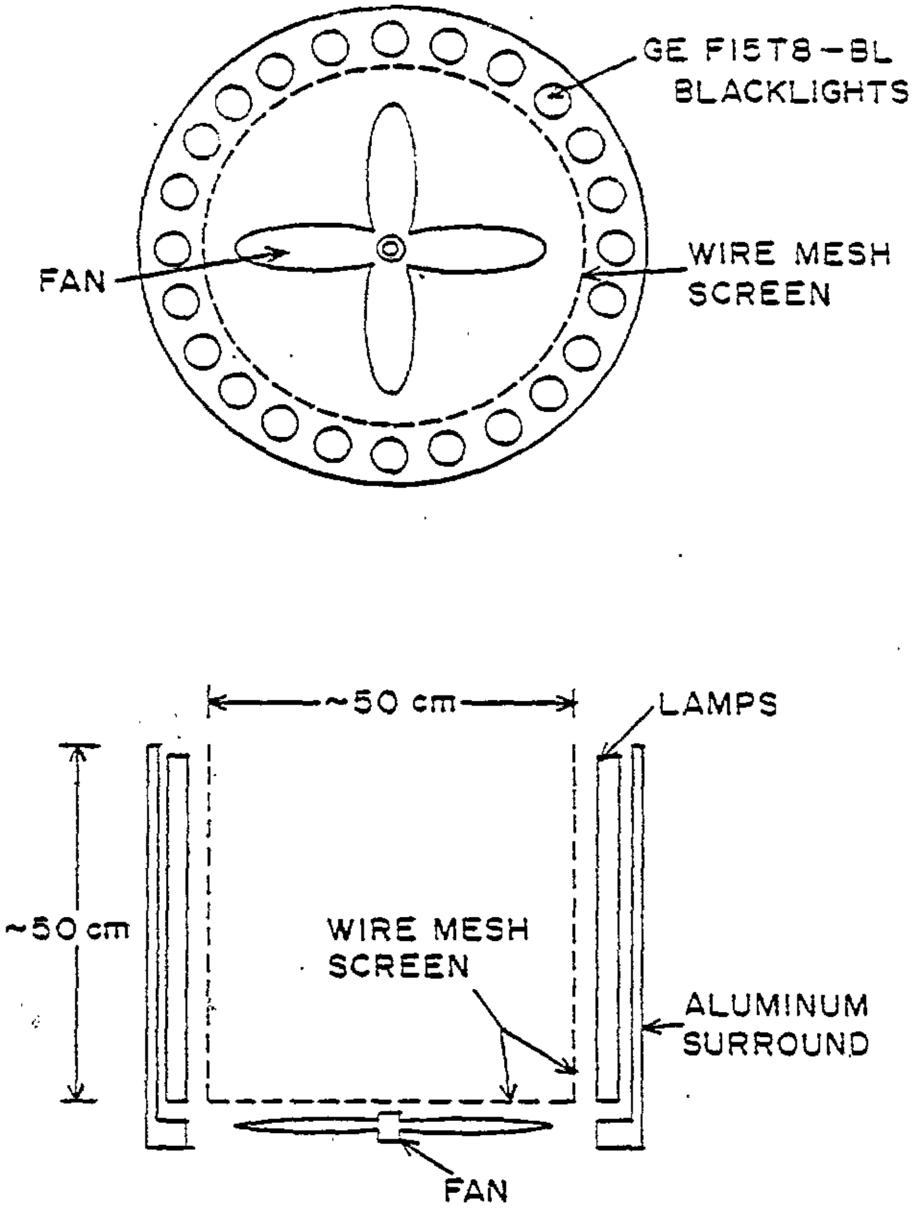


Figure 3. Fluorescent Lamp Assembly

circuit. This allows the use of three differing light intensities. In the bottom of the assembly is a fan which circulates a large volume of air to minimize heating of the reaction chamber. A cylindrical wire mesh screen inside the lamp ring (Figure 3) keeps the reaction bag from contact with the lamps or the fan.

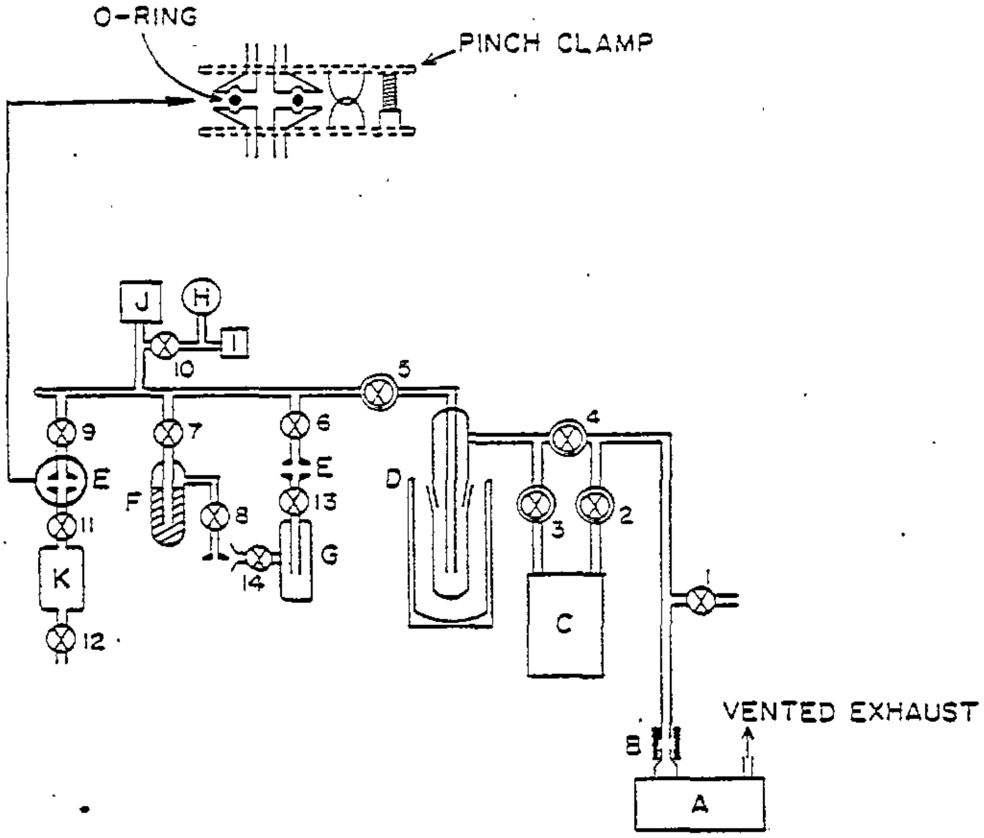
H. Vacuum Gas-Handling System

A gas-handling system is necessary for the preparation and gas handling of methyl nitrite and may also be useful for the preparation and purification of the test or reference compounds. A suitable system is shown diagramatically in Figure 4. Such a system should be constructed from Pyrex, since the use of other materials, such as various metals, can lead to wall adsorption problems. The components of such a gas handling system are discussed below.

1. Vacuum Pumping System

Two pumps, working in tandem, are necessary to provide good vacuum, i.e., pressures $\leq 10^{-5}$ torr. The forepump (A) must be capable of achieving pressures ≤ 0.05 torr. A rotary pump such as a Welch Model 1402 Duo-Seal or equivalent is recommended for this purpose. The forepump is attached to the rest of the vacuum system by heavy-walled rubber vacuum tubing (B), which also serves to damp-out transmission of vibrations to the vacuum line. The exhaust from this pump should be vented into a hood. The second, and high-vacuum, pump required is a multistage oil diffusion pump (C), a CVC (Consolidated Vacuum Corporation) VMF-10 or VMF-20 or equivalent being suitable. The working fluid should be a silicone oil (e.g., Dow-Corning DC703) since it is less susceptible to destructive oxidation should the system be inadvertently opened to air while the diffusion pump is still hot. The diffusion pump fluid must have a room temperature vapor pressure of $\leq 10^{-6}$ torr.

The pumping system must be equipped with a trap (D) cooled by liquid nitrogen (i.e., at 77 K) to reduce pump oil contamination and back-streaming. The cone and socket portions of this trap (Figure 4) may be conveniently sealed using Apiezon W wax (which requires gentle heating to apply).



A	ROTARY PUMP
B	RUBBER TUBING (THICK WALLED)
C	DIFFUSION PUMP
D	TRAP AT LIQUID NITROGEN TEMPERATURE
E	#7 OR 9 O-RING JOINTS
F	MOLECULAR SIEVE 4A TRAP
G	CH_3ONO TRAP
H	THERMOCOUPLE GAUGE
I	IONIZATION GAUGE
J	CAPACITANCE MANOMETER
K	~500cm^3 PYREX BULB

⊗	0-4 OR 0-5 mm STOPCOCKS
⨂	0-8 OR 0-10 mm STOPCOCKS

Figure 4. Schematic of Gas Handling Vacuum Rack

2. Vacuum Rack

A suitable assembly of the vacuum rack is shown in Figure 4. The stopcocks should be of Teflon with Viton "o"-rings, such as the Kontes #K-826500 or K-826510 series. The "o"-ring joints (#7 or #9 size are suitable) must be chosen to be compatible with those on the methyl nitrite trap (G). These "o"-ring joints should be clamped by pinch clamps with a screw lock device (Thomas #18A, available from VWR Scientific, Inc., for example).

3. Pressure Gauges

Two, or preferably three, pressure gauges are required:

(a) An ionization gauge to measure high vacuum, i.e., pressures $\lesssim 10^{-3}$ torr, to verify that the vacuum system is operating correctly and that there are no leaks.

(b) If available, a thermocouple gauge is desirable to monitor, on a semi-quantitative basis, pressures in the range $\sim 10^{-3}$ to 1 torr. This gauge is used to monitor the pressures in the gas handling system prior to turning on either the diffusion pump (which requires pressures of $\lesssim 0.1$ torr) or the ionization gauge. A convenient pressure monitoring system which includes both these gauges is the CVC Products, Inc., Model GIC-300A ionization gauge with associated thermocouples, or equivalent.

(c) The third pressure gauge is needed to accurately monitor pressures of methyl nitrite during its preparation in the range ~0.01 to 760 torr. For this purpose a capacitance manometer should be used, such as an MKS Baratron 310 BHS-1000 with an associated 170-6C electronics unit and a digital readout (this particular system has a usable range of <0.1 to 1000 torr). While these vacuum gauges exhibit a slow zero drift, they can be readily re-zeroed using the ionization gauge, i.e., when the ionization gauge reads $\lesssim 10^{-3}$ torr.

I. Glassware for Preparation of Methyl Nitrite

The glassware required for the preparation of methyl nitrite is shown in Figure 5.

- A 300-mℓ three-necked flask
- A 250-mℓ separating funnel with an appropriate ground glass joint.
- Two bubblers fitted with 12/5 ball and socket joints.

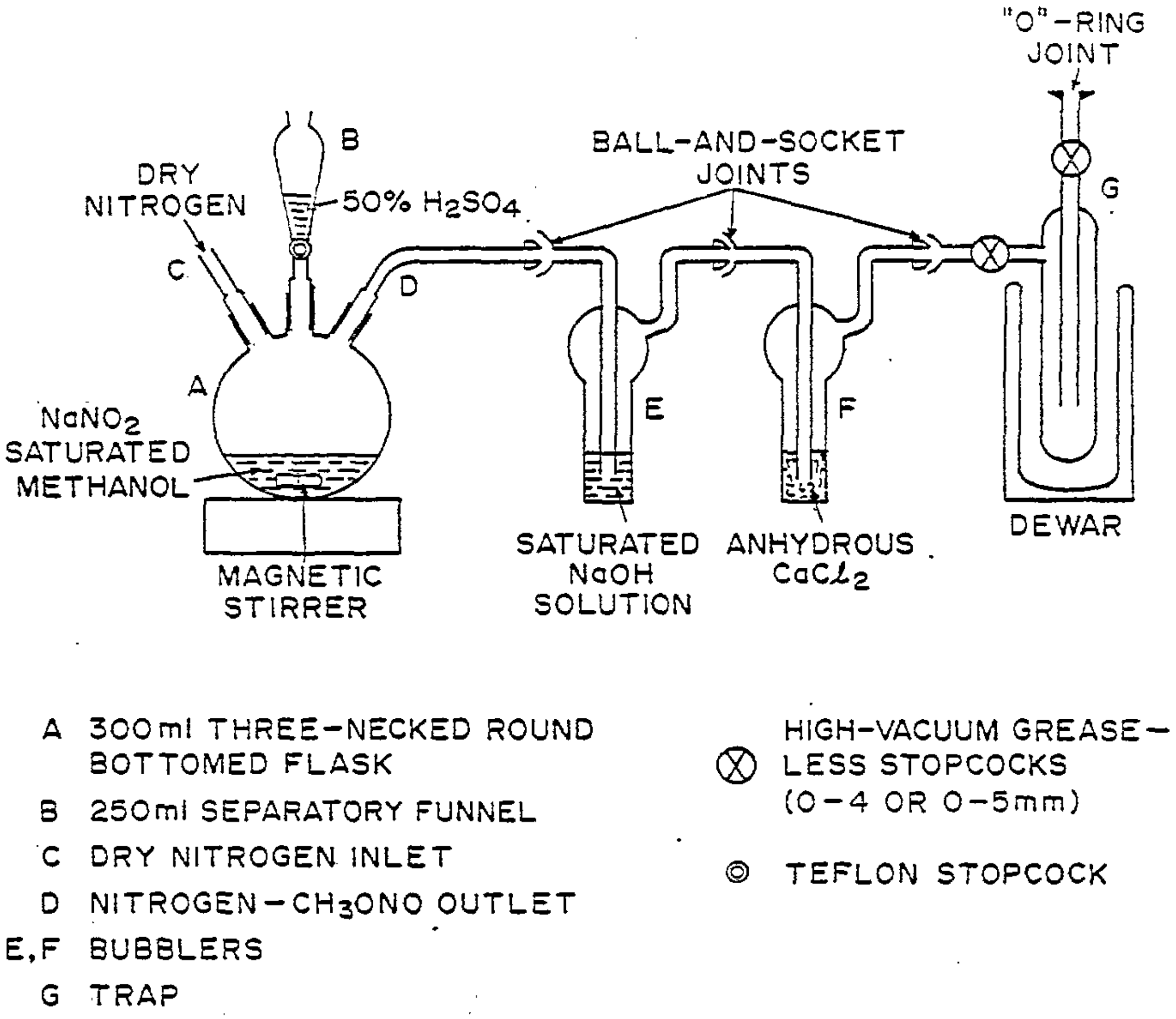


Figure 5. Schematic of Glassware Assembly for Methyl Nitrite Production

- A Pyrex trap fitted with high vacuum greaseless Teflon stopcocks, a ball and socket joint, and an "o"-ring joint (Figure 5).
- Other associated glass fittings as shown in Figure 5.

J. Flowmeter

A rotameter (Matheson 604 flowmeter or its equivalent) with a flow range of ~1 to 10 liter min^{-1} is an effective means for controlling and monitoring the rate of fill of the reaction chamber. When not flushing a test compound into the chamber, the fill rate may be relatively rapid, i.e., ~7-10 liter min^{-1}. However, when a liquid or a solid needs to be introduced into the chamber, this is accomplished by flushing the compound of interest from an ~1-liter bulb or for a solid, from a pyrex tube (1/4 in o.d) packed with the solid with pure air into the bag at a lower flow rate, i.e., ~3 liter min^{-1}. At high flow rates the test compound may not completely vaporize before the bag is filled). A slower flow rate still may be useful for particularly low volatility compounds, though use of a heat gun will aid vaporization in these cases.

Rotameters are often accompanied by a manufacturer's calibration curve for air. Although this calibration curve could be used, it is advisable to determine accurately the flow rate calibration curve. Flow rates should be determined at several (at least five) rotameter settings covering the flow rates to be used (i.e., 1-10 liter min^{-1}). At these flow rates a wet test meter (Precision Scientific Model No. 63126 or equivalent) is preferable, although a 1000 cm^3 or (preferably) a 2000 cm^3 bubble flowmeter can also be used. If neither a wet test meter nor a bubble flowmeter is available, a bubble flowmeter can be readily constructed by narrowing one end of a large glass tube (~5 cm diameter), as shown in Figure 6.

By adding water from a 100 cm^3 volumetric flask which has been filled to the mark and noting the water level after each successive addition of water, indelible lines can be drawn on the glass of the flowmeter at intervals of 100 cm^3, with the flowmeter in a vertical position, and, as shown in Figure 6, the zero line being above the narrow portion of the flowmeter. To the narrow end of the glass tube a glass "T" is attached by Tygon tubing, and the lower arm is enclosed with a disposable pipette

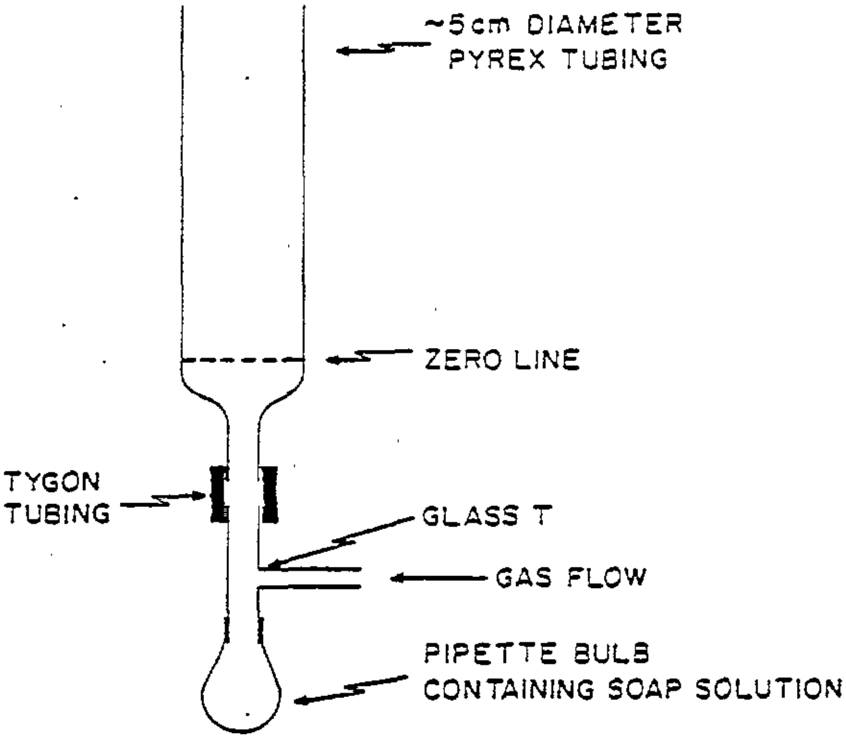


Figure 6. Design of a Bubble Flowmeter

bulb. A Tygon tubing line which carries the gas is attached to the other arm of the "T".

The pure air should first be passed through the rotameter, and its setting adjusted and noted. When using a wet test meter, measure the time, t, for a change of volume, V. For a bubble flowmeter, first squeeze the pipette bulb (containing soap solution, e.g., SNOOP [a registered trade name of Nupro Company]) to start a soap bubble and again measure the time, t, for the soap bubble to pass through a known volume V (the sidewalls of the bubble flowmeter should be well washed with soap solution so that bubbles will not break). For both types of flowmeters at least three repeat readings should be taken at each rotameter setting. The volumes V should be such that the corresponding times t exceed 10 seconds. The flow rate F (in liter min^{-1}) is given by

$$F = \frac{V(\text{cm}^3) \times 60}{t(\text{sec}) \times 1000} \qquad \text{(VII)}$$

K. Temperature Measurement

A thermometer or thermocouple suitable for measuring the temperature in the immediate vicinity of the reaction bag is required. A simple thermometer covering the range 0 to 100 C, with an accuracy of ±0.1 C, is suitable.

SECTION III

EXPERIMENTAL PROTOCOL

A. Operation of Gas Handling System

The gas handling system is required for the synthesis of the methyl nitrite and its preparation for injection into the reactor for the rate constant determinations. It can also be used for the injection of the test or reference organics, if desired. The start-up, shut-down and maintenance of this system is described in this section.

1. Start-Up

The following describes briefly the typical start-up operation of the vacuum gas handling system (Figure 4).

(1) With all stopcocks closed, switch on rotary pump (A), then open stopcock 4 and place a Dewar of liquid nitrogen around trap D.

(2) Open stopcock 10 and monitor the pressure using the thermocouple gauge (H). If the pressure is >0.1 torr, then open stopcock 5. When the pressure as read by the thermocouple gauge (H) is <0.1 torr, turn on the diffusion pump (C), open stopcocks 2 and 3 and close 4. When the diffusion pump has reached operating temperature, the pressure in the vacuum manifold should be $<10^{-5}$ torr as read by the ionization gauge (I). At this point the capacitance manometer (J) can be zeroed. The ionization gauge (I) should only be used when, as indicated by the thermocouple gauge (H), the pressure is $\lesssim 10^{-3}$ torr.

(3) The ~500-mℓ Pyrex bulb cell (K) can now be evacuated by opening stopcocks 9 and 11. If the bulb is at a substantial pressure, then prior to opening these stopcocks, the diffusion pump should not, if possible, be exposed to pressures >0.1 torr to avoid degradation of the pump oil. Rather, in this situation bulb (K) should be evacuated to <0.1 torr using the rotary pump alone, i.e., with stopcocks 2 and 3 closed and 4 open.

2. Shut-Down

The gas-handling system can be shut down by the following procedure: (a) close stopcocks 5 to 11, (b) switch off the diffusion pump, (c) when the diffusion pump is cool, close stopcocks 2 and 3 and open 4, (d) remove the Dewar from trap (D) and allow it to warm up, (e) then close stopcock 4 and switch off the rotary pump. Stopcock 1 should then be opened, to prevent back-up of the rotary pump oil. With this procedure, the vacuum manifold, the trap (D) and the diffusion pump are left under vacuum.

3. Maintenance

If the vacuum system, including the bulb (K) [i.e., all stopcocks open except stopcocks 1, 4, 6 and 7] does not pump down to $<10^{-4}$ torr, then either a leak or contaminant offgassing problem is present. Closing stopcocks 11, then 9, will give indications as to the region of the problem, i.e., if, on closing stopcock 9 the pressure drops, then there may be a leak around the "o"-ring joint on the ~500 mℓ bulb (K), which then should be replaced. If, however, the pressure drops on closing stopcock 11 (with 9 open) then either the bulb has a leak, or offgassing from previous runs is occurring. Leaks can be checked using a Tesla coil. Such maintenance procedures should be routinely carried out on all portions of the vacuum gas handling system. This includes changing the rotary pump oil at frequent intervals.

B. Preparation of Methyl Nitrite

Methyl nitrite (CH_3ONO) is prepared by the dropwise addition of 50% H_2SO_4 to a solution of methanol (CH_3OH) saturated with $NaNO_2$. For the protocol described here, the use of ~50 cm^3 of each (50% H_2SO_4 and sodium nitrite saturated methanol) is sufficient. A schematic of the apparatus needed is shown in Figure 5 (Section II). A solution of methanol saturated with sodium nitrite is placed in the three-necked flask (300 mℓ volume) (A). The 50% H_2SO_4 is placed in the funnel (B) equipped with a Teflon stopcock. Ultra-high purity nitrogen is passed through the flask via inlet and outlet joints (C) and (D). Bubblers (E) and (F) contain a saturated NaOH solution and anhydrous $CaCl_2$, respectively, while trap (G) is fitted with high vacuum greaseless stopcocks (Kontes #K-826500 or equivalent) and the necessary ball and socket and "o"-ring joints, as shown. The system should be purged with a nitrogen flow for ~10 minutes prior to commencing the dropwise addition of H_2SO_4 into the $NaNO_2$ saturated CH_3OH. The trap (G) should be cooled to 196 K by means of a Dewar filled with a dry ice/acetone slush just prior to beginning the reaction. The CH_3ONO produced is swept out of the reaction vessel by the N_2 stream, any H_2SO_4 carried over is removed by passage through the NaOH solution, and the CH_3ONO-N_2 stream is then dried by passage through the trap containing anhydrous $CaCl_2$. The CH_3ONO is collected in the cooled trap (G).

After the reaction has terminated, the N_2 flow is turned off, stopcocks 13 and 14 on the trap (G) are closed, and the trap, still cooled to dry ice/acetone temperature by the Dewar, is connected to the vacuum system (Figure 4) via the "o"-ring joint (E). The Dewar containing dry ice/acetone is then replaced by a Dewar containing liquid nitrogen.

After preparation of the methyl nitrite, as described above, the trap (G) is degassed by opening stopcocks 6 and 13, with the trap still immersed in liquid nitrogen. After pumping down to $<10^{-4}$ torr, stopcock 13 is closed, and the methyl nitrite can be stored indefinitely at liquid nitrogen temperatures under vacuum. The trap (G) and Dewar should be covered with an opaque cover (e.g., aluminum foil) in order to avoid photolysis of the methyl nitrite.

C. Experimental Procedure for the Determination of Rate Constants for Reaction with the Hydroxyl Radical

1. Filling the Reaction Bag

Prior to each new experiment, the reaction bag should be completely emptied using a metal bellows pump whose exhaust is expelled into a hood. The bag should then be filled with pure air and pumped out again to remove any test compound or other reactants or products from the previous run. The desired amounts of the reactants (i.e., methyl nitrite, NO, the test compound and the reference organic) are then introduced (see below, Section III.C.2), and the reaction bag is filled (i.e., visually filled but not excessively so as to cause undue stress on the seams) with ultra-zero air, using a flow rate in the range of ~7-10 liter min^{-1}, as monitored by the rotameter.

The reaction bag should be kept in the dark during the injection of the reactants, since methyl nitrite photolyzes rapidly.

2. Introduction of Initial Reactants

a. Injection of Methyl Nitrite

This protocol calls for introduction of 0-10 ppm of methyl nitrite into the reaction bag, depending on how rapidly this test organic (and reference compound) react. A convenient method of introducing CH_3ONO is to admit the desired pressure of CH_3ONO from the trap (G) into the ~500

cm^3 Pyrex bulb (K) by gradually warming the trap until the desired pressure is attained. The desired pressure, P, to introduce into the bulb is given by

$$p(\text{torr}) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{atmospheric pressure (torr)}] \times [\text{volume of reaction bag (liters)}]/[\text{volume of bulb } (cm^3)] \qquad \text{(VIII)}$$

The volume of bulb (K) should be accurately measured by, for example, the volume of water it holds. For a 500 cm^3 bulb and a 75-liter reaction bag, 1.14 torr in the 500 cm^3 bulb corresponds to 10 ppm (at 760 torr) in the reaction bag.

The bulb (K) is first pumped down to $\leq 10^{-4}$ torr, then with stopcocks 5, 7 and 10 closed and stopcocks 6, 9, 11 and 13 open, the liquid nitrogen Dewar removed from trap (G), and the pressure is allowed to rise to the desired level, as read by the capacitance manometer (J). Stopcock 13 is then closed, the liquid nitrogen Dewar replaced around trap (G), and, after allowing the pressure to equilibrate, the pressure is read and stopcock 11 is closed. The high vacuum manifold, including trap (F), is evacuated, i.e. stopcocks 2, 3, 5, 7, 9, and 10 open, the rest closed. After evacuation to $\leq 10^{-4}$ torr, stopcocks 5 and 10 are closed and nitrogen (of a stated purity level of $\geq$99.99%) is introduced into the vacuum rack through the molecular sieve trap (F) to attain a pressure of ~10 torr. Stopcock 11 is then opened and the pressure of nitrogen increased to ~10 torr above the ambient atmospheric pressure. Stopcocks 8, 9 and 11 are then closed. The bulb (K) is then attached to the reaction bag as shown in Figure 7, stopcocks 11 and 12 are opened and the contents of bulb (K) flushed into the reaction bag by a monitored flow of ultra-zero air.

b. Injection of NO

This protocol requires the introduction of ~5 ppm of NO into the reaction bag. For NO (and other gaseous reactants which are commercially available in high pressure cylinders) this is most conveniently carried out using all-glass syringes as described below. The volume, V, of NO or other gaseous compound required to achieve the desired concentration in the reaction bag is given by:

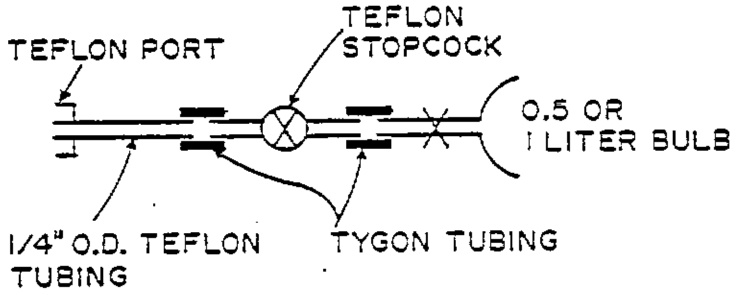


Figure 7. Attachment of Pyrex Bulbs to the Injection Port

$$V(\mathrm{cm}^3) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{volume of reaction bag (liters)}] \qquad \text{(IX)}$$

Using the reaction bag described in this protocol, approximately 0.375 cm^3 of gas are required to yield the desired concentration of 5 ppm in the bag. To obtain such a small volume of gas, pure NO from a high pressure cylinder is used to fill a 10-mℓ all-glass gas syringe (with the syringe being emptied and filled with NO several times to assure that dilution by air is minimized), 7.5 mℓ of NO is then transferred from the 10-mℓ syringe into a 100-mℓ all-glass gas syringe containing ~92.5 mℓ of pure N_2. N_2 rather than air must be used to dilute the NO to avoid its oxidation to NO_2, which will occur relatively rapidly when high concentrations of NO are mixed with O_2. For this transfer the two syringes are connected tip-to-tip by an ~0.4 in. long Tygon tube, as shown in Figure 8. The syringes are pumped back and forth a few times to ensure mixing. From this 100-mℓ syringe, 5.00 mℓ is then taken in the 10-mℓ syringe and injected into an ~1-liter bulb modified as shown (Figure 9), which as been pre-flushed with pure air for ≥ 5 minutes. The contents of this closed 1-liter bulb are then flushed into the reaction bag with pure air.

c. Injection of Test Compound and Reference Organic

Concentrations of the test compound and reference organic used in the development of this protocol have been in the range of 0.5 to 2 ppm by volume. The following protocol details the introduction of a compound to yield a concentration of ~1 ppm in the reaction bag. The specific technique employed depends on whether the compound is gaseous, liquid, or solid at room temperatures.

(1) Gaseous Compounds

If the test compound or reference organic is gaseous at room temperature, it can be injected either using a gas handling system as described above for methyl nitrite, or using all glass syringes as described above for NO. For most compounds, the latter technique is more convenient. If 1 ppm of the compound in the reaction bag is desired, then 1.00 mℓ of the diluted compound in the 100-mℓ syringe is injected into the ~1-liter bulb rather than the 5.00 mℓ as described above for NO. In addition, pure air rather than N_2 can be used as the diluent gas.

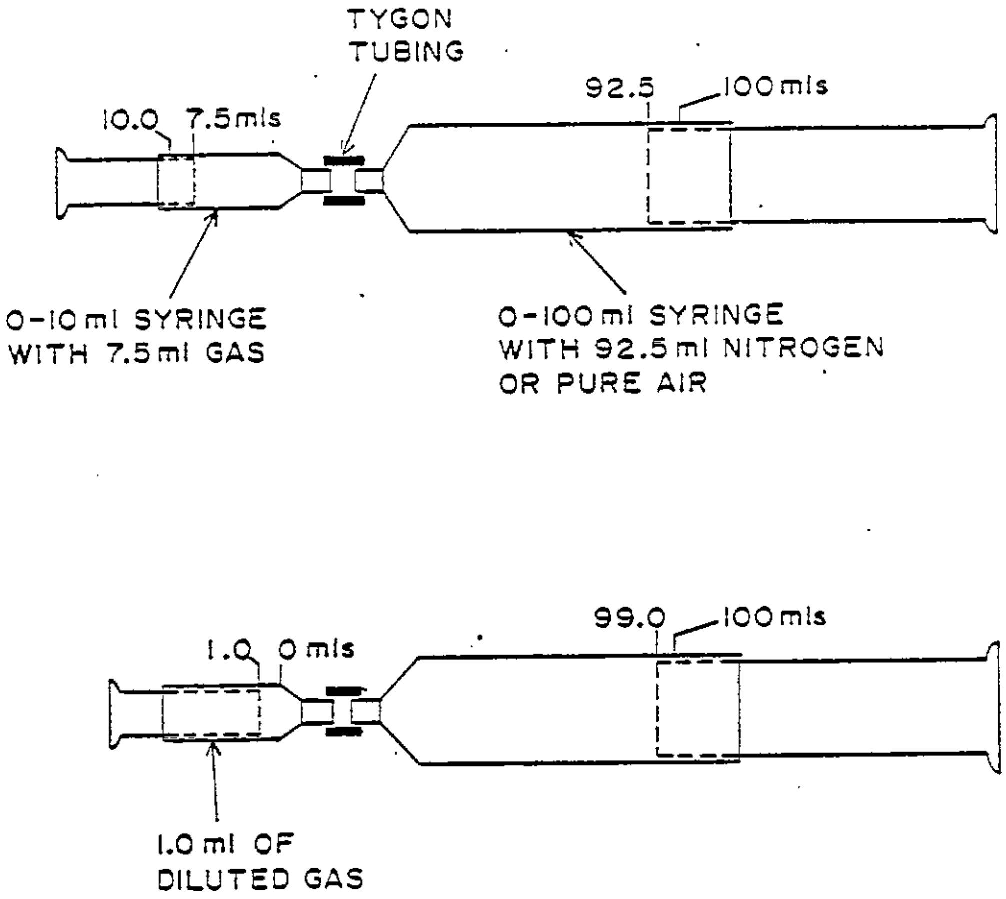


Figure 8. Syringe-to-Syringe Gas Transfer. (The volumes shown are for injection of 1 ppm of a gaseous compound into a 75-liter reaction vessel.)

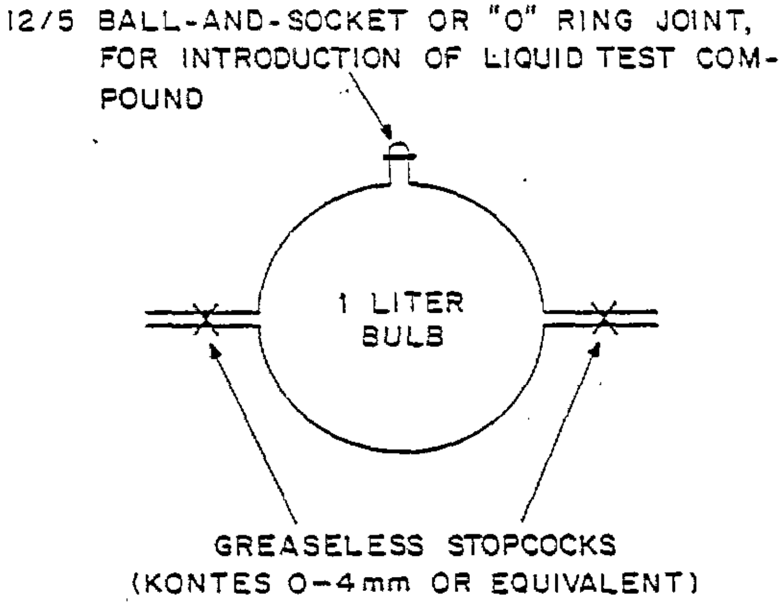


Figure 9. Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds

(2) Liquid Compounds

If the test compound or reference organic is a liquid, a different method of injection and of calculating the amount needed is necessary. For the reaction bag described in this protocol approximately 0.5 μl of liquid will give a concentration appropriate for an experiment aimed at an initial concentration of ~1 ppm, since for the liquid case:

$$V\ (\mu\ \text{liters}) = 10^{-4} \times [\text{desired concentration (ppm)}] \times \frac{[\text{Volume of bag (liters)}] \times [\text{Molecular Weight (g)}]}{[\text{Density } (\text{g cm}^{-3})] \times 2.46} \qquad \text{(X)}$$

at room temperature.

The calculated [see equation (X) above] amount of the liquid test compound is then injected into a 1-ℓ bulb, modified as shown in Figure 9, which has been preflushed with pure air into the hood for ≥5 minutes. The dosed 1-ℓ bulb is then attached to the reactor as shown in Figure 7 and its contents are then flushed into the bag with pure air at a known flow rate, which should be ~3.5 liter min^{-1} for a more volatile liquid or less (~1-2 liter min^{-1}) for a nonvolatile liquid. Evaporation of the lower volatility liquids may be aided by gentle use of a heat gun to warm the 1-liter bulb (taking care not to pyrolyze the compound). If heat must be applied, any tendency of a compound to air oxidize or polymerize will lead to low volatility residues and hence errors when carrying out liquid injections. The compounds should, if such problems are known to be likely, be first distilled by conventional means, i.e., vacuum distillation with liquid nitrogen trapping, vapor transfer from trap-to-trap at dry ice temperature, or by distillation at atmospheric or subatmospheric pressure and N_2 rather than air should be used as the flush gas.

(3) Solid Compounds

If the test or reference compound is a solid at room temperature, the desired mass (m) of compound to inject is given by

$$m(\text{g}) = \frac{10^{-7} \times [\text{desired concentration (ppm)}] \times [\text{volume of bag (liters)}] \times [\text{molecular weight (g)}]}{2.46} \qquad \text{(XI)}$$

If the compound has a melting point below ~50 C, is relatively volatile, and is known to be stable above its melting point, it can be injected in a manner analogous to that described above for liquids. In this procedure, the desired, weighed amount of compound is placed in the 1-liter bulb shown in Figure 9, which has been previously flushed with N_2, the bulb is attached to the reactor as shown in Figure 7, the compound is carefully heated with a heat gun until it melts, and then it is flushed into the reactor.

For solid compounds for which the above method is not suitable, an alternate technique must be employed. In this method, a 3 to 6-in. x 0.25-in. o.d. Pyrex tube is loosely packed with the compound, which is held in place with Pyrex wool. Tests should be carried out to assure that none of the solid compound is blown from the tube when air flows through it at ~2 liter min^{-1}. The tube is then attached to a simple dilution system as shown in Figure 10, which is in turn attached to the reactor. The compound is injected into the reactor by flushing the tube with ultrahigh purity air at a controlled rate in the range of 1-2 liter min^{-1} for the necessary amount of time to achieve the desired concentration in the reactor, with the diluent flow being at least a factor of 2 higher. The tube should not be heated. The diluent is necessary to avoid exposure of the injection inlet tube to the test organic at its vapor pressure, which may result in condensation. If the compound's vapor pressure at room temperature is known, the length of time to flush a desired quantity into the chamber is given by:

$$\begin{matrix}\text{time} \\ \text{min)}\end{matrix} = \frac{10^{-6} \times [\text{desired concentration (ppm)}] \times [\text{volume of bag (liter)}]}{[\text{vapor pressure (atm.)}] \times [\text{flow rate (liter min}^{-1})]} \qquad \text{(XII)}$$

If the compound's vapor pressure is not known, the time required to obtain a given reactant concentration in a given volume at a given flow rate will need to be determined experimentally. To avoid contamination of the reactor, a different reaction bag should be used for these trial injections than used in the reactivity experiments, unless it is known that the amounts injected in the trials will be less than those required for the reactivity experiments. Ultrazero air should be used as both the flush and the diluent gas.

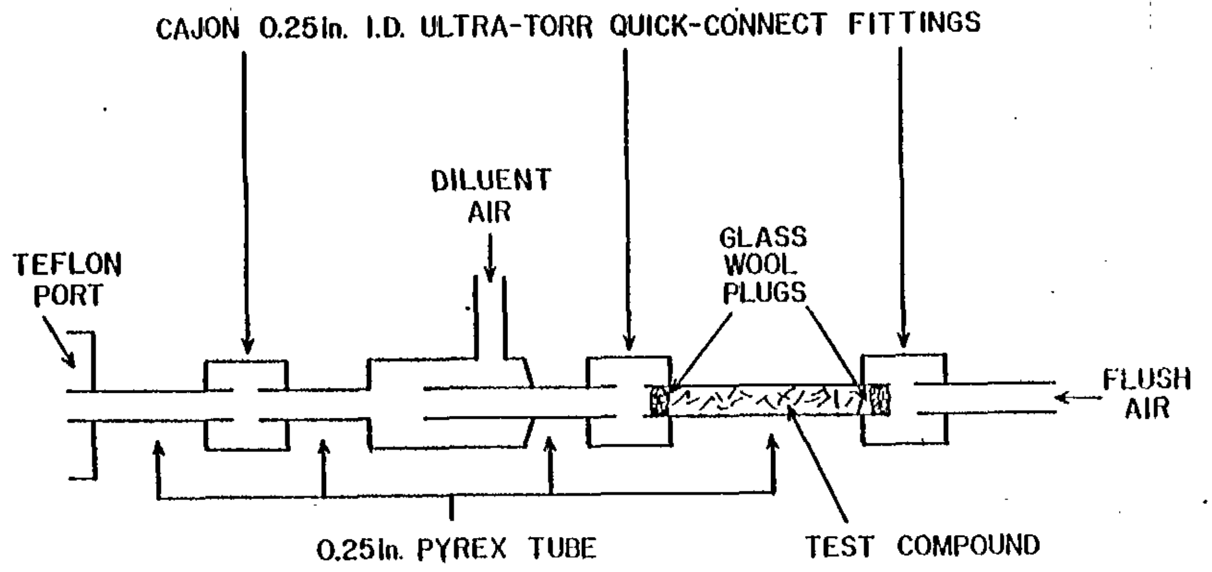


Figure 10. Apparatus for Introducing Solid Compounds into the Reaction Chamber

If the compound is relatively nonvolatile, the amount of air used to inject it may be comparable to the bag volume, so in these cases the reactor should be nearly empty prior to the injection of the organic. This protocol is not intended for use for compounds whose vapor pressure is less than ~10 ppm (~0.01 torr), since it would not be possible to use this technique to achieve concentrations of ~1-2 ppm in the reaction bag.

3. Pre-Irradiation Analyses

When the reactants have been injected in the reaction bag and mixed, the concentrations of the test compound and the reference organic are determined. The discussion in this and in the following section is based on gas chromatography being employed for the analysis of these species. Analogous considerations apply if other analytical techniques are employed.

Samples for analyses by gas chromatography are conveniently taken by a 100-mℓ all-glass, gas-tight syringe. The syringe is flushed by withdrawing and expelling 100 mℓ of the gas to be sampled two or three times prior to taking the sample for analysis. While the data analysis does not strictly require absolute concentrations [equations (V) and (VI) in Section I involve only relative concentrations], the gas chromatograph(s) should, if possible, be calibrated for the test compound and reference organic. A minimum of three gas chromatographic samples should be analyzed prior to turning on the lamps.

Based upon literature results, the reproducibility of these analyses will depend on the particular organic compounds being studied. A reproducibility of ±2% should be aimed at, and this can be achieved for the $\lesssim C_9$ alkanes and the smaller alkenes. For other classes of compounds, such as organics of low volatility or organics which tend to be adsorbed on the reaction walls, an analytical reproducibility of only ±5% may be achievable. The minimum rate constant measurable with this protocol is directly related to this analytical reproducibility. Thus with a reproducibility of ±2%, the lowest rate constants which can be measured will be $\sim 3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. For lower analytical reproducibilities, only higher rate constants can be measured. Clearly, for fast reacting organics with rate constants $\gtrsim 1 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}, an analytical reproducibility of ~±5% is adequate.

If the first two analyses agree to within the necessary reproducibility, then immediately after the third sample is taken from the reaction bag, the lamps can be turned on. If the first two analyses disagree by more than the expected reproducibility, then further samples should be taken until duplicate analyses are reproducible. In between gas chromatographic sampling, the NO-NO_x and O_3 monitors should be sampling from the reaction bag, and their outputs displayed on stripchart recorders. Before beginning monitoring from the bag, these analyzers should be allowed to warm up according to the manufacturer's specifications. Teflon sampling lines (1/4 in. o.d.) should be used between the bag and the O_3 and NO-NO_x monitors in order to avoid losses experienced with, for example, Tygon or nylon tubing. The first three to five minutes sampling should be neglected since initial flushing of the sample lines is needed.

4. Irradiation Procedure

When stable concentration readings have been established (see above), the desired number of lamps are turned on, together with the cooling fan. The temperature beside the reaction bag should be monitored during the irradiation. Samples are taken for analysis as often as possible. If gas chromatography is employed for these analyses, this is constrained by the retention times of the test compound and the reference organic. O_3 and NO-NO_x monitoring should be carried out between sampling. Sampling for gas chromatographic analysis of the test compound and the reference organic must be carried out simultaneously.

With the protocol developed here, the irradiation should be terminated, and the last analytical samples taken, after ~30 minutes for full light intensity, ~45 minutes for two-thirds maximum light intensity or ~60-90 minutes for one-third maximum light intensity. Since it is preferable to have two to four analyses during the irradiation, the optimum light intensity is then determined by the gas chromatographic retention times. As an example, Figure 11 shows a typical set of gas chromatograms for an n-butane + propene system, for which analyses were carried out every 15 minutes during the 45 min irradiation. In Figure 12, an example of the OH radical concentration as a function of time, derived from such analyses, is shown.

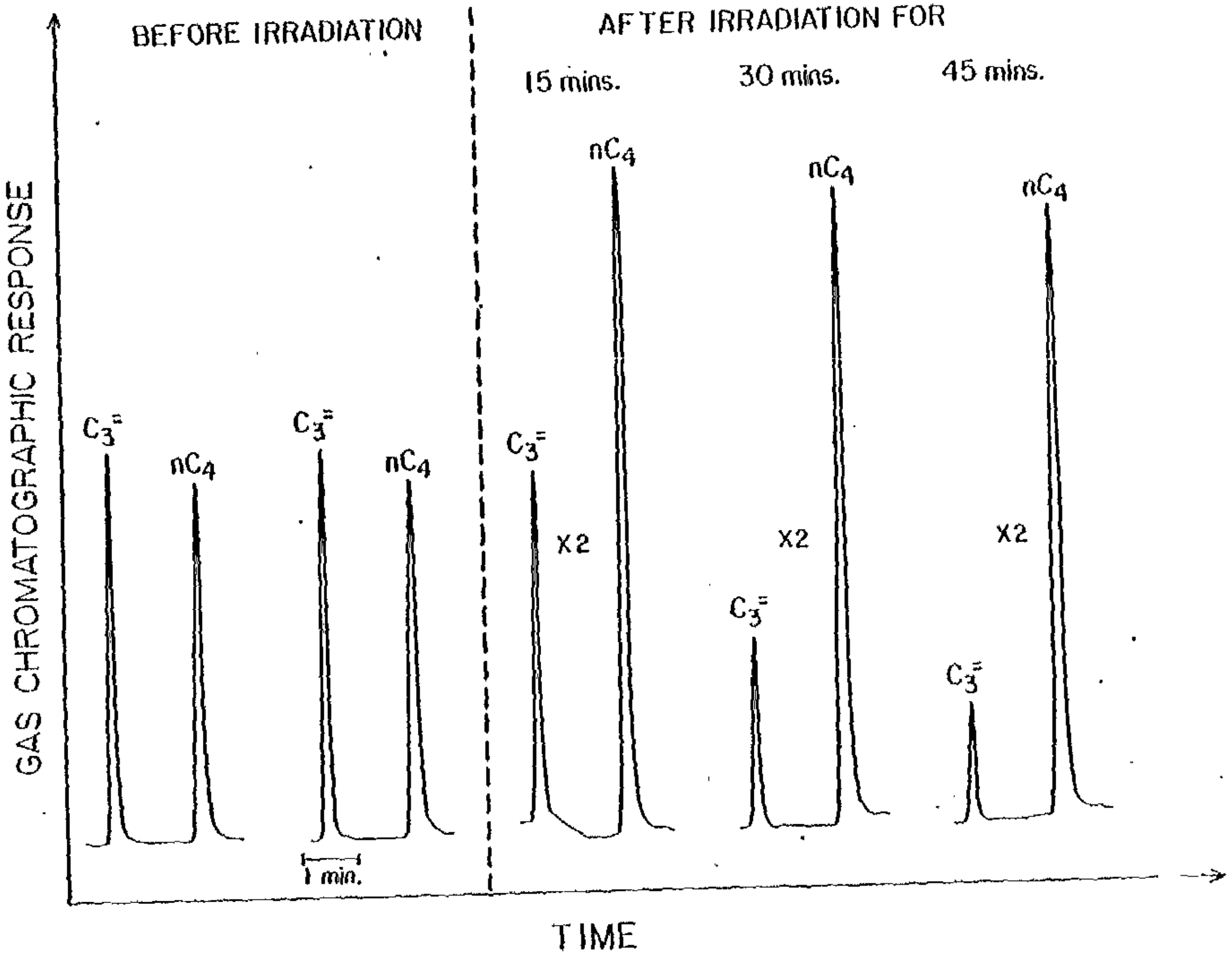


Figure 11. Example of Gas Chromatographic Analysis of Propene ($C_3^=$) and n-Butane (n-C_4) During a CH_3ONO/NO/Propene/n-Butane/Air Irradiation

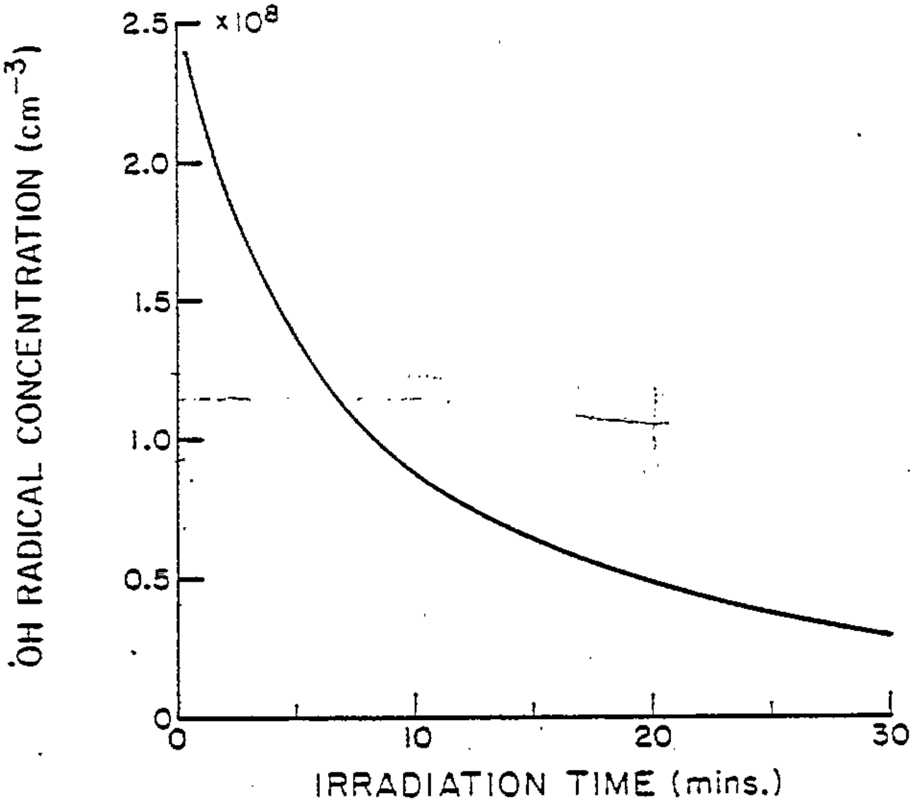


Figure 12. OH Radical Concentrations During a Typical Irradiation at Full Light Intensity with an Initial Concentration of CH_3ONO of 10 ppm

For compounds which are suspected of reacting rapidly with OH radicals, the irradiations should be carried out with one-third light intensity and low (~4 ppm) concentrations of CH_3ONO, with short irradiation times (<5 minutes). In this case, only one analysis will probably be able to be carried out for each irradiation, and a larger number of irradiations will be necessary (See, for example, Atkinson and Aschmann 1984).

For organics which exhibit an absorption spectrum in the actinic region with a significant photolysis rate (Pitts et al. 1981), at least three sets of irradiations should be carried out, with CH_3ONO concentrations of 0, ~5 ppm and ~15 ppm. Three concentrations are necessary because the origin cannot be used as a point in plots of equation (V). For organics which do not photolyze, at least two sets of irradiations should be carried out with CH_3ONO concentrations of ~5 and ~10 ppm.

5. Safety Considerations

Full safety precautions consistent with the known or unknown toxic, mutagenic or carcinogenic hazards of the test compounds must be taken. If the test compound is known to be hazardous or toxic, or if there is a reason to believe that it is, then handling should be carried out in a hood with disposable gloves, and if the compound is a liquid it should be measured using a variable micropipette with disposable tips. Used gloves and tips should be disposed of according to safety regulations. If the toxicity of a liquid compound is not a problem, a 10 $\mu\ell$ capacity Hamilton liquid syringe may be used, but it should be cleaned immediately after use by alternately drawing in and expelling methanol or some other appropriate solvent five to ten times and then completely drying it by flowing dry nitrogen or pure air through the body of the syringe. Similar precautions should be taken with hazardous or toxic gases or solids. Obviously, if the hazards or toxicological characteristics of a compound are not known, then the compounds should be treated as if they are known to be hazardous or toxic.

D. Data Analysis

The concentrations of the test compound and reference organic, as determined by gas chromatography or some other suitable analytical technique, are used to plot equation (V). An example of a plot of equation (V) is shown in Figure 13 for irradiations of three hydrocarbons and ethane. Least squares analyses of the slopes of these plots yield the rate constants ratios k_1/k_2. The intercept with these compounds is zero since they do not photodissociate, but an intercept is observed if the compound photodissociates or undergoes a light-induced wall loss.

The rate constant, k_1, can then be calculated from the slope of equation (V) and the known value of k_2, the rate constant for the reference compound. This rate constant can then be used to classify the atmospheric reactivity of the test compound. In particular, its rate constant can be compared with those for other organics to determine where it fits relative to those on the reactivity scale. For example, if it is determined that compounds which react slower than ethane can be considered to be unreactive, then if the value of k_1 so determined is less than 2.75×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, the OH rate constant for ethane (Atkinson, 1985), then the test compound can be considered to be unreactive by this criterion.

E. Reference Organics

These organics are chosen for ease of analyses and must have accurately known OH radical rate constants. They should not photolyze and, preferably, they should not react with O_3 or NO_3 radicals. If the reference compound does react with O_3 or NO_3 radicals, care should be taken to assure that sufficiently high levels of NO are present during the experimental runs to suppress the levels of these species. In addition, the OH radical rate constant for the reference compound should be similar to that for the test compound, preferably to within a factor of two to three. Table 1 gives a list of recommended reference organics, together with their OH radical reaction rate constants at room temperature.

F. Information to Be Reported

A report of the results should include for each test compound the following:

a. The compound's name, formula and physical properties (boiling and melting points).

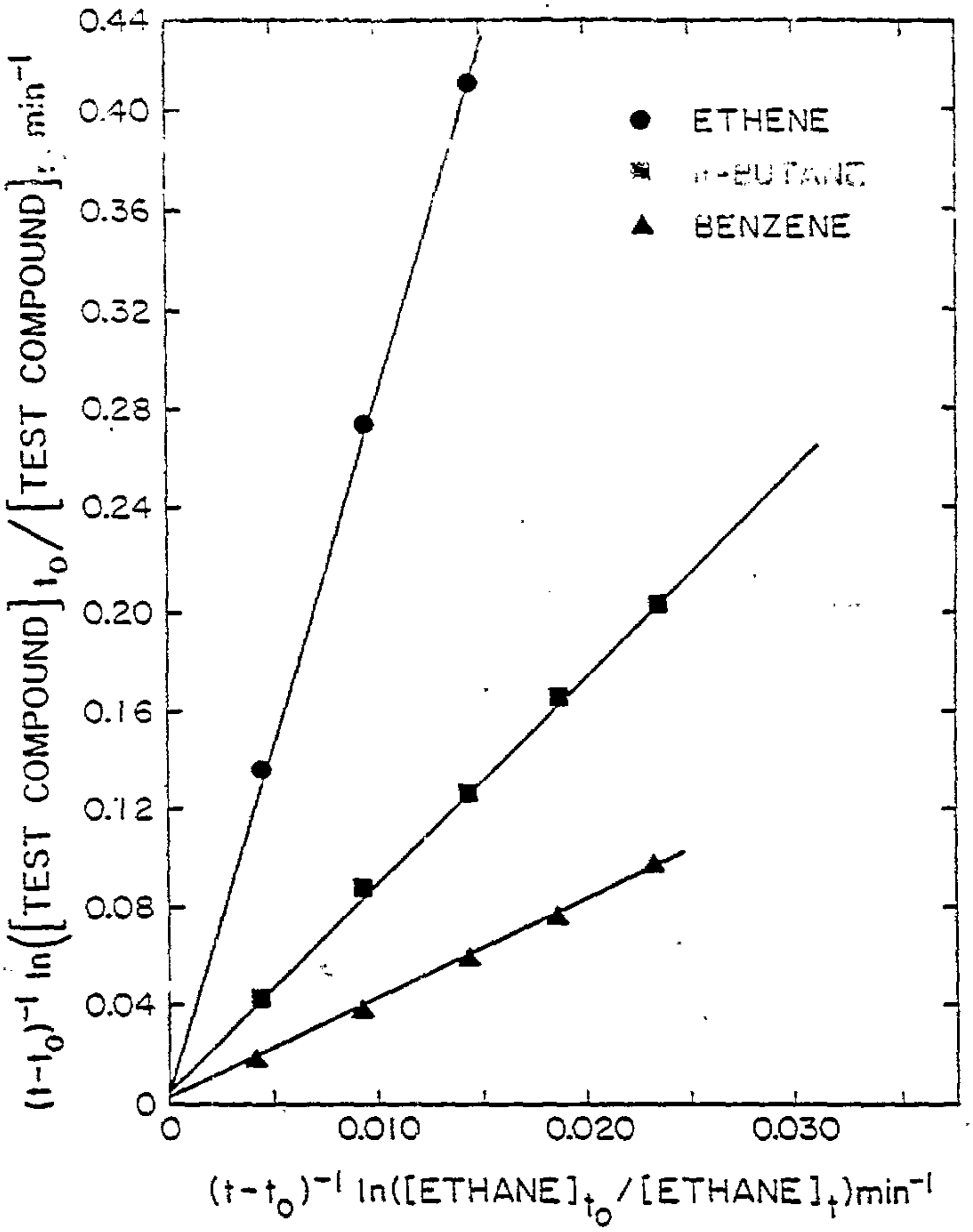


Figure 13. Plot of Equation (V) for Several Hydrocarbons Using Ethane as the Reference Organic

Table 1. List of Several Organics for Which Accurate OH Radical Rate Constants are Available, and Which do not Photolyze

Organic	$10^{12} \times k^{OH}$ (cm^3 $molecule^{-1}$ sec^{-1})[a]
Ethane	0.28
n-Butane	2.5
Cyclohexane	7.4
Ethene[b]	8.5
Propene[b]	26
2-Methyl-2-butene[b]	87
Isoprene [b]	100

[a] At 298 K, from Atkinson (1985).

[b] These compounds react with O_3 (Atkinson and Carter 1984) and are not suitable as reference compounds unless NO is in large excess of O_3. (This is generally true with short reaction times when excess NO is added.)

b. The chemical's physical form used during injection (gas or liquid at room temperature), method of purification and purity including analysis of impurities).

c. The temperature during each run.

d. The name and formula of the reference organic used and the rate constant, k_2, used in the data analysis.

e. The initial concentrations of the reference organic and test compound, NO and CH_3ONO.

f. An indication of the analytical technique(s) employed for the test and reference compounds.

g. The data obtained (i.e., the concentrations of the reference organic and test compound prior to and during irradiation, and the values of $(t-t_o)^{-1}$ ln([reference organic]$_{t_o}$/[reference organic]$_t$) and $(t-t_o)^{-1}$ ln([test compound]$_{t_o}$/[test compound]$_t$).

h. Plots of equation (V) or, if the test compound does not photolyze, equation (VI).

i. The value of k_1/k_2 and hence of k_1 determined by least squares analysis from such a plot.

j. A discussion of any special problems encountered in the experiments employing the test compound, or any special procedures which had to be employed, and the results of any experimental tests which might reflect on the accuracy of the value of k_1 obtained.

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16. ABSTRACT

An experimental protocol for the determination at room temperature of rate constants for the reactions of hydroxyl radicals with organic chemicals in the gas phase is described in detail. This protocol provides a basis for evaluating the reactivity of organic substances which are emitted into the environment and which are consumed primarily by reaction with hydroxyl radicals. The experimental technique is based upon monitoring the disappearance rates of the test compound and of a reference organic in irradiated methyl nitrite-NO-organic-air mixtures. Irradiations, employing blacklamps emitting in the actinic region, are carried out in ~ 75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite, zero to ~ 15 ppm; NO, ~ 5 ppm; test compound, ~ 1 ppm; reference organic, ~ 1 ppm. The test compound and reference organic are monitored by gas chromatography or other appropriate techniques and NO, NO_x, and O_3 by chemiluminescence instruments. Using this technique, OH radical rate constants $\geq 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} can be measured.

17. KEY WORDS AND DOCUMENT ANALYSIS

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