

FORM 9
 CHECK POINT FOR CHEMICAL HAZARD

REV. 7/21/82

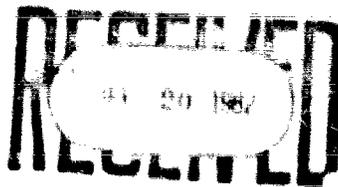
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23	ENVIRONMENTAL FATE AND EFFECT OF CHLORINATED SOLVENTS		
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25	METHYLENE CHLORIDE		75-09-2
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ENVIRONMENTAL FATE AND EFFECT OF CHLORINATED SOLVENTS

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The Dow Chemical Company, Midland, Michigan 48640

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A seminar on the environmental fate and effect of chlorinated solvents will be based on the slides shown on the following pages. The verbal presentation will be based on the four papers which are reproduced on the pages following the slides.

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US Production of Chlorinated Solvents in 1972

CH_2Cl_2	471,000,000 lbs.
CHCl_3	235,000,000
CH_2CCl_2	441,000,000
$\text{CHCl}=\text{CCl}_2$	440,000,000
$\text{CCl}_2=\text{CCl}_2$	735,000,000

US Tariff Commission Report, March 1973.

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Distribution of Chlorinated Solvents in the Environment

Atmosphere

Water

Soil

CHCl_3 , CCl_4 , CFCl_3 , $\text{CHCl}=\text{CCl}_2$, $\text{CCl}_2=\text{CCl}_2$

Found in the atmosphere and natural water bodies

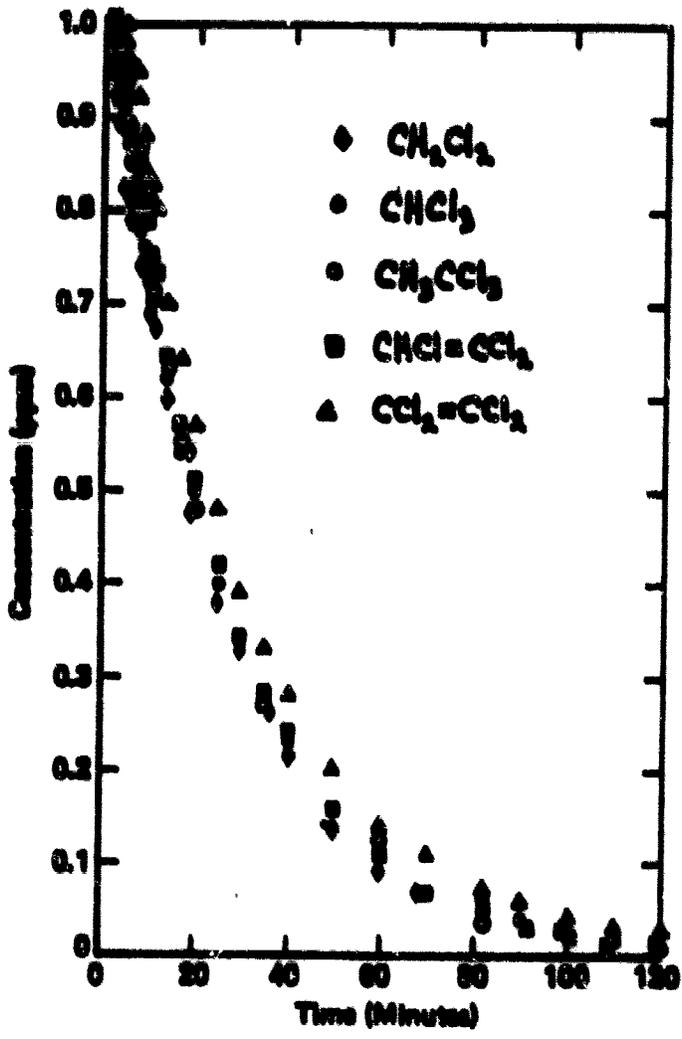
[0.03 - 70 ppt (10^{12})]

Murray and Riley, 1973; Lovelock, Maggs, and Wade, 1973;
Klopper and Fairless, 1972.

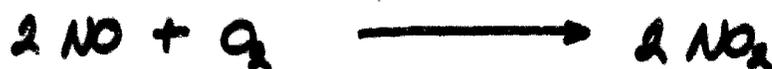
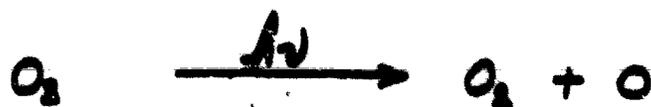
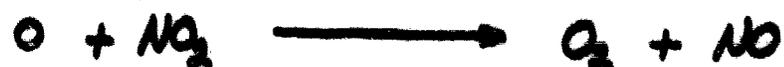
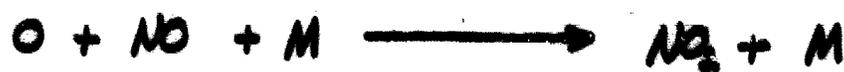
Compound	Solubility in water (25°C)	Vapor pressure (25°C)	Calcd	Partition coefficient K = C ₁ /C ₂ Found
CH ₂ Cl ₂	11,800 ppm	126 mm	0.10	0.11
CHCl ₃	7,950	200	0.16	0.18
CH ₂ Cl ₂	1,300	123	0.18	
CHCl=CCl ₂	1,100	77	0.18	
CCl ₂ =CCl ₂	400	11	0.19	0.50

Brown, NTS

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Addition of organic compounds -

1) Disrupts NO , NO_2 , O_2 , O_3 equilibrium.

a) NO concentration decreases.

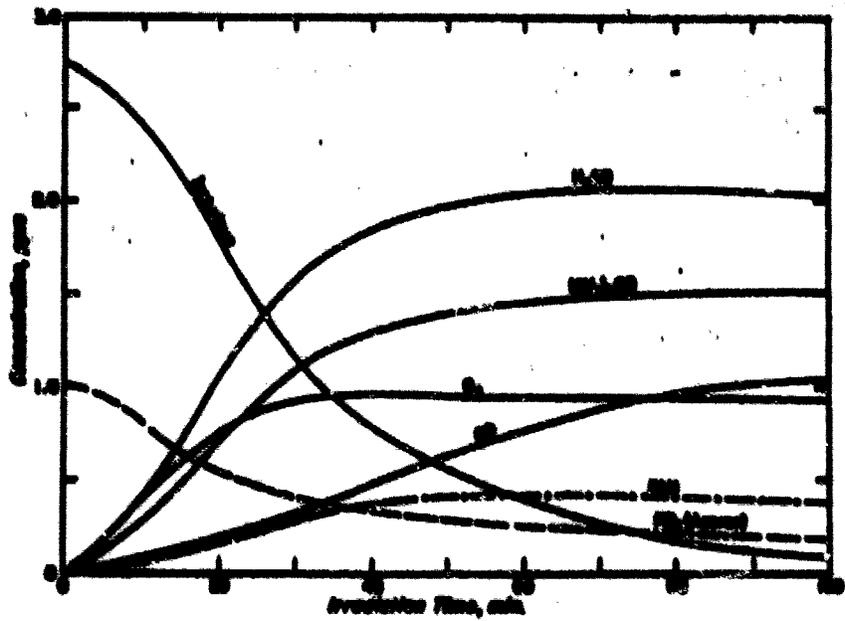
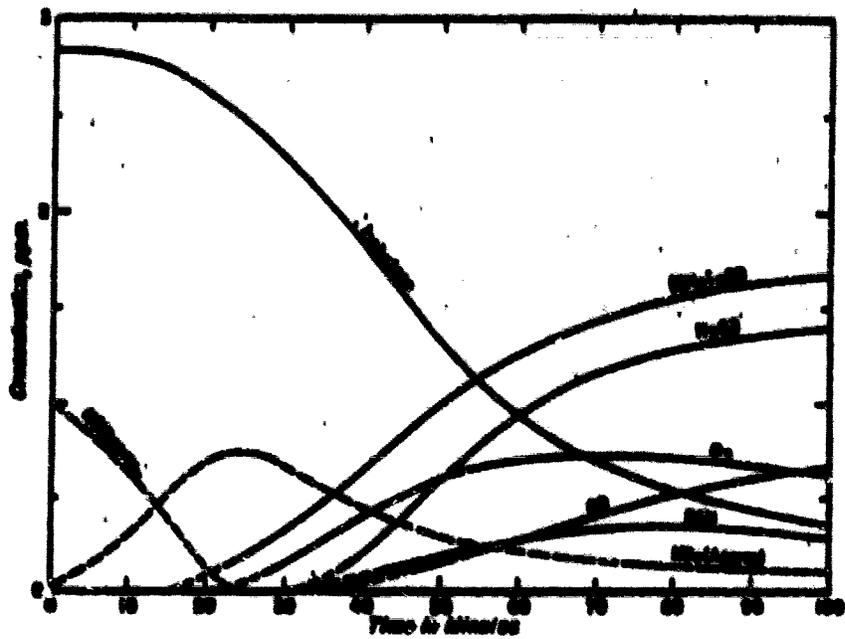
b) NO_2 concentration increases and then decreases.

c) O_3 concentration increases after most of NO has disappeared.

2) Organic compounds disappear.

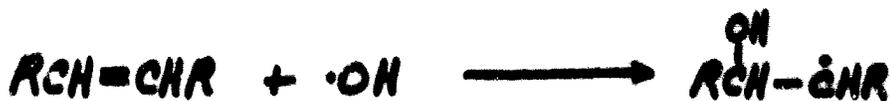
3) Reaction products are formed [RCHO , R_2CO , RONO , RCO_2NO_2 (PAN), CO , etc.].

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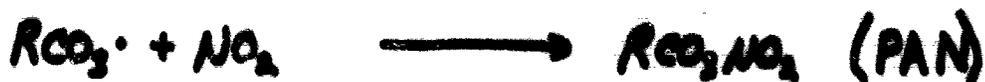
Leighton, 1961.

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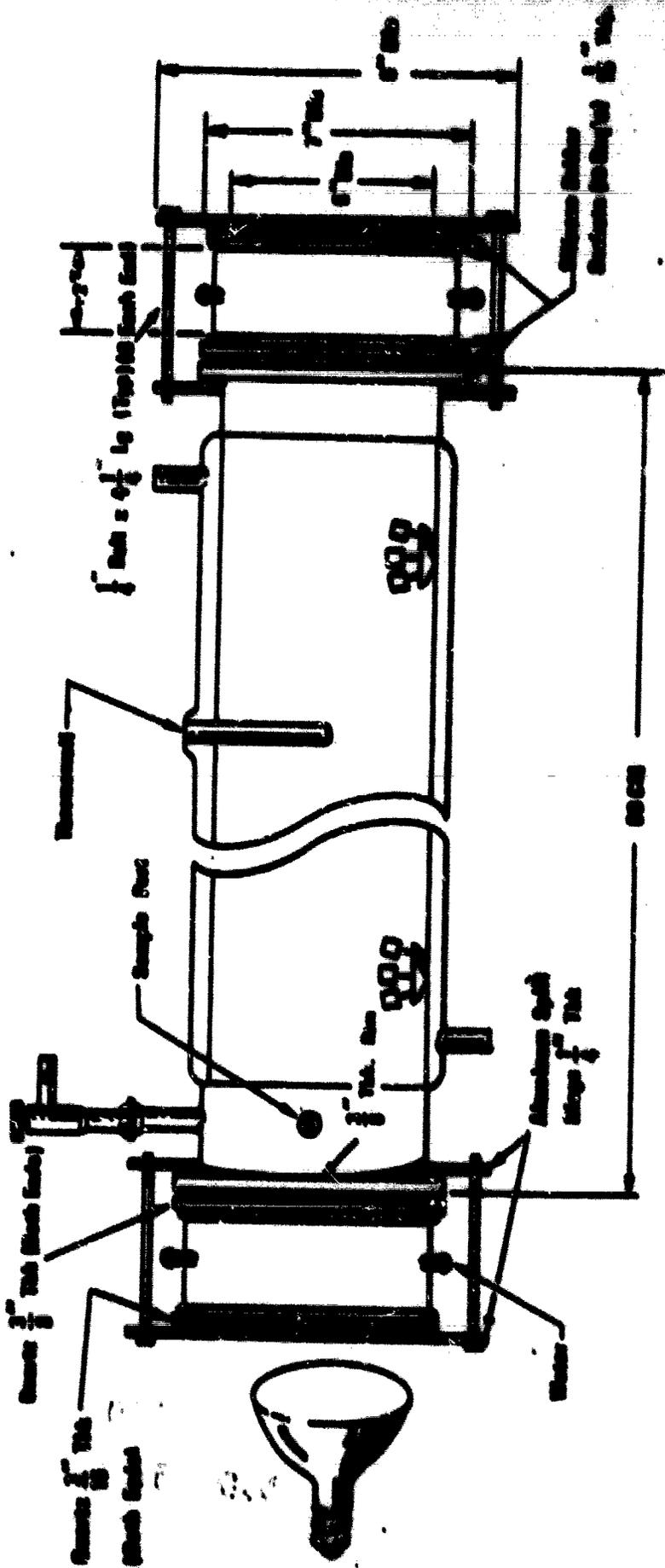


Kerr, Calvert, Demerjian, 1972; Altshaller, Bufalini, 1965, 1971.

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Usual Reaction Conditions

10 ppm organic compound

5 ppm NO (or NO₂)

95% relative humidity

UV light intensity ~2.5 x bright sunlight

(medium pressure Hg arc, $\lambda > 290$ nm)

26-28° C

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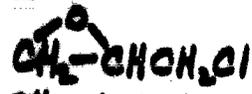
Abilities and Relative Photoactivities of Standard Compounds Determined at Different Laboratories

Compound	Stanford Research Institute	General Motors Corporation	Battelle Memorial Institute	National Air Pollution Control Administration	This work
	50% (18 hr.) 0.92	18% (6 hr.) 0.90	~92% (5 hr.) ~0.5	—	50% (6.8 hr.) 0.99
Ph.Me	—	39% (6 hr.) 0.87	~50% (5 hr.) ~0.6	—	50% (6.8 hr.) 0.99
CH ₂ =CH ₂	50% (7.5 hr.) 1.0	45% (6 hr.) 1.0	~50% (3 hr.) 1.0	50% (2.7 hr.) 1.0	50% (2.9 hr.) 1.0
C ₆ H ₅ COCH ₃	50% (7.0 hr.) 1.1	—	—	50% (2.6 hr.) 1.4	50% (2.5 hr.) 0.99
	50% (0.97 hr.) 17	85% (6 hr.)	~50% (0.2 hr.) ~15	—	50% (0.23 hr.) 15

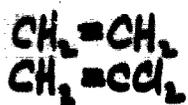
Effect of Light Intensity

<u>Compound</u>	<u>Relative light intensity</u>	<u>$t_{1/2}$</u>	<u>Relative reactivity</u>
↳	1.00	11 minutes	1.00
	0.50	23	0.48
	0.25	40	0.26
CH ₂ =CH ₂	1.00	2.8 hr.	1.00
	0.50	5.2	0.52
	0.25	10.0	0.28
CHCl=CCl ₂	1.00	3.5 hr.	1.00
	0.50	6.9	0.56
	0.25	9.5	0.37

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Compound	With NO	With NO ₂
CH ₂ Cl ₂	23.5 hr (<5%)	28 days (<5%)
CH ₂ Cl ₂	21.0 (<5%)	6 (<5%)
t-BuOH	34.5	
	16.0	
CH ₂ ClCHCl ₂	15.9	
	15.9	15.2 hr.
EtOAc	14.6	
COCl ₂ =CCl ₂	14.2	8.3
MeCOEt	9.8	
MeNO ₂	9.2	
PhCl	8.7	
	6.9	6.5
Ph Me	6.8	
n-BuOH	6.5	
Ph Et	5.0	
	4.7	
CH ₂ =CHCl	4.3	
s-BuOH	4.0	
CHCl=CCl ₂	3.5	2.9
MeCO-i-Bu	3.5	
i-BuOH	3.5	
	3.4	
MeOCH ₂ CHOHMe	3.1	
	3.1	
	2.9	
	3.0	3.0
	2.9	2.8

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2.9

2.1

0.87

0.60

0.30

0.16

2.5

0.19

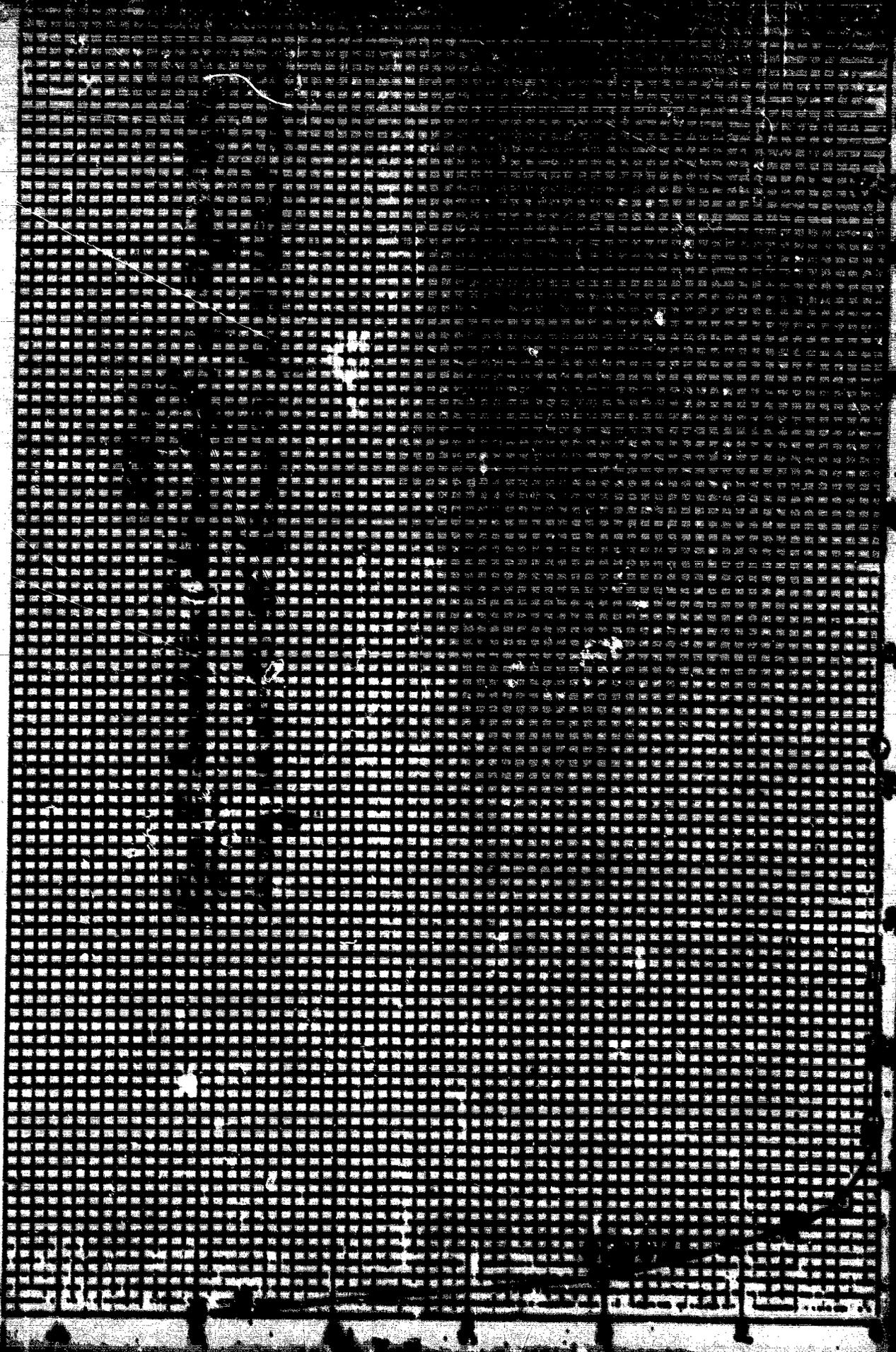
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Effect of Concentration

<u>Compound</u>	<u>Initial concentrations (ppm)</u>		<u>$t_{1/2}$</u>	<u>Relative reactivity</u>
	<u>Compound</u>	<u>No</u>		
✓	10	5	26 min	1.0
	20	10	28	1.2
	40	20	17	1.5
	100	50	13	2.0
CHCl=CCl ₂	10	5	9.5 hr	1.0
	20	10	3.0	1.2
	40	20	1.5	2.3
	100	50	1.0	3.5
CCl ₂ =CCl ₂	10	5	11.2	1.0
	40	20	7.0	1.6
	100	50	3.8	3.0

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Effect of NO Concentration

$\text{CHCl}_3 = \text{CCl}_4 - 10 \text{ ppm}$

NO Concentration

t_k

0 ppm

10.9 hr.

2.5

1.8

5

2.0

10

2.5

20

2.5

40

2.5

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Effect of Relative Humidity

$\text{CHCl}=\text{CCl}_2$ - 10 ppm

<u>Relative Humidity</u>	<u>NO Concentration</u>	<u>t_f</u>
0%	5 ppm	20 hr
35	5	2.1
70	5	3.0
0	0	50
35	0	109

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Competition Reactions

Relative reactivity with NO_2 :



CC=CC reactivity increased in the presence of CC=CC

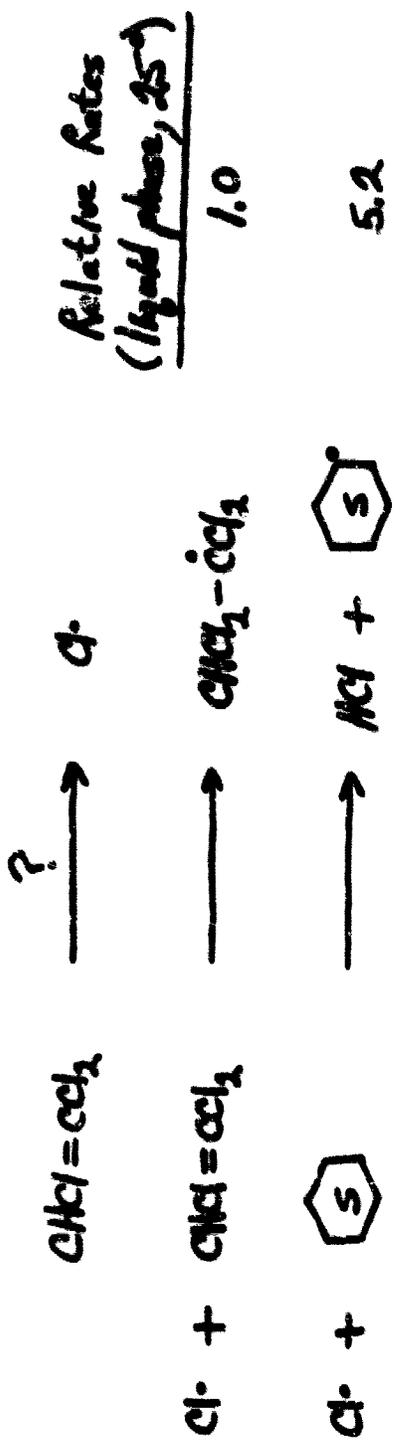
CC=CC reactivity decreased in the presence of C1=CC=CC=C1

"Leveling Effect"

Bufalini and Altshuler, 1967.

Reactivity of $\text{CHCl}=\text{CCl}_2$ in Competition Reactions

Compound	$\xrightarrow{\text{CHCl}=\text{CCl}_2}$	$\xrightarrow{\text{Compound Alone}}$	$\xrightarrow{\text{Compound in Mixture}}$
—	3.5 hr	—	—
CH_2Cl_2	3.5	\Rightarrow 24 hr	\Rightarrow 24 hr
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	7.0	15.9	6.4
EtOAc	6.1	17.6	12.5
$\text{CCl}_2=\text{CCl}_2$	2.8	14.2	5.0
MeCOEt	5.8	9.8	7.4
	8.7	7.6	9.9
Ph Me	7.6	6.8	5.2
t-BuOH	8.5	6.5	3.0
s-BuOH	7.8	3.5	3.3
	6.0	3.4	2.4
$\text{MeOCH}_2\text{CH}_2\text{OMe}$	10.5	3.1	2.5
$\text{CH}_2=\text{CH}_2$	4.8	2.9	2.5
	6.1	0.87	0.82
	8.3	0.80	0.16



Poutsma and Hinman, 1964.

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Photoactivity of S in Competition Reactions

Compound	$t_{1/2}$ S	$t_{1/2}$ Compound Alone	$t_{1/2}$ Compound in Mixture
—	6.9 hr	—	—
CH_2Cl_2	9.0	$\gg 24$ hr.	$\gg 24$ hr.
CH_2Cl_2	6.8	$\gg 24$	$\gg 24$
$\text{CH}_2=\text{CHCl}$	5.4	4.3	5.5
$\text{CHCl}=\text{CCl}_2$	4.9	3.5	8.7
$\text{MeCO}_2\text{-bu}$	8.3	3.5	3.9
	5.4	3.0	13.1
$\text{CH}_2=\text{CH}_2$	6.1	2.9	4.1
$\text{CH}_2=\text{CCl}_2$	5.0	2.1	3.8

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Photoactivity of $\text{CH}_2=\text{CH}_2$ in Competition Reactions

<u>Compound</u>	t_k <u>$\text{CH}_2=\text{CH}_2$</u>	t_k <u>Compound Alone</u>	t_k <u>Compound in Mixture</u>
—	2.9 hr	—	—
CH_3CCl_3	2.9	$\gg 24$ hr.	$\gg 24$ hr.
	4.0	15.9	12.4
	4.1	6.9	6.1
<i>n</i> -BuOH	3.7	6.5	3.8
$\text{CHCl}=\text{CCl}_2$	2.6	3.6	4.8
	4.1	0.87	0.73
	3.2	0.30	0.37

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Photoactivity of in Competition Reactions

<u>Compound</u>	t_k 	t_k <u>Compound Alone</u>	t_k <u>Compound in Mixture</u>
—	0.30 hr.	—	—
CH_3CCl_3	0.24	$\gg 24$ hr.	> 24 hr.
CH_2Cl_2	0.26	$\gg 24$	> 24
<u>n</u> -BuOH	0.32	6.5	4.3
$\text{CHCl}=\text{CCl}_2$	0.16	3.5	8.3
$\text{CH}_2=\text{CH}_2$	0.37	2.9	3.2
	0.37	0.87	0.37

Photoreactivities in a Multicomponent System

<u>Compound</u>	$t_{1/2}$	
	<u>In Mixture</u>	<u>Alone</u>
	12.9 hr.	15.0 hr.
$\text{CHCl}=\text{CCl}_2$	11.1	3.5
$\text{CH}_2=\text{CH}_2$	3.5	2.9
	0.35	0.87
	0.35	0.30

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Effect of $\text{CHCl}=\text{CCl}_2$: S Ratio

Concentrations		Ratio	No Concentration	t_x	
$\text{CHCl}=\text{CCl}_2$	S	$\frac{[\text{CHCl}=\text{CCl}_2]}{[\text{S}]}$		$\text{CHCl}=\text{CCl}_2$	S
10 ppm	0 ppm	∞	5 ppm	3.5 hr	—
10	0.01	1000	5	3.3	—
10	0.1	100	5	2.7	~0.9 hr
10	0.2	50	5	3.5	1.3
10	2	5	5	5.6	2.2
10	10	1	5	>16	5.5
2	10	0.2	5	>20	6.7
0	10	0	5	—	6.9
10	2	5	10	6.6	2.8
10	10	1	10	8.7	4.9

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Effect of CHCl_3 : $\text{CH}_2=\text{CHET}$ Ratio

Concentrations		Ratio	No Concentration	$t_{\frac{1}{2}}$	
CHCl_3	$\text{CH}_2=\text{CHET}$	$\frac{[\text{CHCl}_3]}{[\text{CH}_2=\text{CHET}]}$		CHCl_3	$\text{CH}_2=\text{CHET}$
10 ppm	0 ppm	∞	5 ppm	3.5	—
10	2	5	5	4.2	4.1
10	10	1	10	7.0	6.4
0	10	0	5	—	15.9

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Compound	t _{1/2}		Relative Reactivity			
	NO (5 ppm)	NO ₂ (5 ppm)	O ₃ (15 ppm)	NO	NO ₂	O ₃
<chem>CH2=CHC(=O)OC</chem>	15.9 hr	15.2 hr	0.83 hr	0.23	0.19	0.51
<chem>C1=CC=CC=C1</chem>	6.9	7.5	1.0	0.51	0.38	0.42
<chem>C=CC(=O)C</chem>	3.5	2.9	0.42	1.0	1.0	1.0
<chem>C=C</chem>	2.9	2.5	—	1.2	1.2	—
<chem>C1=CC=CC=C1</chem>	0.87	0.19	—	4.0	15.1	—
<chem>C=C</chem>	0.30	0.17	—	117	15.9	—

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Competition Experiments with NO, NO₂, O₃

Compound Pair	$t^{1/2}$		Reactivity Ratios	
	NO (p ppm)	NO ₂ (p ppm)	NO	NO ₂
<chem>C1=CC=CC=C1</chem>	4.9 hr	5.0 hr	1.8	2.1
<chem>C=CCl</chem>	8.7	10.5		1.2
<chem>C=C</chem>	6.4	8.0	1.1	1.9
<chem>C=C</chem>	7.0	10.5	1.7	1.0
<chem>CCCCC</chem>	0.57	0.13	1.0	1.1
<chem>C1=CC=CC=C1</chem>	0.57	0.15		

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Possible Oxidation Products and Reactive Intermediates from $\text{CHCl}=\text{CCl}_2$

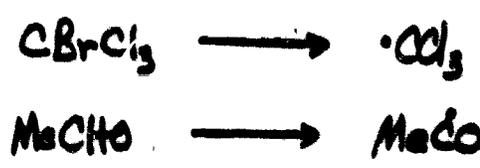
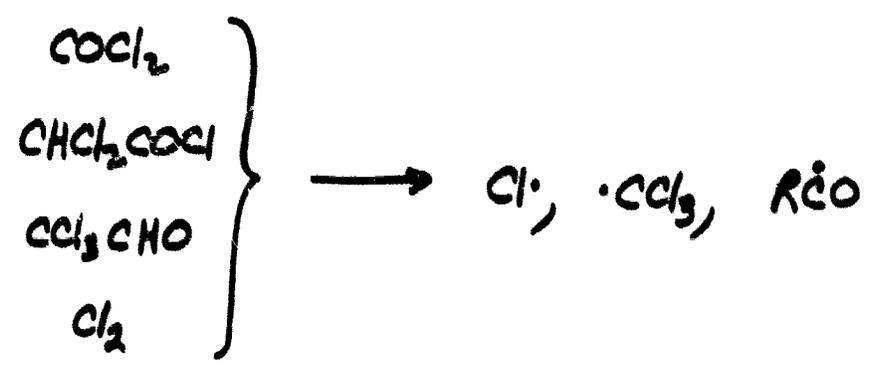


Photo-reactivity of $\text{CHCl}=\text{CCl}_2$ with Possible Oxidation Products and
Other Co-reactants

<u>Co-reactant</u>	<u>t_k</u>
NO (5 ppm)	3.5 hr
CCl_3CHO (2)	3.2
CCl_3CHO (5)	0.93
CCl_3CHO (10)	0.95
MeCHO (10)	15.7
MeCHO (10) + NO (5)	10.7
CBrCl_3 (10)	5.0
CBrCl_3 (10) + NO (10)	1.3
Cl_2 (1)	3.1
Cl_2 (1) + NO (5)	0.93
Cl_2 (2)	0.18
Cl_2 (5)	< 0.05
Cl_2 (10)	< 0.05
COCl_2 (5)	5.1
COCl_2 (5) + NO (5)	2.2

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Photoactivity of $\text{CH}_2=\text{CHET}$ with Possible $\text{CHCl}=\text{CCl}_2$ Oxidation Products

<u>Co-reactant</u>	<u>$t_{1/2}$</u>
NO (5 ppm)	15.9 hr.
NO_2 (5)	15.2
$\text{CHCl}=\text{CCl}_2$ (10) + NO (10)	6.4
CCl_3CHO (10)	3.3
CCl_3CHO (10) + NO (10)	3.1
CCl_3CHO (10) + NO_2 (10)	3.1
CHCl_2COCl (10) + NO (10)	9.1

Compound	$t_{1/2}$			
	NO (5 ppm)	MeCHO (10 ppm)	MeCHO + NO (10 ppm) (5 ppm)	CCl_3CHO (10 ppm)
 <chem>C1CO1</chem>	15.9 hr.	—	—	3.3 hr.
 <chem>C1CCCCC1</chem>	6.9	98 hr.	22 hr.	3.4
<chem>CH3=CCl2</chem>	3.5	15.6	15.3	0.45
<chem>CH2=CH2</chem>	2.9	—	10.6	3.1
 <chem>C1=CCCCC1</chem>	0.87	12.2	0.50	1.8
 <chem>CCC=C</chem>	0.30	6.3	0.22	2.3

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Competition Experiments with Cl_2 (5 ppm)

Compound Pair (10 ppm each)	$t_{1/2}$
$\text{CHCl}=\text{CCl}_2$	< 0.12 hr. (100%)
$\text{CCl}_2=\text{CCl}_2$	< 0.12 (100%)
$\text{CH}_2=\text{CH}_2$	0.37
$\text{CCl}_2=\text{CCl}_2$	1.7
$\text{CH}_2=\text{CH}_2$	0.57
$\text{CHCl}=\text{CCl}_2$	0.58

Relative Rates for $\text{R}_2\text{C}=\text{CR}_2 + \text{Cl}_2 \xrightarrow[27^\circ\text{C}]{\text{Gas Phase}} \text{R}_2\text{CClCClR}_2$

$\text{CH}_2=\text{CH}_2$	$\text{CHCl}=\text{CCl}_2$	$\text{CCl}_2=\text{CCl}_2$
20,000	4	1

P. Goldfinger, et. al., 1963.

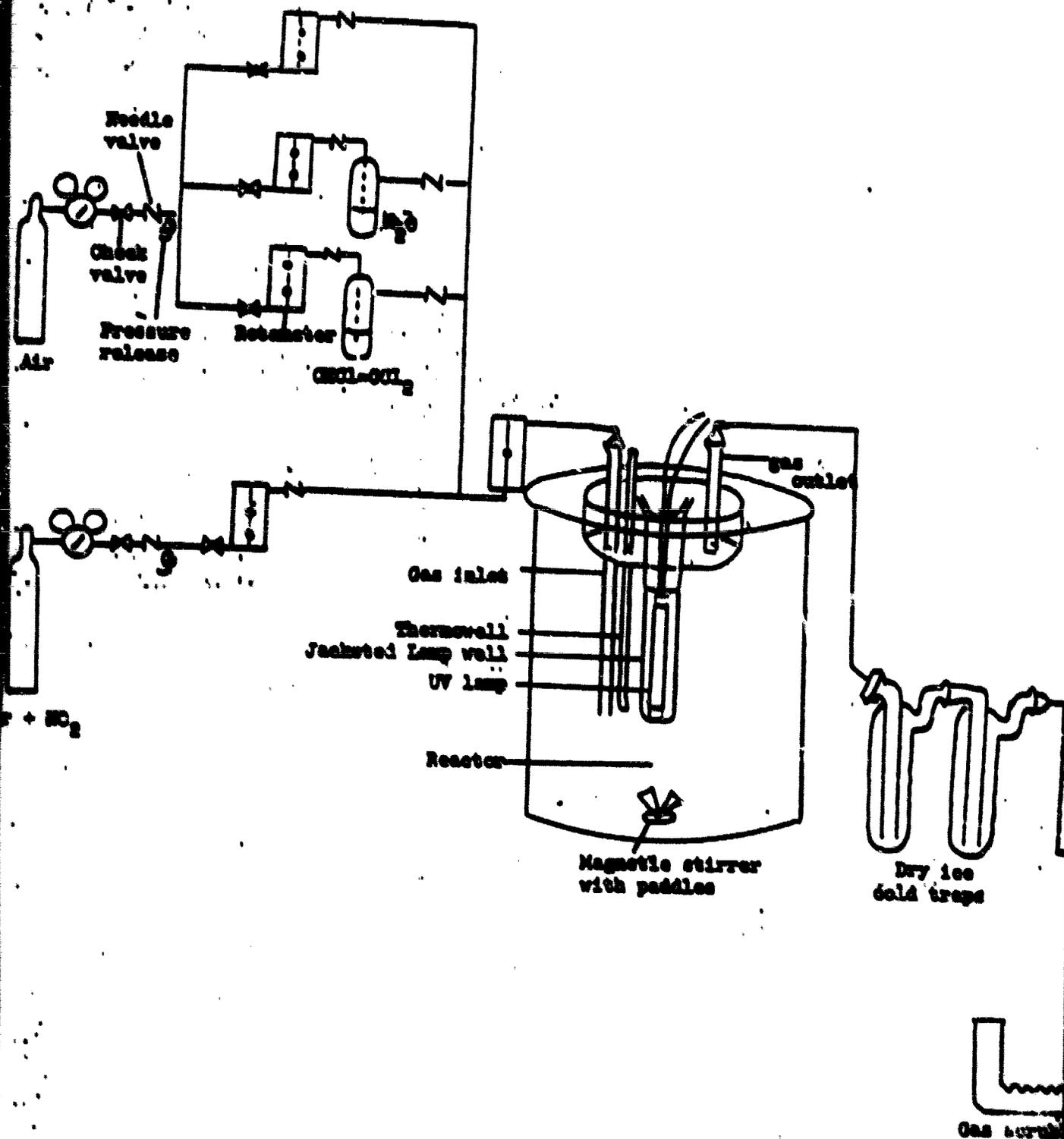
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Other Possible Reactive Intermediates

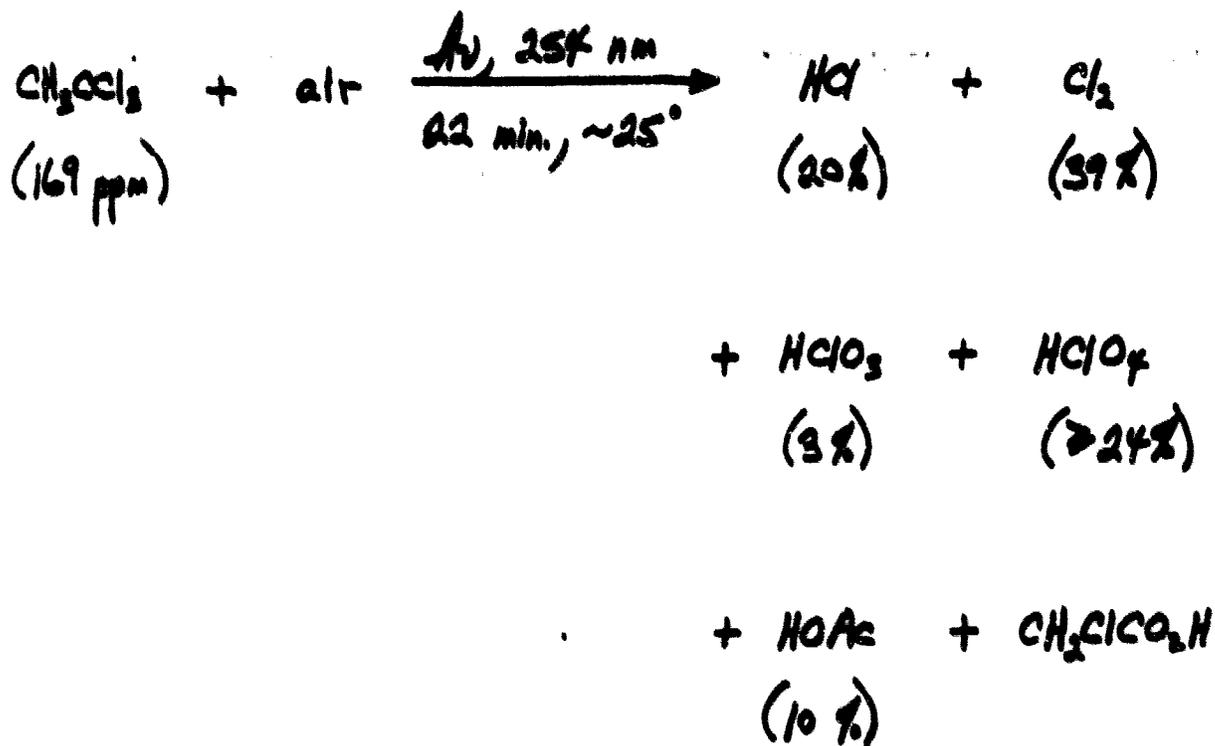
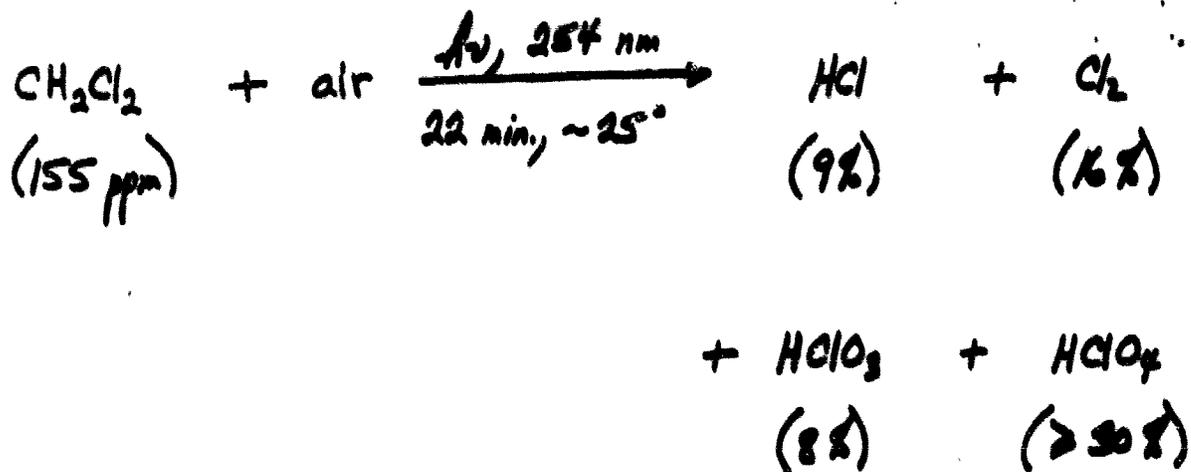


Pitts, et. al, 1969; Stedman, et. al, 1970; Kiryashin and Blaklov, 1968
Johnston, et. al, 1969; Pierrard, 1969.

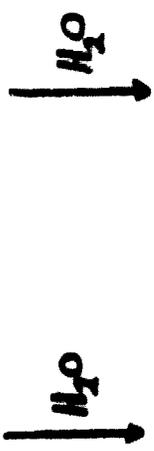
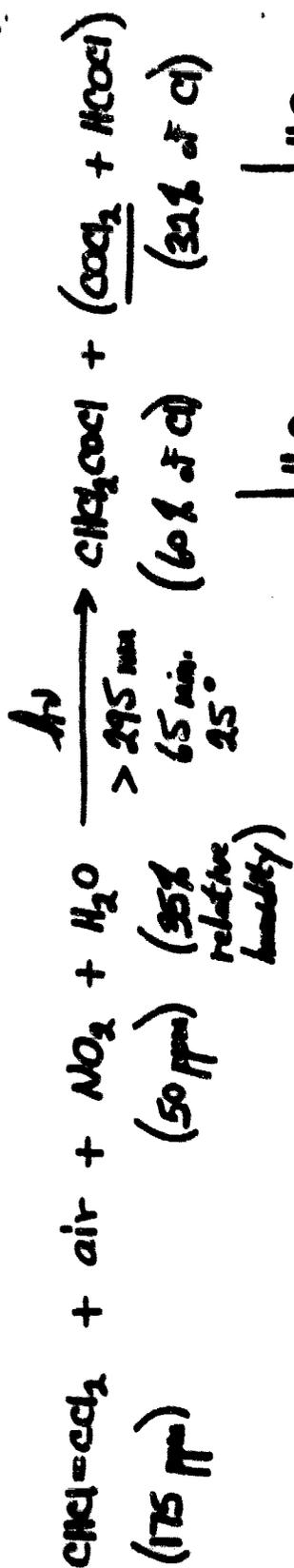
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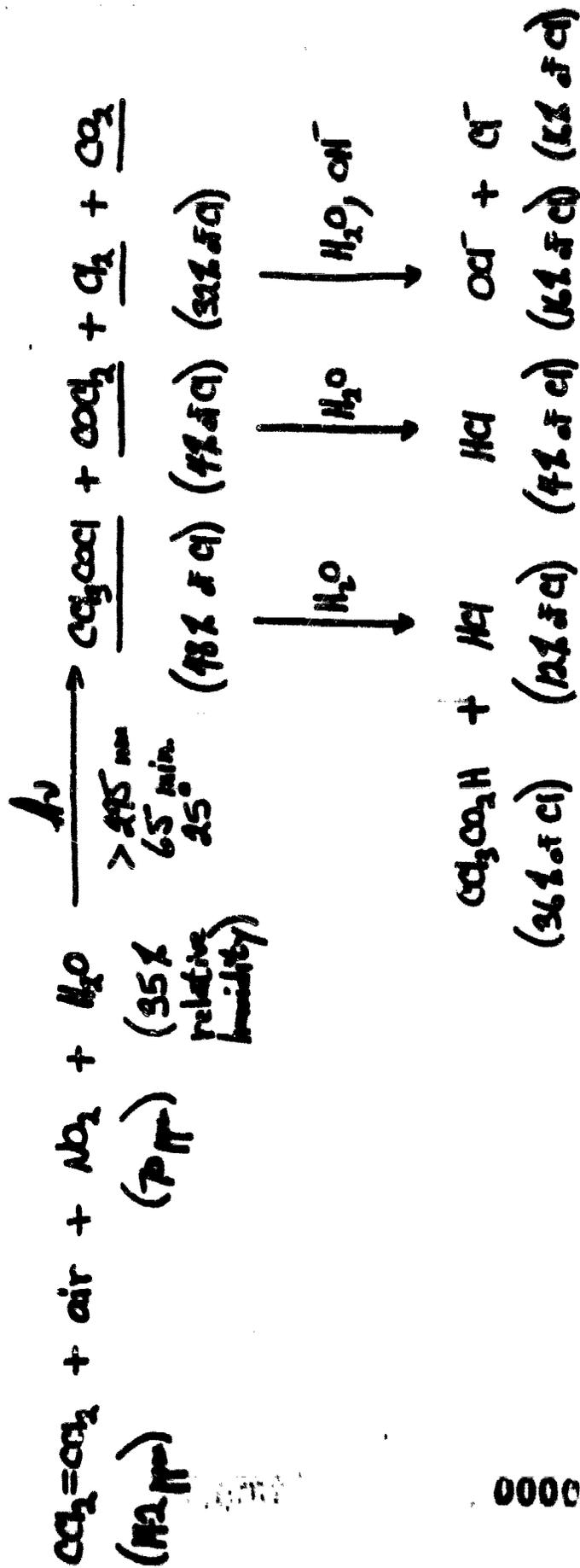
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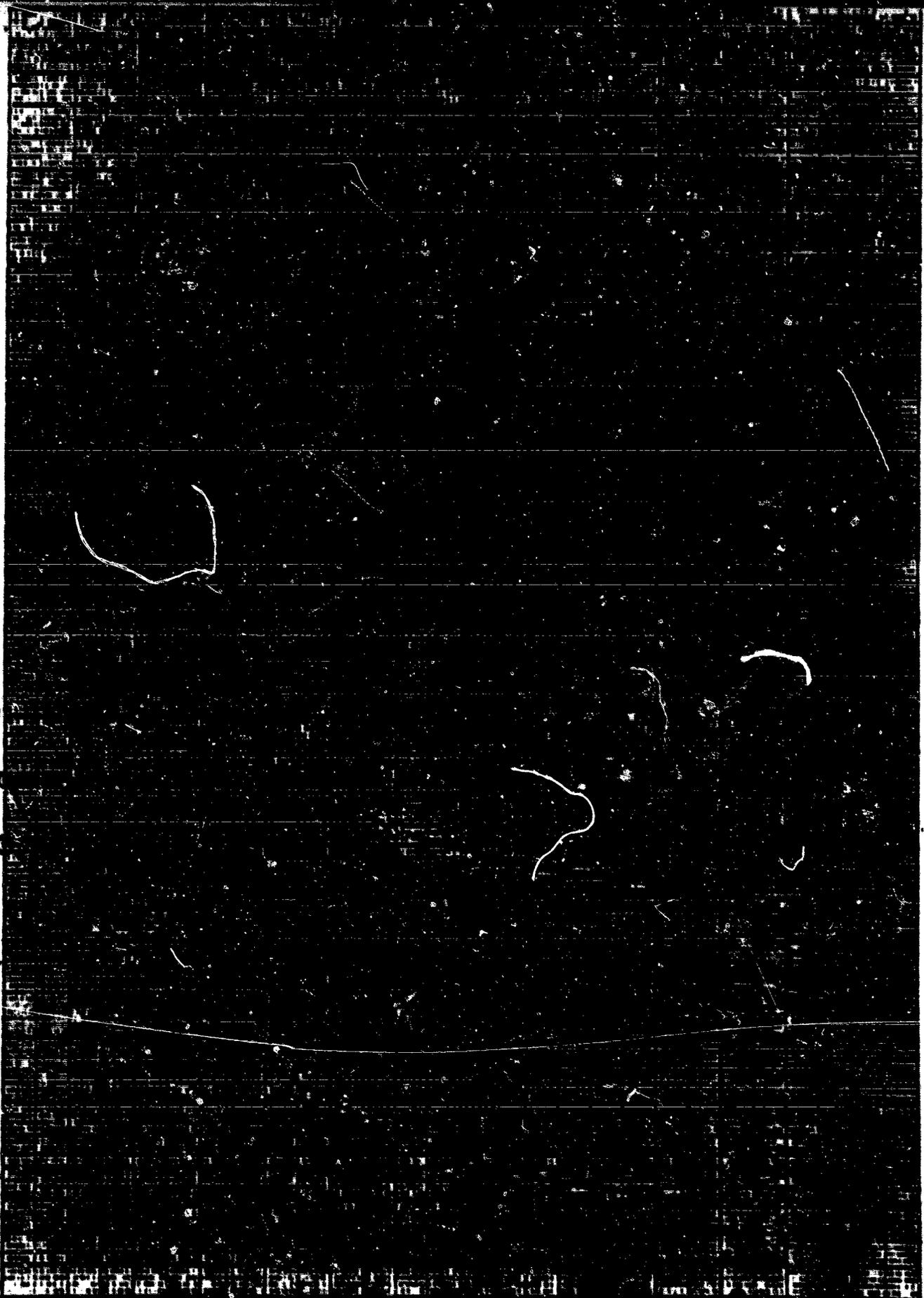


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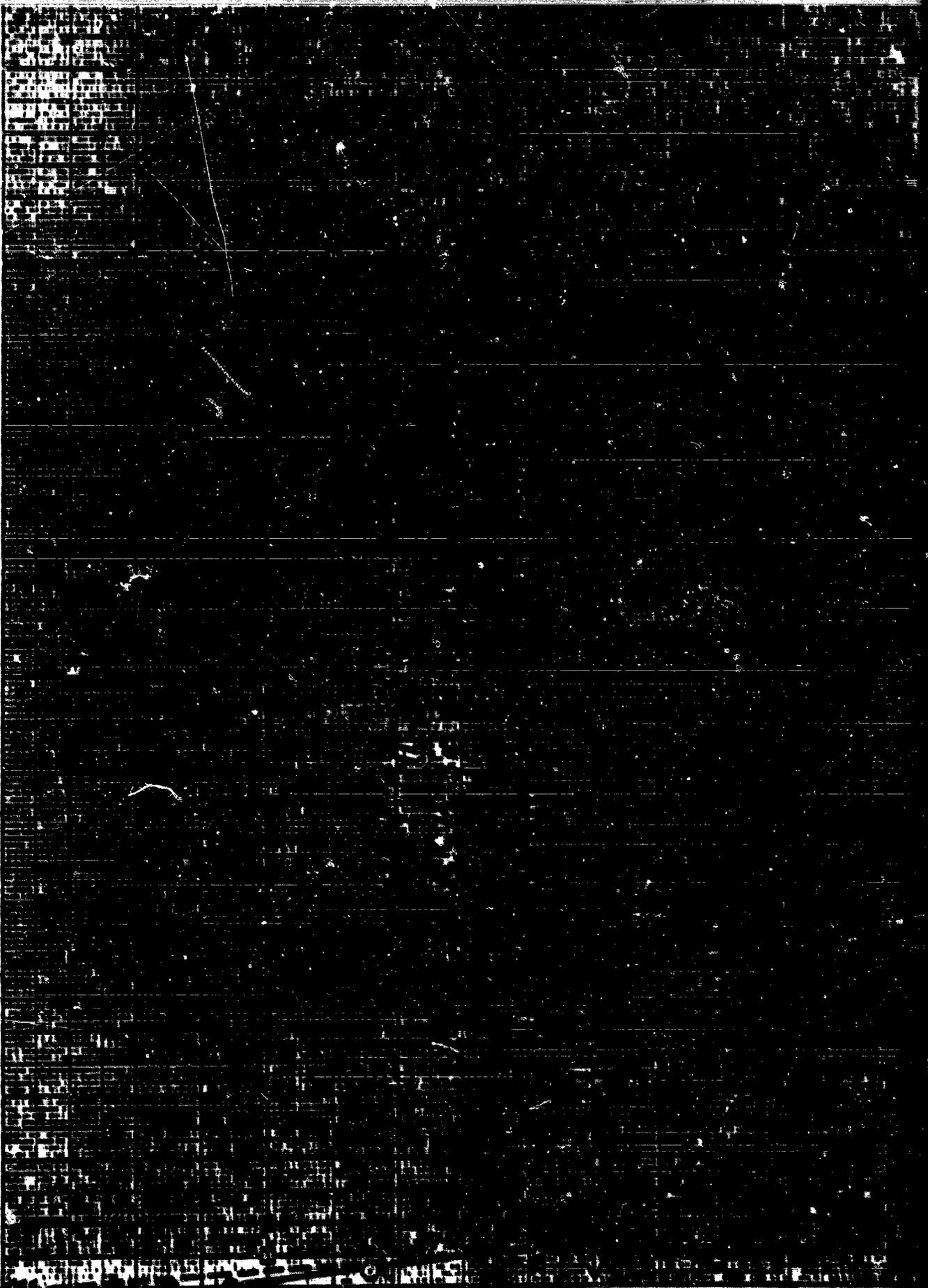
Concentration of Output (ppm) $\frac{1}{10}$

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

0 1 2 3 4 5 6 7 8 9 10



NO. 201 TO THE BUCH 46 1242
MAY 1942
MILWAUKEE, WISCONSIN

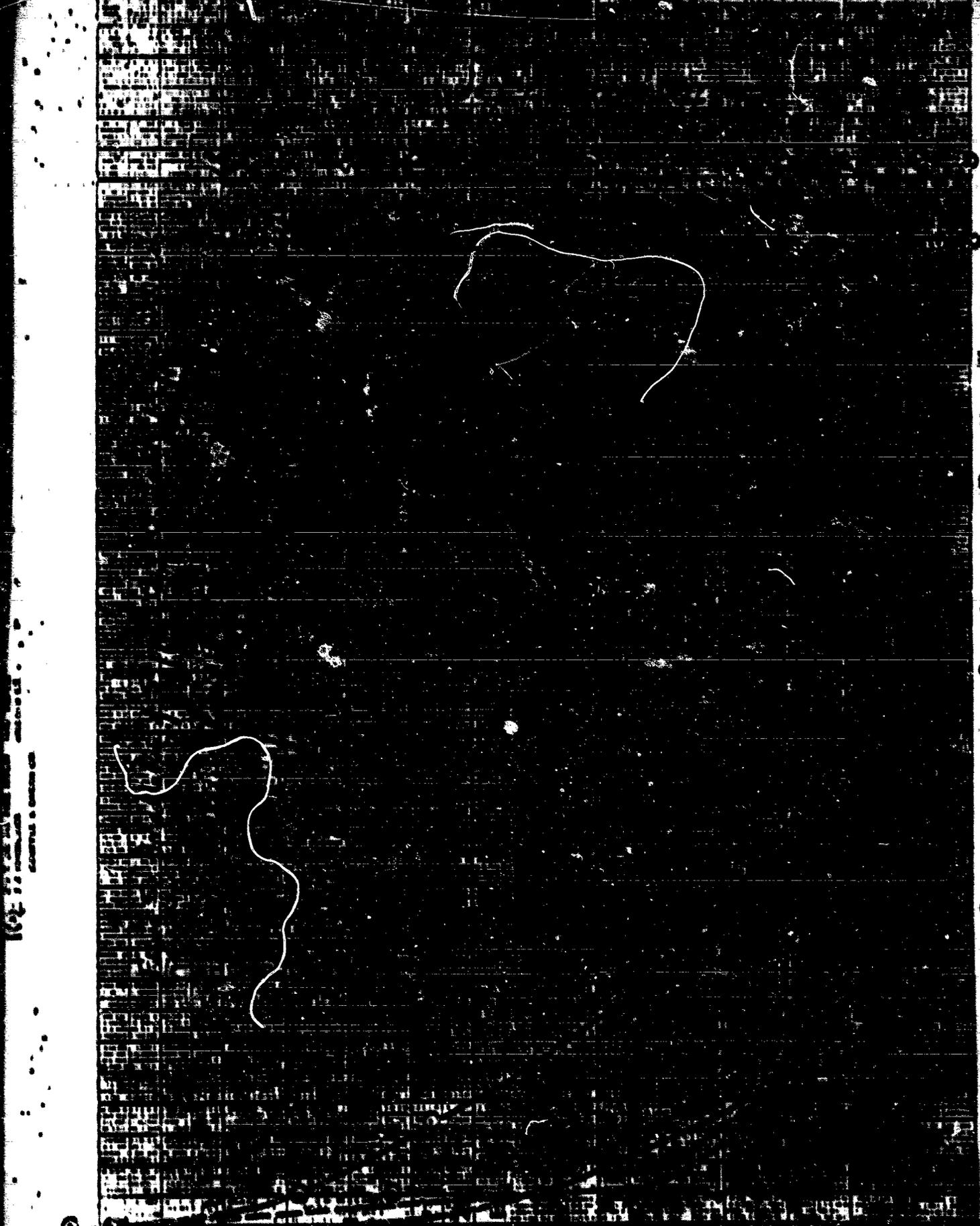


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Concentration of Oxide (ppm)

Concentration of Oxide (ppm)

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

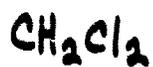


102-17-2000
SECRET
CONTROL & SAFETY OF

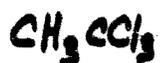
21 22 23 24 25 26 27 28 29 30

Summary

Smog potential as judged by
reactivity and oxidant formation

Compound

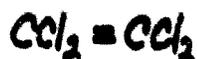
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Acknowledgments

Dr. Corwin J. Brodeweg

Dr. Michael J. Mintz

Dr. Jack P. Arrington

Mrs. Nancy B. Tetertiller

Mrs. Violet L. Stevens

Mr. George J. Kallos

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Organic Photochemistry, XIII. ¹ Environmental Fate and Effect of Chlorinated Solvents. II. ² Simulated Atmospheric Photochemistry of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Hydrocarbons

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Abstract

In order to estimate the reactivity of chlorinated solvents in the atmosphere, laboratory studies were carried out on the photolysis rates of four common chlorinated solvents, six other chlorinated hydrocarbons, and 23 other organic compounds under simulated atmospheric conditions. Most reactions included nitric oxide or nitrogen dioxide, and water vapor in the air; the rates of disappearance of the organic compounds were measured. Under simulated sea level atmospheric conditions ($\lambda > 290$ nm), vinylidene chloride, cis- and trans-dichloroethylene, trichloroethylene, and vinyl chloride were moderately reactive when compared with the reactivity of a series of standard hydrocarbons. Chlorobenzene, tetrachloroethylene, and 1,1,2-trichloroethane

¹Part XII: (Dilling et al., 1973).

²Part I: (Dilling et al., 1974a).

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had a low reactivity. Methylene chloride and 1,1,1-trichloroethane were nonreactive under sea level conditions, but were rapidly decomposed under simulated high altitude conditions (λ 854 nm principally).

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The fate and effect of chlorinated solvents which may be discharged to the environment (Murray and Riley, 1973a; Murray and Riley, 1973b; Farber, 1973) are important from an ecological standpoint. In the preceding paper (Cilling et al., 1974a) we showed that the major portions of several chlorinated solvents evaporated relatively rapidly from dilute aqueous solutions under simulated environmental conditions. We therefore undertook a study of the reactivity of several of the more important chlorinated solvents in use today, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), and also several other related chlorinated compounds under simulated atmospheric conditions.

To the best of our knowledge no studies have been reported on the photo-reactivity (rate of disappearance) of CH_2Cl_2 and CH_3CCl_3 under simulated atmospheric conditions. However it has been reported (Altschuler and Bufalini, 1971) that chlorinated saturated hydrocarbons were virtually unreactive. An indication of the expected low reactivity of CH_2Cl_2 and CH_3CCl_3 can be found in other chemical studies on these compounds. Liquid CH_2Cl_2 was unreactive toward oxygen even at temperatures up to 140° (Carlisle and Levine, 1932). CH_3CCl_3 in the liquid phase was very resistant to oxidation with oxygen under relatively mild conditions (Archer, 1970), but did react under high pressure (Young, 1958). The quantum yield for the chlorine initiated photooxidation of CH_3CCl_3 in the vapor phase was much lower than was the quantum yield for the photooxidation of $\text{CCl}_2=\text{CCl}_2$ (Bertrand et al., 1971).

Considerably more work has been done on the behavior of $\text{CHCl}=\text{CCl}_2$ under simulated atmospheric conditions than on the other chlorinated solvents considered in this paper. There is reasonably good agreement on the effect of $\text{CHCl}=\text{CCl}_2$ based on some criteria. Based on other criteria the agreement is not

as good. In general $\text{CHCl}_2\text{-CCl}_2$ is of intermediate reactivity when compared with other common atmospheric contaminants (Schuck and Doyle, 1979; Manning, 1967; Wilson et al., 1969a; Altshuler and Bufalini, 1971). The data were variable and easily affected by changes in experimental conditions (Manning, 1967; Wilson et al., 1969a; Wilson et al., 1969b). The rates of formation of smog components and their maximum observed concentrations fell rapidly as the $\text{CHCl}_2\text{-CCl}_2$:nitric oxide (NO) ratio decreased; at ratios less than one, the photoreactivity of $\text{CHCl}_2\text{-CCl}_2$ was completely inhibited (Wilson et al., 1969b; Wilson, 1969). At any fixed $\text{CHCl}_2\text{-CCl}_2$:NO ratio the reactivity of $\text{CHCl}_2\text{-CCl}_2$ decreased as the absolute concentrations fell as measured both by $\text{CHCl}_2\text{-CCl}_2$ disappearance and appearance of smog components (Wilson, 1969).

$\text{CHCl}_2\text{-CCl}_2$ was moderately reactive under simulated atmospheric conditions as judged by its rate of disappearance (Schuck and Doyle, 1979; Wilson, 1969; Wilson et al., 1969b; Wilson et al., 1969c; Altshuler and Bufalini, 1971). It was less reactive than propylene (MeCH=CH_2) (Schuck and Doyle, 1979; Wilson et al., 1969a) but there was disagreement concerning its reactivity relative to the standard compound ethylene ($\text{CH}_2=\text{CH}_2$). Some workers found $\text{CHCl}_2\text{-CCl}_2$ disappeared more slowly than $\text{CH}_2=\text{CH}_2$ (Wilson, 1969; Wilson et al., 1969b; Wilson et al., 1969c) while others found $\text{CHCl}_2\text{-CCl}_2$ reacted more rapidly than $\text{CH}_2=\text{CH}_2$ (Schuck and Doyle, 1979; Altshuler and Bufalini, 1971). The effect of several other variables on the rate of disappearance of $\text{CHCl}_2\text{-CCl}_2$ have been determined. These variables include $\text{CHCl}_2\text{-CCl}_2$:NO ratio and their absolute concentrations, and replacement of NO with nitrogen dioxide (NO_2) (Wilson et al., 1969c).

In general $\text{CCl}_2=\text{CCl}_2$ had a relatively low reactivity under simulated atmospheric conditions (Schuck and Doyle, 1979; Manning, 1967; Altshuler and Bufalini, 1971).

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Experimental

Short Term (5th Hr) Sea Level Simulated Photoirradiation Reactor Design and Operation. The reactor (9.98 liters) is shown in Figure 1. All materials in the reactor to which the reaction mixture was exposed were constructed of glass, quartz or Teflon—except for two silicone rubber gaskets for seals at the ends. The reactor and light sources were enclosed in a wooden box so that there would be little exposure of the ultraviolet light to the chemist and for protection in case of implosion of the reactor while under vacuum.

The reactor temperature (26-28°) was controlled by a constant temperature bath which circulated water through the jacket surrounding the reactor as well as through the 2 inch cylinders attached to the ends of the reactor. The cooling water in the cylinders at the ends was necessary to remove the heat from the sunlamps.

In order to continually circulate the contents within the reactor, an internal, leak-proof and inert circulation system was designed. Stirrers (Figure 2) were used; they were constructed from watch glasses, Teflon blades, and bar magnets, and were rotated by external magnetic stirrers. The effectiveness of these stirrers was demonstrated by the addition of a sample of cyclohexene ($\alpha\text{-C}_6\text{H}_{12}$) to the reactor. Uniform mixing occurred in less than one minute with the stirrers on, while it took over 14 minutes with the stirrers off (Table I). See below for reactor loading and sampling techniques.

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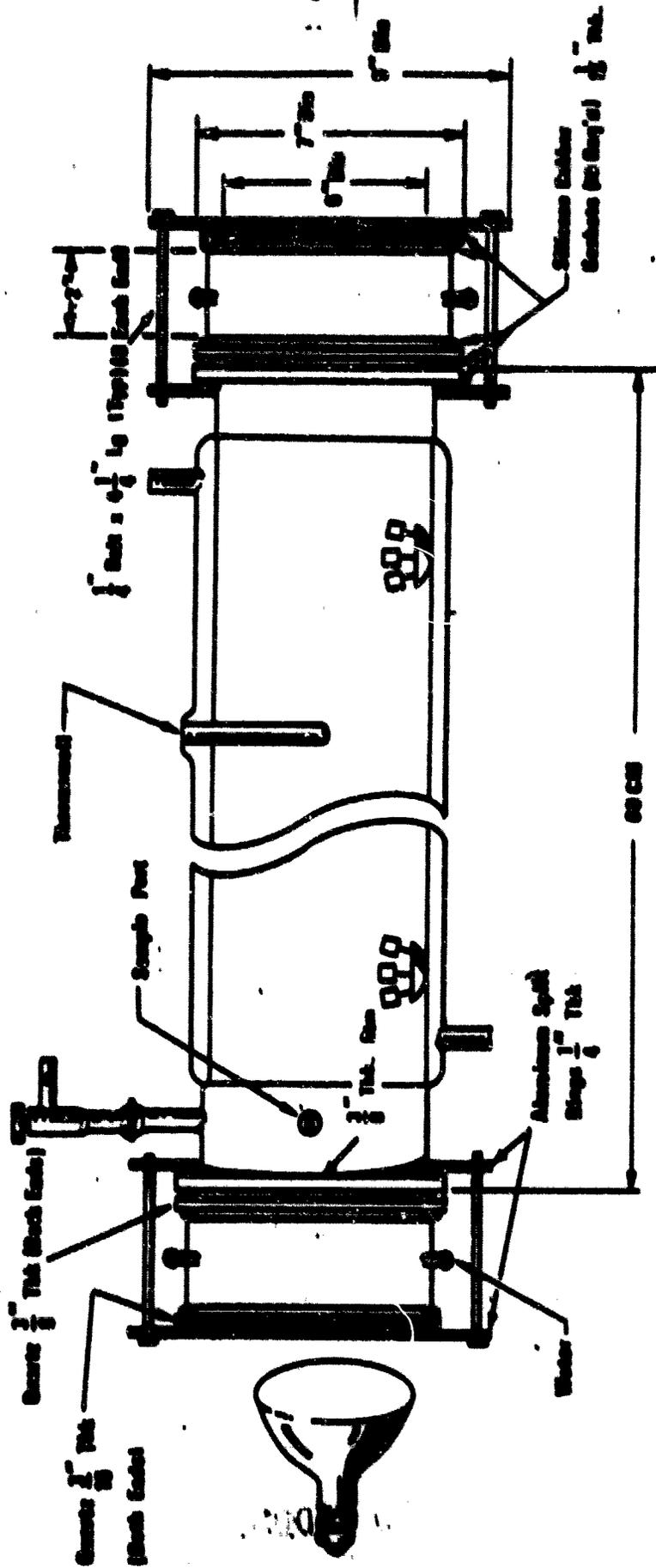


Figure 1. Short Tube Sea Level Simulated Photolysis Reactor

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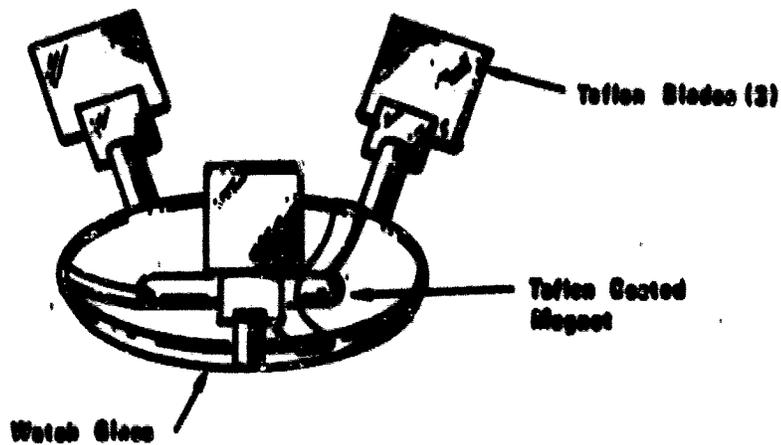


Figure 2. Stirring Devices For Photochemical Reactor

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Table I. Effectiveness of Air Circulation

With stirrers on

<u>Time</u>	<u>$g-C_6H_{12}$ 50 peak height</u>
0 seconds	$g-C_6H_{12}$ added
60	74
800	73
340	73

With stirrers off

0 seconds	$g-C_6H_{12}$ added
90	380
4 minutes	184
7	190
11	184
14	118
16	Stirrers turned on
17	82
19	83
23	82

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The ultraviolet light sources were two General Electric 275 watt reflector sunlamps (Keller, 1967a) whose short wavelength cut off was 290 nm as determined with an International Light Inc. IL600 Research Photometer and an IL660 Photomultiplier Power Supply. The 290 nm cut off is about the same cut off as that of sunlight at the earth's surface (Keller, 1967a). These lamps were used since to a rough approximation they simulate sunlight (Kicksic et al., 1974; Keller, 1967a) and are easily maintained; the output in the ultraviolet range is approximately that of sunlight, and the lamp design was convenient for use with our reactor. A General Electric ultraviolet meter, model 80W40Y17, was used to compare the ultraviolet light output of the sun with that from the sunlamps. Figure 3 shows the ultraviolet light output of two sunlamps. The data were obtained by leaving one end of the reactor open while the lamp and cooling jacket at the other end were in operation. The light intensity was determined by taking readings within the reactor at various distances from the lamp. The process was repeated with the second lamp in place of the first one. The upper curve in Figure 3 is the combined intensity of both lamps. An average of ~ 90 E-vitons/cm² is estimated. The intensity of natural sunlight at noon one summer day in Freeport, Texas, was 35 E-vitons/cm². Thus, the ultraviolet light intensity within the reactor varied from about 2 to 4 times that of natural sunlight; the estimated average is ~ 2.6 times. This higher intensity does not affect our conclusions to any significant extent since all the reaction rates were compared in a relative manner. It should be noted that the contents within the reactor received approximately two times more ultraviolet radiation than if these same contents were to occupy a similar volume in space between the lamps if the reactor were not there. The increased light within the reactor very likely resulted from the

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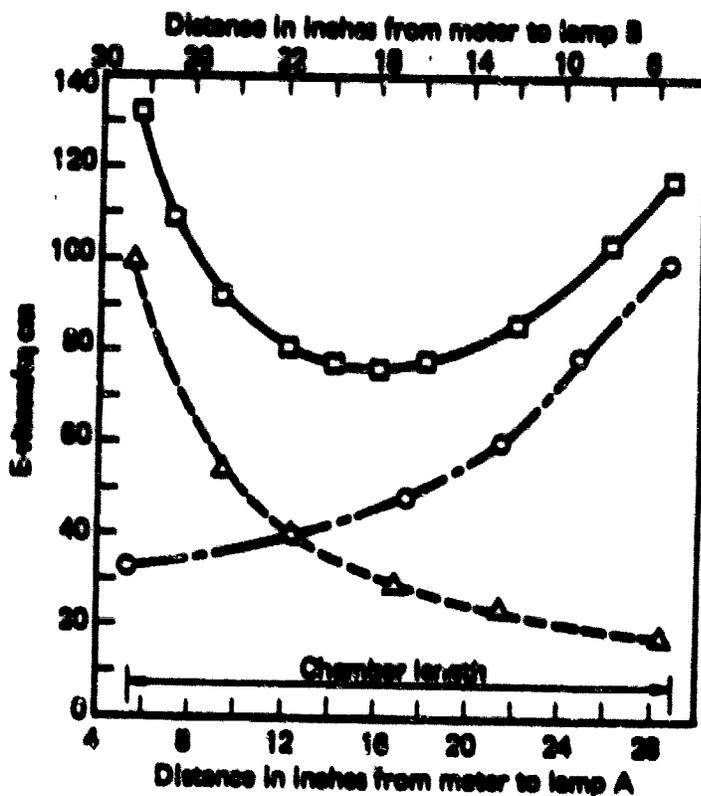


Figure 3. Ultraviolet light intensity inside reactor; intensity from lamp A (- - -); intensity from lamp B (- · - ·); combined intensity from lamps A and B (—).

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multiple reflections within the reactor walls. Since the sunlamps gradually deteriorated, they were periodically replaced. To determine when this was necessary, a series of standard materials were periodically run and compared. A constant voltage transformer was used to stabilize the output from the sunlamps. There should be essentially no loss of ultraviolet light from the sunlamp which passes through 2 inches of distilled water and two thicknesses ($3/16$ and $3/8$ inch) of 101 quartz (Kollar, 1969a).

The reactor leak rate or rate of loss of contents through glass wall absorptions, absorption in the Teflon, or permeation through the silicone rubber gaskets was minimal, too low to determine. The loss of sample through "leakage" was probably less than the experimental error in sampling and analysis. It is estimated that there was less than 5% loss in an 8 hr run, and certainly not greater than 10% in a 24 hr run.

The reactor was cleaned by evacuating to -0.9 mm for an hr or more. The cleanliness of the reactor was periodically checked by filling with pure air and analyzing the air by gc for any residual solvent or impurities. No evidence of contaminant buildup was found during this work.

Sampling Techniques and Analysis. The rate of solvent disappearance in the reactor was determined with a hydrogen flame ionization gas chromatograph (FAM 5790). Initially, 1 cc samples were removed with a syringe from the sample port which was stoppered with a serum cap. These samples were then transferred to the gas chromatograph, and upon elution, the peaks were either measured by peak height or by peak area with an Infotronics CMS-100 Electronic Integrator which was connected to a Teletype Printer. All-glass hypodermic syringes, labeled B-O Yale, were used. Later, an automatic sampling device was incorporated into the analysis. This device gave excellent reproducibility while the syringe

technique was sometimes erratic and required several sample injections in order that ^a data point could be determined with confidence. A small diaphragm pump (Universal Electric Co., Model 143-005) was used to circulate the reactor contents through a Beckman gas sampling valve. All tubing between the reactor, pump and sampling valve was stainless steel (SS) 0.045 inch ID with a capacity of ~0.3 cc/ft. A four-way Asco solenoid valve (Model 8345A) was used to change the valve positions on the gas sampling valve. All of the operations connected with the analysis by gas were completely automated by a multiple timing device.

The gas conditions were as follows: helium flow through column, ~85 cc/minute (85 psi); hydrogen flow at the flame head, ~10 cc/minute (4 psi); air flow at the flame head, ~300 cc/minute (33 psi); detector block temperature, 280°; injection port temperature, usually near the column temperature; column temperature, variable but usually less than 130°. All analyses were carried out under isothermal conditions except when low and high boiling compounds were investigated together. The columns used were a 12 ft x 1/8 inch SS packed with Poropak Q, 7 ft x 1/8 inch SS packed with 20% Orinote, and 6 ft x 1/8 inch SS packed with 10% UC-W98 (silicone rubber). Table II shows the relative response of various chlorinated compounds along with some hydrocarbons. The lower limits of detectability for most of these materials were not determined, but in most cases were probably 0.1 to 1 ppm or less.

To check the reproducibility of the addition of materials to a constant volume of air and the linearity of the analytical method, liquid gig-CHCl-CHCl was added in incremental volumes from a 0.01 microliter syringe to 10 liters of nitrogen in a Saran[®] bag. After each solvent addition, the air was analyzed by gas. The following data were obtained (volume of gig-CHCl-CHCl added and gas peak height given): 0.15 μ l, 14.3 units; 0.30 μ l (~10 ppm), 31.5 units; 0.60 μ l,

Table II. Response to Various Chlorinated Compounds by Flame Ionization Detector GC

Compound ^a	Column	Area	Relative response
CH ₂ Cl ₂	Orinite	191	1.0
CH ₂ =CH ₂	Poropak Q	303	1.6
Vinyl chloride (CH ₂ =CHCl)	Orinite	397	2.1
Vinylidene chloride (CH ₂ =CCl ₂)	Orinite	455	2.4
<u>cis</u> -Dichloroethylene (cis-CHCl=CHCl)	UC-W98	465	2.4
<u>trans</u> -Dichloroethylene (trans-CHCl=CHCl)	Orinite	619	3.2
CHCl=CCl ₂	Orinite	432	2.3
CCl ₂ =CCl ₂	Orinite	442	2.3
CH ₃ CCl ₃	UC-W98	625	3.3
<u>trans</u> -2-Butene (trans-MeCH=CHMe)	Orinite	920	4.8
2-C ₆ H ₁₀	Orinite	937	4.9

^aSample size was 1 cc and all areas were based on a sensitivity of 1 x 4 with a compound concentration of 10 ppm in air.

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60.8 units; 0.90 μ l, 86.3 units. In another experiment, 0.89 μ l cis-CHCl-CHCl . was added to the reactor (9.38 liters) and gc analysis gave a peak height of 31.75 units. The excellent agreement between the reactor and the Saran[®] bag indicated that there were no peculiar wall effects or adsorption effects with either container.

Materials. Ultra high purity air (synthetic, 20% O₂, 80% N₂) obtained from Matheson showed no impurities by gc. NO and NO₂ were from Matheson and were used as received. Water was redistilled. CH₂Cl₂ (uninhibited) was redistilled, and the center cut was used. CH₃OCl₂ (uninhibited) was redistilled, and the center cut, by 74°, was used. CHCl-CCl₂ (NI-TRI[®]) which contained 20 ppm diisopropyl amine was used without purification unless otherwise stated. CCl₂-CCl₂ was redistilled. cis-CHCl-CHCl from Matheson was redistilled to give a center cut, by 58-60°. trans-CHCl-CHCl from Eastman was redistilled to give a center cut, by 48°. CH₂=CH₂ from Matheson and research grade trans-40 CH=CH₂ from Phillips Petroleum were used as received. C₆H₁₂ was redistilled. Other materials were either redistilled or shown to be pure by gc.

Example of a Typical Photolysis. After the reactor was evacuated to 0.2-0.3 mm for an hour or more, 47.9 μ l of NO, taken from an exit tube of a cylinder with a syringe, was added to the reactor with the stirrers on to give a final concentration of 5 ppm. The NO was added at this point to prevent the premature oxidation of NO to NO₂ since NO is readily oxidized at "high" concentrations of NO in air. While the reactor was still under vacuum, 94 μ l of distilled water was added and evaporated with a heat gun from outside the chamber to give a relative humidity of 35-40%. Pure air was then added from a Saran[®] bag to the reactor until the pressure inside the chamber was equalized with atmospheric pressure. Finally, 0.94 μ l of CHCl-CCl₂ was added to the reactor from a can

microliter syringe (type with plunger in needle of syringe) to give a concentration of 10 ppm (all concentrations on a molar or gas volume basis). The $\text{CHCl}_2\text{-CCl}_2$, as well as most other solvents except alcohols, evaporated from the end of the syringe needle in less than one minute. The reactor temperature was maintained at 26-28° throughout the reaction. Constant volume samples (1 cc) were analyzed by gc periodically as follows (time and peak height given): 0 minutes, 85 units; 17, 78; 34, 75.5; 51, 70; 68, 66.5; 85, 61; 102, 57.5; 119, 53.5; 136, 52; 153, 49; 170, 46; 187, 44; 204, 42; 221, 40; 238, 40; 255, 37; 272, 35; 289, 34.5; 306, 33. The half life of the $\text{CHCl}_2\text{-CCl}_2$ was thus 3.3 hr. The first samples analyzed, before the lamps were turned on, were used as standards to which subsequent samples during the reaction were compared. The rate of compound disappearance during the reaction was then determined directly from the reduction in peak height (most of the peaks were highly symmetrical) or reduction in peak area. The compound half-life or the percent that reacted in 6 to 8 hr (for compounds which reacted slowly) was used as a measure of the reactivity of the compound. The 6-8 hours reaction time is equivalent to 2-3 days of intense noon-time sun for 6 hr each day. The chlorinated solvent concentration was generally chosen at 10 ppm in order to obtain reasonable gc responses throughout the run.

When NO_2 was introduced into the reactor in a manner similar to that described for NO above, the dimerization equilibrium was taken into account for purposes of calculating the correct volume of gas at atmospheric pressure.

Some of the reactions were run in duplicate or more. Average values are given in the tables; duplicate values obtained within several weeks generally agreed within -10% of each other. The variation in compound half-lives among the different tables is probably due to variations in light intensity inside the

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reactor. The reactivities listed within a given table are consistent within that table.

Long Term Sea Level Simulated Photolysis. Reactor Design and Operation.

The photo reactor used in this work was designed to minimize the possibility of leakage over periods of several weeks. Consequently, there were only two non-glass seals, a 4 mm Teflon stopcock near one end and a capillary tubing sample port which was sealed with a silicone rubber septum near the other end. The reactor was a flat-ended pyrex cylinder similar in shape and size to the one shown in Figure 1; the volume was 11.6 liters. At each end was positioned the same type of sunlamp described above. Midway between each lamp and the end of the reactor (16 cm) was a 3/8 inch thick quartz plate to reduce the warming of the photoreactor by the sunlamps; the reactor did not have a water jacket. The ends of the reactor were further cooled by forced air which had been passed over a cold water cooling coil. The entire system was placed in a hood to maintain adequate air flow to dissipate the heat. The temperature was measured by a thermocouple taped to the outside of the reactor near the center of the cylinder. The hood in which the apparatus was placed was covered by black cloth to eliminate the possibility of eye injury from the ultraviolet radiation.

The simulated atmosphere used in the photoreactions was obtained by premixing, in the desired proportions, a dry air stream with an air stream saturated with water and one containing a known amount of NO_2 . The gas streams were monitored by flowmeters (Dilling and Tefertiller, 1974) and the photo reactor was flushed with the gas mixture for a period of time calculated to replace 99.9% of the ambient air in the photoreactor (Dilling et al., 1974b). A sample of the gas mixture was then removed and analyzed for NO_2 using a modified Saltzman (1974) procedure. This procedure involved withdrawing a 47.8 cc gas sample

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into an evacuated tube which contained 10 ml of the absorbing reagent. The calibration curve was determined in the same manner with air-NO₂ mixtures prepared directly by pressure-volume measurements on a vacuum line. Finally a quantity of the chlorinated solvent calculated to give 50 ppm (on a molar basis) in air was injected by syringe through the septum into the reactor. The system was allowed to equilibrate overnight, and gas samples were removed for analysis before turning the lamps on.

Sampling Techniques and Analysis. Gas samples were removed at intervals with Hamilton gas-tight syringes and analyzed by gc.

Two gc systems were used to analyze for the chlorinated solvent concentration. The first system, which employed a thermal conductivity detector, was a F & M 500 instrument equipped with a 10 ft x 1/4 inch column packed with 20% Apieson L on chromosorb WAW. The column temperature was 125°, the detector 300°, and the injection port 140°. The helium flow rate through the column was 45 cc/minute. A 10 cc gas sample was used. The peak areas were measured with a planimeter. A liquid standard of CH₂OCCl₂ in CCl₄ was used for calibration in experiments with the former compound.

The second and more precise gc system employed a hydrogen flame ionization detector. An Aerograph Hy-Fi Model 550-B, with a Bendix electrometer, was equipped with a 10 ft x 1/8 inch column packed with 20% N,N-bis(2-cyanoethyl)-formamide on chromosorb W. The column temperature was generally 97° and the carrier gas was nitrogen. A 2 cc gas sample was used. A gas standard was used to calibrate the gc. It consisted of 50 ppm of the chlorinated solvent in air in a 12.6 liter Pyrex glass sphere which had two openings, a 4 mm Teflon stopcock and a capillary sampling port closed by a silicone rubber septum. Samples from this bulb were reproducible for at least 6 weeks, indicating no leakage from the bulb.

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Materials. NO_2 free from air (mass spectroscopy) was prepared by condensing material from Matheson at 0° and degassing to 10^{-2} mm in three freeze-pump-thaw cycles (-78° to 0°). NO_2 in air was obtained from Matheson; the NO_2 concentration was found to be 25 ppm by the modified Saltzman method. Dry air was obtained by passing Matheson dry cylinder air through a drying tower which contained phosphorous pentoxide dispersed on calcium sulfate. CH_2Cl_2 and carbon tetrachloride (CCl_4) were distilled in glass materials from Burdick and Jackson. The CH_2OCl_2 was the same as described above.

Analysis of CH_2Cl_2 Reaction Mixture. The contents of the reactor from the reaction shown in Figure 6 (after 13 days irradiation) were removed from the reactor by rinsing it with 20 ml of 0.01 N sodium hydroxide solution and 40 ml of water. The combined rinses were evaporated to a small volume, acidified with nitric acid, and titrated with 0.100 N silver nitrate solution (Dilling and Tafertiller, 1974). The titration required 0.36 ml to reach an end point. This represents 77% of the chlorine present in the initial CH_2Cl_2 (1.91 μl , 0.0470 mg atoms of chlorine).

High Altitude Simulated Photolysis. The photo-reactor was a Pyrex sphere of 12.1 liters capacity having a $\frac{1}{4}$ in Teflon stopcock and a capillary tubing sample port closed by a silicone rubber septum. The reactor had a 60/90 silicone greased ground glass joint into which was inserted a low pressure immersion mercury arc lamp. Air blowers were directed at the top and bottom of the reactor to dissipate the small amount of heat generated by the lamp. The temperature of the reactor was measured by a thermocouple taped to the outside of the flask near the middle between the blowers.

The short wavelength light source was a 10 watt Hanovia low pressure mercury arc lamp which was in the form of a coil. The emission from this lamp was measured at a distance of 2.4 meters from the lamp with the International Light photometer described above. The intensity at various wavelengths were as follows: 254 nm, 3.5 μ watts/cm²; 265, 0.016; 297, 0.032; 313, 0.11; 334, 0.0043; 366, 0.023; 405, 0.022; 436, 0.022; 488, 0.002. The total energy at 254 nm was

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2.7 watts. Radiation of 185 nm may have been emitted (Calvert and Pitts, 1966a), but it was not measured. The intensity of short wavelength light outside the earth's atmosphere was calculated from data given by Keller (1963c). The total intensity in the 140-260 nm range was 0.887 milliwatts/cm², in the 140-280 nm range 0.714 milliwatts/cm², and in the 140-300 nm range 1.672 milliwatts/cm².

The materials used and the techniques employed for loading the reactor and for sampling and analyzing the reaction mixtures were the same as described above for the long term photolyses.

(a) CH₃COCl₂ (50 ppm) was stable for ^{at least} 14 days in the dark in the presence of ozone, which had been generated by photolyzing air in the reactor.

No significant problems were encountered from adsorption of CH₃COCl₂ on the reactor walls as shown by measuring the amount of material present in the gas phase after multiple injections.

Results and Discussion

Short Term (< 24 Hours) Sea Level Simulated Photolysis. We chose to carry out this research with small photoreactors (~10 liters) because of certain disadvantages of large smog chambers (e.g. Dimitriadis, 1967; Doyle, 1970) including the following. The chamber cannot be built completely out of an inert and impermeable material such as glass, since a rigid framework made of some kind of metal such as aluminum (Wilson et al., 1968) is needed for support. It cannot be evacuated for cleaning purposes. Cleaning must be done through a purging process which requires a lengthy time and large volumes of air. The ambient air must be purified at the chamber site through a complicated process to remove oxidants, oxides of nitrogen, any organic compounds, etc., since it is not practical to use purified cylinder air. Temperature control is more

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difficult than with a small reactor. However, large chambers have certain advantages which include the following. The construction of the lighting system has greater flexibility since a wide variety of lamps can be used to obtain better spectral distribution and intensity which simulates sunlight. Since relatively large volumes of air are available for analysis, wet chemical analysis can be obtained for NO , NO_2 , O_3 , aldehydes, etc., which are important in evaluating photochemical smog production. However, we have been able to measure total oxidant formation with the small reactor (Dilling et al., 1974b). Eye irritation data can only be obtained by exposing a panel of human subjects to the contents of a large chamber through the use of eyeports.

Correlation of the results from one study to another is often difficult since many of the variables such as lighting, temperature, chamber construction materials, air purity, and other reaction conditions are difficult to evaluate and control. To best compare results from various reactors, standard materials are run which range from very slow reacting materials to compounds which are highly reactive. Table III shows a comparison from several different laboratories, of the absolute photochemical reactivities (rate of compound disappearance) and approximate relative reactivities of several standard hydrocarbons ($n\text{-C}_6\text{H}_{14}$, toluene (PhH), *trans*- $\text{H}_2\text{C}=\text{CH}_2$) and of $\text{ONCl}-\text{CCl}_2$ compared with $\text{CH}_2=\text{CH}_2$. There is a relatively good correlation between the five sets of data. The variation in absolute reactivities between groups in Table III can be attributed largely to the differences in light intensity and reactant concentrations.

There is a good correlation between reactivity and light intensity (see below).

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Table III. Absolute and Relative Photochemical Reactivities of Chloral, Dichloroacetal, and Chloroacetaldehyde at Different Laboratories

Compound	Stanford Research Institute ^a	General Motors Corporation ^b	Battelle Memorial Institute ^c	National Air Pollution Control Administration	This work ^d
$\text{C}_2\text{H}_5\text{Cl}$	50% (13 hr) ^e 0.42 ^f	15% (6 hr) ^g 0.40	~4% (5 hr) ~0.5	--	50% (6.5 hr) 0.43
None	--	35% (6 hr) 0.57	~5% (5 hr) ~0.6	--	50% (6.8 hr) 0.43
CH_2Cl_2	50% (7.5 hr) 1.0	45% (6 hr) 1.0	~5% (3 hr) 1.0	50% (3.7 hr) 1.0	50% (2.9 hr) 1.0
CHCl_2Cl	50% (7.0 hr) ^h 1.1	--	--	50% (2.6 hr) 1.4	50% (3.5 hr) 0.83
$\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}_3$	50% (0.44 hr)	85% (6 hr)	~5% (0.2 hr)	--	50% (0.23 hr)
	17		-15		13

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(Reactions continued on next page)

Footnotes to Table III.

^aData from Wilson et al. (1969c); initial concentrations (ppm) of organic compound and NO: *o*-C₆H₁₂, CH₂=CH₂, and CNCl-CCl₂, 8 and 2; *trans*-MeCH=CH₂; 3 and 1.3. ^bData from Neuse and Olsson (1968a, 1968b); initial concentrations, 2 ppm organic compound, 1 ppm NO. ^cData from Levy (1968); initial concentrations, 4 ppm organic compound, 2 ppm NO. ^dData of Kopynski cited by Altshuler and Bufalini (1971). ^eInitial concentrations, 10 ppm organic compound, 5 ppm NO. ^fData given as percent disappearance of organic compound in the indicated length of time. ^gRelative reactivity compared with CH₂=CH₂ as 1.0. ^h*trans*-Hexane used instead of *o*-C₆H₁₂. ⁱExtrapolated from data at different light intensity by assuming an inverse relationship between light intensity and half-life.

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Table IV shows a summary of the results of the photochemical reactivity of a variety of chlorinated compounds along with the standard hydrocarbons and other materials. All of the data are based on the rate of disappearance of the compound under the same reaction conditions. The compounds are listed in order increasing reactivity with NO.

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Table IV. Photochemical Reactivity of Chlorinated Compounds, Standard Hydrocarbons, and Other Materials Under Simulated Atmospheric Conditions

Compound ^b	Time (hr) for 50% disappearance of compound unless otherwise indicated ^a	
	With NO ^c	With NO ₂ ^d
CH ₃ COCl ₂	23.5 (< 5%) ^e	8.0 (< 5%) ^e
CH ₂ Cl ₂	21.0 (< 5%) ^e	7.5 (< 5%) ^e
<i>t</i> -Butyl alcohol (<i>t</i> -BuOH)	15.2 (22%) [34.5] ^f	
Epichlorohydrin [<i>g</i> -CH(CH ₂ Cl)CH ₂ O]	16.0	
1,1,2-Trichloroethane (CH ₂ ClCHCl ₂)	7.0 (22%) [15.9] ^f	
1-Butene oxide (<i>g</i> -CH=CHCH ₂ O)	14.9 (47%) [15.9] ^f	15.2 ^f
Ethyl acetate (EtOAc)	7.0 (24%) [14.6] ^f	
CCl ₂ -COCl ₂	12.5 (44%) [14.2] ^f	7.0 (42%) [8.3] ^f
Methyl ethyl ketone (MeOEt)	8.5 (33%) [9.8] ^f	
Nitromethane (iONO ₂)	9.2	

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Table IV. continued ...

Chlorobenzene (PhCl)	7.9 (43%) [8.7] ²	
$n\text{-C}_6\text{H}_{12}$	6.9	6.9 7.9 ²
PhEt	6.8	
<i>n</i> -Butyl alcohol (<i>n</i> -BuOH)	6.5	
Ethyl benzene (PhEt)	5.0	
Trioxane [$\text{-(CH}_2\text{O)}_3$]	4.7	
$\text{CH}_2\text{-CHCl}$	4.3	
<i>n</i> -Butyl alcohol (<i>n</i> -BuOH)	4.0	
CHCl-CCl_2	3.9	2.9
Methyl isobutyl ketone ($\text{MeCO}_2\text{-Bu}$)	3.5	
Isobutyl alcohol (<i>i</i> -BuOH)	3.5	
Dioxane [$\text{-O(C}_2\text{H}_4)_2\text{O}$]	3.4	
1-Methoxy-2-propanol ($\text{MeOCH}_2\text{CH(OH)Me}$)	3.1	

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Table IV: continued.....

<i>p</i> -Xylene ^b (<i>p</i> -Me ₂ C ₆ H ₄)	3.1	
<i>p</i> -Xylene ^b (<i>p</i> -Me ₂ C ₆ H ₄)	2.9	
<i>cis</i> -CHCl-CHCl	3.0	3.0
<i>trans</i> -CHCl-CHCl	2.9	2.8
CH ₂ =CH ₂	2.9	2.5
CH ₂ =CCl ₂	2.1	
Cyclohexane (<i>c</i> -C ₆ H ₁₀)	0.87	0.19 ^e
Diisobutylene (<i>i</i> -BuCH ₂ CH=CH ₂)	0.60	
<i>trans</i> -MeCH=CHMe	0.30	0.17 ^e
<i>N</i> -Methylpyrrole (<i>c</i> -C ₄ H ₇ NMe)	0.16	

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^aAll reactions carried out with 39% relative humidity. ^bAll compounds at 10 ppm in air initially unless specified otherwise. ^cAll initial concentrations 5 ppm. ^dAll initial concentrations 16.8 ppm except as noted. ^eCorrected for reactor "leakage" which was estimated to be -5% in 5 hr. ^fEstimated value for 50% disappearance of compound. ^gInitial NO₂ concentration 5 ppm. ^h*p*-Me₂C₆H₄ and *p*-Me₂C₆H₄ measured simultaneously at initial concentrations of 2 and 8 ppm respectively.

It is obvious that CH_3CCl_3 and CH_2Cl_2 are essentially unreactive for up to a day with either NO or NO_2 present. $\text{OCl}_2=\text{CCl}_2$ is less reactive than $\text{p-C}_6\text{H}_4$ while the remaining chlorinated ethylenes including $\text{CHCl}=\text{CCl}_2$ are comparable to the reactivity of $\text{CH}_2=\text{CH}_2$. Thus, those chlorinated compounds which are less reactive than $\text{p-C}_6\text{H}_4$, especially CH_3CCl_3 and CH_2Cl_2 , would not be expected to produce significant photochemical smog symptoms, whereas $\text{CHCl}=\text{CCl}_2$ and the remaining chlorinated ethylenes, may be expected to produce photochemical smog symptoms. In general the relative reactivities of the materials in Table IV roughly parallel what is known or expected for their reactions with electrophilic radicals.

In several reactions, light intensities were varied in order to determine the effect on the reaction rate since our reactions were carried out with a higher light intensity than real sunlight. The total light intensity was reduced by placing a 30 x 30 mesh SS screen between the sunlamp and the reactor. One screen reduced the light intensity by 50% whereas two screens set at a 45° angle to each other reduced the intensity by 75%. Table V shows a good linear correlation between reactivity and light intensity with the possible exception of $\text{CHCl}=\text{CCl}_2$ at the lowest light intensity. These results also suggest that it is unnecessary to duplicate the intensity of sunlight to study photochemical reactions related to air pollution. It should only be necessary to know how the laboratory ultraviolet radiation intensity compares to that of sunlight and that a realistic wave length range is used. Thus, one could readily calculate what the reactivity of the compound would be in the real atmosphere at any time of the day barring any other complicating factors.

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Table V. Effect of Light Intensity on Reaction Rates

Compound ^a	Relative light intensity	Time for 50% disappearance of compound	Relative reactivity
<u>trans</u> -MeCH=CH ₂	1.00 ^b	11 minutes	1.00
	0.50	23	0.48
	0.25	40	0.26
CH ₂ =CH ₂	1.00 ^b	2.8 hr	1.00
	0.50	5.2	0.52
	0.25	10.0	0.28
CHCl=CCl ₂	1.00 ^b	3.9 hr	1.00
	0.50	6.3	0.56
	0.25	9.5	0.37

^aAll reactions carried out with 10 ppm of the compound, 5 ppm NO, and 35% relative humidity. ^bNormal light intensity used in this work.

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This linear correlation between light intensity and reactivity is also in agreement with the results observed by other workers (Schuck and Doyle, 1959; Tuesday, 1961; Bufalini and Altschuller, 1967). These workers found that the distribution of reaction products was nearly independent of the light intensity with the exception that Q_3 had increased with increased light intensity. In our work no data were obtained on how the photochemical reaction is affected by a variation in the wave length distribution within the 300-400 nm range, but no major effects are expected (Laity, 1971).

Tuesday (1961, 1963) observed an increase in the rate of photooxidation of trans-MeCH-CH₂ (and trans-MeCH-CH₂-C₆H₁₀) when NO₂ was used instead of NO. We also found that trans-MeCH-CH₂ (and trans-MeCH-CH₂-C₆H₁₀) were consumed faster when NO₂ was initially present. However, with slower reacting materials, the difference in reactivity with NO and NO₂ is insignificant ^{except for CCl₂ and CCl₃} (Table IV). Presumably, the reason is that NO must be first oxidized to NO₂ before the photooxidation process can begin (Altschuller and Bufalini, 1965). In the case of slow reactors, there is sufficient time for some of the oxidation of NO to occur, whereas in the case of trans-MeCH-CH₂ and trans-MeCH-CH₂-C₆H₁₀, the initial presence of NO₂ allows an immediate reaction to occur.

In the real atmosphere, the absolute concentrations of organic material and NO may be constantly changing, particularly as the components leave the source of emission and become diluted into the atmosphere. A change in the absolute concentrations of compound and NO from 10:5 to 100:90 (ppm) resulted in a 2 to 3.5-fold increase in reactivity (Table VI). By extrapolation, the reactivity probably would continue to decrease as the concentrations are decreased. Further data on the reactivity of CH₂Cl₂, CH₃CCl₃, CHCl-CCl₂, CCl₂-CCl₂.

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Table VI. Effect of Concentration on Reaction Rates.

Compound ^a	Initial concentrations (ppm)		Time for 50% disappearance of compound	Relative reactivity
	Compound	NO		
<u>trans</u> -MeCN-CH ₃ ^b	10	5	26 minutes	1.0
	20	10	22.5	1.2
	40	20	17	1.5
	100	50	13	2.0
CHCl-CCl ₂	10	5	3.5 hr	1.0
	20	10	3.0	1.2
	40	20	1.5	2.3
	100	50	1.0	3.5
CCl ₂ -CCl ₂	10	5	6.5 ^c hr (29%) [11.2] ^d	1.0
	40	20	7.0	1.6
	100	50	3.8	3.0

^aAll reactions carried out with 35% relative humidity. ^bReactions with trans-MeCN-CH₃ carried out with 0.50 relative light intensity. ^cTime required for 29% disappearance of CCl₂-CCl₂. ^dEstimated value for 50% disappearance of compound.

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and $\text{CH}_2=\text{CHCl}$ at concentrations of 30 ppm in the presence of 12 ppm NO_2 are given in a later paper of this series (Dilling et al., 1974b); these data were obtained in a study of oxidant formation in the presence of these compounds.

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Table VII. Effect of $\text{CHCl}_3\text{-CCl}_4$: NO Ratio on Reaction Rate

Initial concentration (ppm) ^a $\text{CHCl}_3\text{-CCl}_4$	NO	Time (hr) for 50% disappearance of $\text{CHCl}_3\text{-CCl}_4$
10	0	7.0 (38%) ^b [10.9] ^c
10	2.5	1.8
10	5	2.0
10	10	2.5
10	20	2.5
10	40	2.5

^aAll reactions carried out with 35% relative humidity. ^bTime required for 38% disappearance of $\text{CHCl}_3\text{-CCl}_4$. ^cEstimated value for 50% disappearance of $\text{CHCl}_3\text{-CCl}_4$.

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Table VIII. Effect of Relative Humidity and Absence of NO on Reactivity of $\text{CHCl}_2\text{-CCl}_2$ ^a

Relative humidity (%)	Initial NO concentration (ppm)	Time (hr) for 90% disappearance of $\text{CHCl}_2\text{-CCl}_2$
0	5	2.0
35	5	2.1
70	5	3.0
0	0	3.0
35	0	7.0 (30%) ^b [10.9] ^c

^aAll reactions carried out with 10 ppm $\text{CHCl}_2\text{-CCl}_2$ initially. ^bTime required for 30% disappearance of $\text{CHCl}_2\text{-CCl}_2$. ^cEstimated value for 90% disappearance of $\text{CHCl}_2\text{-CCl}_2$.

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Long Term Sea Level Simulated Photolysis. Since CH_2Cl_2 and CH_3CCl_3 were found to be essentially non reactive under the short term photolysis conditions described above, it was of interest to determine if these two important chlorinated solvents would undergo a very slow decomposition under simulated low altitude atmospheric conditions over an extended time period. Experiments were conducted in an essentially leak-free reactor for up to 4 weeks of continuous irradiation.

CH_3CCl_3 (50 ppm) was stable for at least 4 weeks when subjected to continuous irradiation in the presence of 10-11 ppm NO_2 in air with a relative humidity of 37% at 25-27° (Figure 4, data at 19 and 28 days were obtained with a less precise thermal conductivity gas chromatograph).

CH_2Cl_2 (50 ppm) was stable for 4-6 days when irradiated in air with 10 ppm NO_2 at 25-28° and a relative humidity of 37% (Figures 5 and 6). Then within a few days the CH_2Cl_2 reacted completely. In the products of the reaction, from which the data in Figure 6 were obtained, it was possible to titrate 77% of the total chlorine charged (in the CH_2Cl_2) as inorganic chloride after washing the reactor with dilute sodium hydroxide solution.

CH_3CCl_3 would thus appear to be stable in the lower atmosphere for a long time. CH_2Cl_2 may also be stable. The rather abrupt disappearance of the CH_2Cl_2 after several days irradiation is unexplained. It is possible that an impurity in the CH_2Cl_2 inhibited the reaction until the impurity itself had decomposed or that a product was formed at a low concentration which catalyzed the reaction. It is not particularly surprising that CH_3CCl_3 and CH_2Cl_2 were not reactive when irradiated with long wavelength ultraviolet light ($\lambda > 290 \text{ nm}$) since their ultraviolet spectra show no absorption in that spectral region. Apparently these chlorinated solvents are unreactive toward the radicals and atoms derived from the photolysis of NO_2 .

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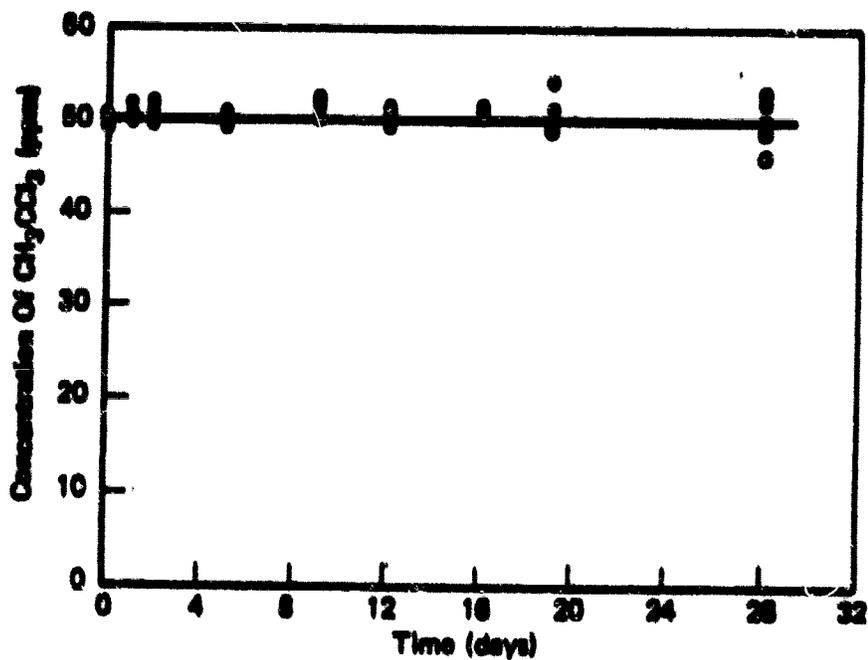


Figure 4. Irradiation of 50 ppm CH₂Cl₂ with 10-11 ppm NO₂ in air with a relative humidity of 37% at 25-27°.

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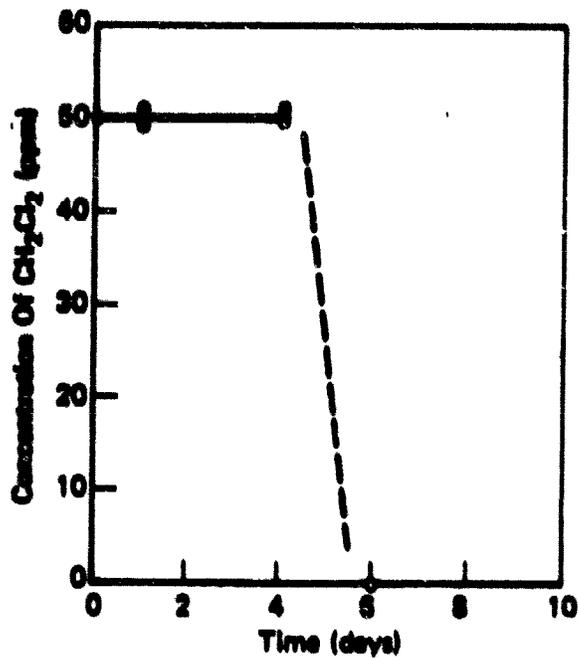


Figure 5. Irradiation of 50 ppm CH₂Cl₂ with 10 ppm NO₂ in air with a relative humidity of 39% at 25-26°.

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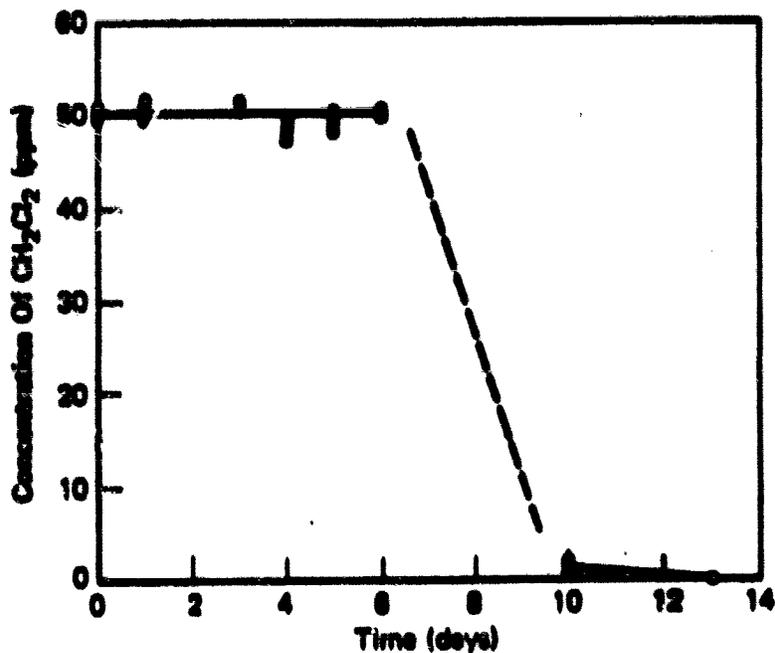


Figure 6. Irradiation of 50 ppm CH_2Cl_2 with 10 ppm NO_2 in air with a relative humidity of 39% at 25-26°.

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High Altitude Simulated Photolysis. Since CH_2OCl_2 and probably CH_2Cl_2 were stable for prolonged times under simulated low altitude atmospheric conditions and both chlorinated solvents evaporated rapidly from water, the question arises as to what is their ultimate fate. One possibility is diffusion into the upper atmosphere (O_3 layer) where short wavelength light (down to 140 nm) is present (Keller, 1969a). Diffusion between the troposphere and the stratosphere was predicted (Machta, 1958) and demonstrated (Manson et al., 1961). In order to qualitatively determine the reactivity of CH_2OCl_2 and CH_2Cl_2 under high altitude conditions we irradiated these materials with short wavelength light. CCl_4 was also studied under these conditions since this compound has been detected in the stratosphere (Lovelock et al., 1973) at an altitude of ~12 kilometers (Lovelock, 1973).

The short wavelength light source was a low pressure mercury arc lamp. The major portion of the emission from this type of lamp occurs at 254 nm (Calvert and Pitts, 1966b). There also may be radiation of 185 nm emitted from this source. The emission from this lamp at 254 nm is 10-40 times as intense as the sun's radiation just outside the earth's atmosphere in the 140-260 or 140-300 nm region. Just within the earth's atmosphere (~40 kilometers altitude) where the sunlight intensity is decreased to ~1/3 of its original intensity in the 200-280 nm range by absorption of its short wavelength radiation by O_3 (Chem. Eng. News, 1966), the lamp would be 30-120 times as intense as sunlight.

The temperature of the atmosphere at the altitude which was simulated is not known; at 11 km the temperature is -50 to -60°C and rises to about 0°C at 30 km (Chem. Eng. News, 1966). The photoreactions were run at 23-33°. The

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photoreactions were run at 740-750 mm pressure; the pressure at high altitudes is lower, 210 mm at 10 km, 0.75 mm at 50 km (Weast et al., 1964). Pressure probably has an effect on the rates of these photoreactions. The rate could be either increased or decreased with a decrease in pressure depending on the mechanism of the photodecompositions. There is relatively little water in the atmosphere at higher altitudes; most is found in the troposphere (< 11 km) (Chem. Eng. News, 1966).

Irradiation of CH_2OCl_2 in dry air or in air with a relative humidity of 39% with or without NO_2 under our simulated high altitude conditions caused a $\geq 90\%$ decomposition of the CH_2OCl_2 within 10 minutes (Figure 7). The reason for the variation in the extent of reaction often 10-20 minutes for the various reaction conditions is not known. Injection of CH_2OCl_2 into the dark reactor which contained O_3 from a previous air photolysis did not lead to any measurable decomposition of the CH_2OCl_2 over a 4 day period.

Simulated high altitude irradiations of CH_2Cl_2 (Figure 8) and OCl_2 (Figure 9) in dry air brought about $> 99\%$ decompositions of both compounds within 10 minutes.

Assuming a linear relationship between light intensity and rate of photodecomposition, one can estimate that these three chlorinated compounds would be greater than 90% decomposed within several hours to a few days if the compounds do diffuse to the upper regions of the earth's atmosphere. Since these chlorinated compounds do absorb ultraviolet radiation at 254 nm and are unreactive in the presence of O_3 in the dark and in the presence of NO and NO_2 with longer wavelength light, we suggest that photodissociation is the initial reaction of these materials.

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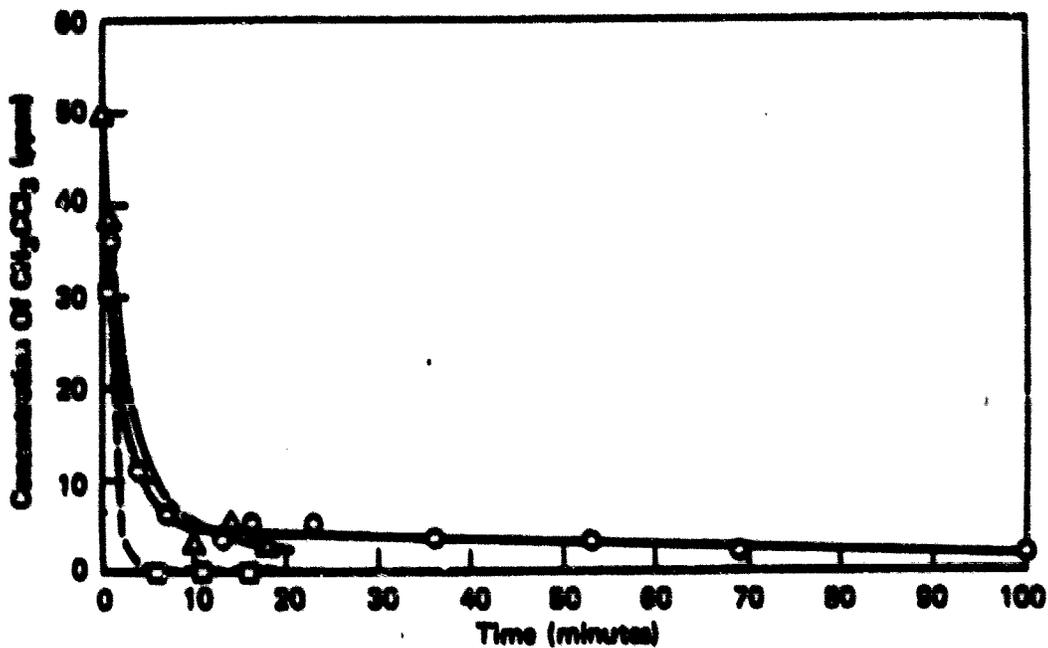


Figure 7. Irradiation (short wavelength) of 50 ppm CH_2Cl_2 in dry air at 24-33° (O, _____); in air with a relative humidity of 39% at 25-33° (□, _____); with 9 ppm NO_2 in air with a relative humidity of 39% at 25-33° (Δ, _____)

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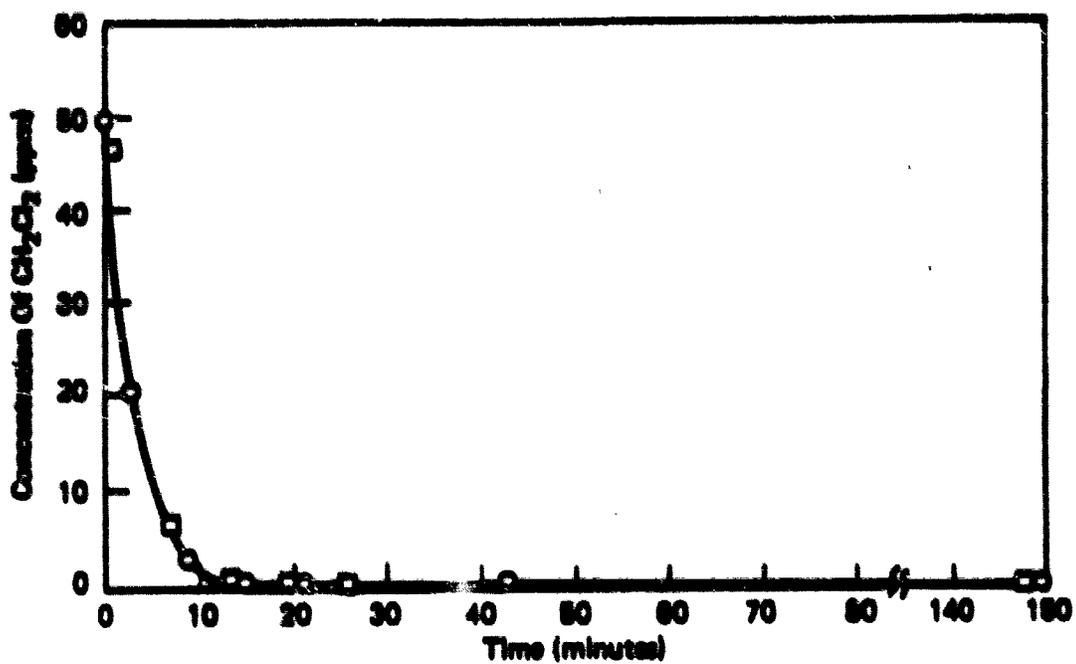


Figure 8. Irradiation (short wavelength) of 50 ppm CH_2Cl_2 in dry air at 23-33° (○ and □ for 2 identical runs)

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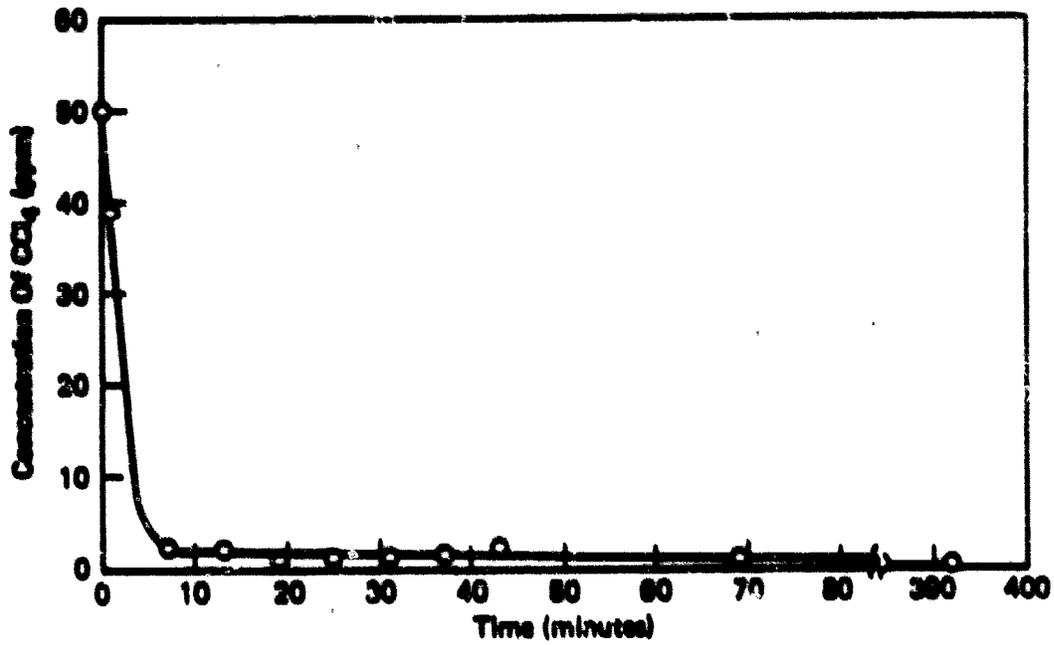


Figure 9. Irradiation (short wavelength) of 50 ppm CCl_4 in dry air at 23-33°.

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Acknowledgment

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Literature Cited

- Altschuller, A. P., Bufalini, J. J., Environ. Sci. Technol., 2, 39-64 (1971).
- Altschuller, A. P., Bufalini, J. J., Photochem. Photobiol., 4, 97-146 (1969).
- Altschuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Slater, N., Ibid., 1, 899-914 (1967).
- Archer, W. L., Dow Chemical Co., Midland, Mich., private communication, 1970.
- Bertrand, L., Exsteen-Meyers, L., Franklin, J. A., Huybrechts, O., Olbregts, J., Ind. J. Chem. Eng., 1, 89 (1971).
- Bufalini, J. J., Altschuller, A. P., Environ. Sci. Technol., 1, 133-8 (1967).
- Bufalini, J. J., Altschuller, A. P., Ibid., 2, 469-72 (1969).
- Calvert, J. G., Pitts, J. N., Jr., "Photochemistry", p 689, John Wiley and Sons, Inc., New York, N. Y., 1966a.
- Calvert, J. G., Pitts, J. N., Jr., op. cit., p 696, 1966b.
- Carlisle, P. J., Levine, A. A., Ind. Eng. Chem., 24, 146-7 (1932).
- Chem. Eng. News, Special Report, "Chemistry and the Atmosphere", 44, 1A-54A, March 28, 1966.
- Dilling, W. L., Tefertiller, N. B., Environ. Sci. Technol., 8, 0000-00 (1974).
- Dilling, W. L., Tefertiller, N. B., Mitchell, A. B., Mal. Photochem., 2, 0000-00 (1973).
- Dilling, W. L., Tefertiller, N. B., Kallos, G. J., Environ. Sci. Technol., 8, 0000-00 (1974a).

- Dilling, W. L., Mints, M. J., Arrington, J. P., Stevens, V. L., ibid., 8,
0000-00 (1974b).
- Dimitriades, B., J. Air Pollut. Contr. Ass., 17, 460-6 (1967).
- Doyle, G. J., Environ. Sci. Technol., 4, 907-16 (1970).
- Farber, H. A., "Chlorinated Solvents and the Environment", paper presented
at AAAPCC Symposium, Atlanta, Ga., January 10-11, 1973; Textile Solvent
Technology - Update '73, pp 6-12.
- Hawking, W. J., "Photochemical Reactivity of Solvents", paper presented at
Aeronautic and Space Engineering and Manufacturing Meeting, Society
of Automotive Engineers, Los Angeles, Calif., October 2-6, 1967.
- Neuss, J. M., Glasson, W. A., "Hydrocarbon Reactivity and Eye Irritation",
paper presented at 155th American Chemical Society National Meeting,
San Francisco, Calif., March 31-April 5, 1968a; Abstracts of Papers,
U S O.
- Neuss, J. M., Glasson, W. A., "Hydrocarbon Reactivity and Eye Irritation",
Research Publication GMR-747, General Motors Research Laboratories,
Warren, Michigan, 1968b.
- Koller, L. R., "Ultraviolet Radiation", 2nd edn., pp 40, 47, John Wiley and
Sons, Inc., New York, N. Y., 1969a.
- Koller, L. R., op. cit., pp 46-49, 1969b.
- Koller, L. R., op. cit., p 108, 1969c.
- Koller, L. R., op. cit., p 130, 1969d.
- Koller, L. R., op. cit., pp 162, 185, 1969e.

- Leiby, J. L., Environ. Sci. Technol., 5, 1218-20 (1971).
- Levy, A., Battelle Memorial Institute, Columbus, Ohio, private communication, 1968.
- Lovelock, J. E., University of Reading, Reading, England, private communication, 1973.
- Lovelock, J. E., Maggs, R. J., Wade, R. J., Nature, 241, 194-6 (1973).
- Machta, L., Second UN Conference on the Peaceful Uses of Atomic Energy, 10, 519-25 (1976).
- Manson, J. E., Junge, C. E., Chagnon, C. W., "Chemical Reactions in the Lower and Upper Atmosphere", Proceedings of an International Symposium, pp 139-53, Interscience Publishers, New York, N. Y., 1961.
- Murray, A. J., Riley, J. P., Anal. Chim. Acta, 61, 261-70 (1973a).
- Murray, A. J., Riley, J. P., Nature, 242, 37-8 (1973b).
- Nicksic, S. W., Markins, J., Fries, B. A., J. Air Pollut. Control Ass., 14, 158-60 (1964).
- Saltman, B. E., Anal. Chem., 26, 1949-55 (1954).
- Schuck, E. A., Doyle, G. J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide", Report No. 29, Air Pollution Foundation, San Marino, Calif., October 1979.
- Tuesday, C. S., "Chemical Reactions in the Lower and Upper Atmosphere", Proceedings of an International Symposium, pp 15-49, Interscience Publishers, New York, N. Y., 1961.
- Tuesday, C. S., Arch. Environ. Health, 7, 188-201 (1963).

000099

- Weast, R. C., Selby, S. M., Hodgman, C. D., Eds., "Handbook of Chemistry and Physics", 45th ed., p F-82, The Chemical Rubber Co., Cleveland, Ohio, 1964.
- Wilson, K. W., "Photoreactivity of Trichloroethylene", Summary Report for Manufacturing Chemists Association on SRI Project FBC-6687, Stanford Research Institute, South Pasadena, Calif., September 1969.
- Wilson, K. W., Doyle, G. J., Hansen, D. A., "Photochemical Reactivity of Trichloroethylene", Interim Report for Manufacturing Chemists Association on SRI Project FBC-6687, Stanford Research Institute, South Pasadena, Calif., December 1968.
- Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical Reactivity of Trichloroethylene and Other Solvents", paper presented at 158th American Chemical Society National Meeting, New York, N. Y., September 7-12, 1969a; Abstracts of Papers, ORPL 36.
- Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., Am. Chem. Soc., Div. of Org. Coat. and Plast. Chem. Preprints, 22, No. 2, 445-9 (1969b).
- Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical Reactivity of Organic Solvents", Technical Report to Manufacturing Chemists Association, Stanford Research Institute, South Pasadena, Calif., September 1969c.
- Young, J. D., Dow Chemical Co., Freeport, Texas, private communication, 1968.

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Organic Photochemistry. XIV.¹ Environmental Fate and Effect of Chlorinated Solvents. III.² Simulated Atmospheric Photoreactivity of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Hydrocarbons in the Presence of Other Organic Materials and Reactive Species

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Abstract

In order to estimate the reactivities of chlorinated solvents in the atmosphere, laboratory studies were carried out on the photolysis rates of mixtures of four common chlorinated solvents, three other chlorinated olefins, and 14 other organic compounds under simulated atmospheric conditions. The reactivity of trichloroethylene was determined, and various competitive reactions were carried out, in the presence of nitric oxide, nitrogen dioxide, ozone, chloral, acetaldehyde, bromotrichloromethane, chloroform, phosgene, and dichloroacetyl chloride. The presence of other organic materials and nitric

¹Part XIII: (Dilling et al., 1974).

²Part II: (Dilling et al., 1974).

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oxide reduced the photochemical reactivity of trichloroethylene. Vinyl chloride, vinylidene chloride and gig-dichloroethylene behaved like 1-chloroethylene whereas the presence of other organic materials did not significantly affect the photochemical reactivities of methylene chloride and 1,1,1-trichloroethane. Trichloroethylene increased the photochemical reactivity of tetrachloroethylene. The reactivities of most hydrocarbons increased in the presence of trichloroethylene. Chlorine atoms (or other similar species) are suggested as possible reactive intermediates.

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The fate and effect of chlorinated solvents which may be discharged to the environment (Murray and Riley, 1973; ^{a.) Murray and Riley, 1973} Farber, 1973) are important from an ecological standpoint. In the preceding paper (Dilling et al., 1974) the reactivities (rates of disappearance) of four of the more important chlorinated solvents in use today, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), and several related compounds were determined under simulated atmospheric conditions.

Changes in the reactivity of one organic compound in the presence of another have been reported (Altschuler et al., 1966; Bufalini and Altschuler, 1967; Wilson, 1969; Wilson et al., 1969). For example, Bufalini and Altschuler (1967) reported that the photochemical reactivity of 1-butene ($\text{EtCH}=\text{CH}_2$) increased in the presence of trans-2-butene (trans- $\text{MeCH}=\text{CHMe}$) and nitrogen dioxide (NO_2) compared with the reactivity of $\text{EtCH}=\text{CH}_2$ in the absence of trans- $\text{MeCH}=\text{CHMe}$. On the other hand the reactivity of $\text{EtCH}=\text{CH}_2$ decreased in the presence of mesitylene ($\text{C}_6\text{H}_3\text{Me}_3$). Since the order of increasing photochemical reactivities of these materials by themselves with NO_2 was $\text{C}_6\text{H}_3\text{Me}_3 < \text{EtCH}=\text{CH}_2 < \text{trans-MeCH}=\text{CHMe}$, these authors concluded that leveling effects should exist when combinations of materials were present, e.g., organic contaminants in the atmosphere. That is, the presence of slow-reacting hydrocarbons would decrease the reactivity of the faster reacting hydrocarbons and conversely, the presence of fast-reacting hydrocarbons would increase the reactivity of slower-reacting hydrocarbons. Photolysis of propylene ($\text{MeCH}=\text{CH}_2$)-nitric oxide (NO) mixtures in the presence of $\text{CHCl}=\text{CCl}_2$ produced slight accelerations of both the formation and decay of oxidant as compared with the photolysis of $\text{MeCH}=\text{CH}_2$ - NO alone; there was no significant difference in the level of eye irritants (Wilson, 1969; Wilson et al., 1969).

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Therefore it was of interest to determine how the presence of other organic materials affected the photochemical reactivities of the chlorinated solvents. These types of data are important in evaluating how the chlorinated solvents, as well as other materials, behave in a real atmosphere which contains a mixture of slow- and fast-reacting components.

Experimental

General. The reactor design and operation, sampling techniques and analyses, materials, and an example of a typical photolysis have been described in the preceding paper under the heading, Short Term (< 24 Hr) Sea Level Simulated Photolyses (Dilling et al., 1974). In most cases the ratio of organic materials to NO was kept near 2:1 because the highest reactivity generally occurs at this ratio (Tuesday, 1963). All experiments were carried out at 26-28°, 35% relative humidity, and with the same light intensity as previously described (Dilling et al., 1974) unless otherwise specified.

Preparation of Ozone-Air Mixtures. A stream of air was passed into a flask in which was suspended a screen electrode. The electrode was charged by a small Tesla coil. The exit gas which contained a mixture of ozone (O_3) and air was collected in a 20 liter Saran[®] plastic bag which was then used to fill the previously evacuated photochemical reactor. According to a published procedure (Byers and Saltman, 1959), the concentration of O_3 in the air stream was determined by bubbling the O_3 -air stream at a constant rate for a specified length of time through two gas scrubbing towers. The towers contained a solution of 20 g of potassium iodide in 40 ml of 0.002 N sodium thiosulfate, 50 ml of 0.025 N potassium dihydrogen phosphate, and 50 ml of 0.025 N disodium hydrogen phosphate. The above solution was then titrated with a standard 0.002 N iodine solution which contained 0.04% potassium iodide; a 1% starch solution was used

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as an indicator. The air flow through the O_3 generator was adjusted so that the concentration of O_3 used in the photochemical reactions was 10-20 ppm.

Results and Discussion

Since various formulations of $CHCl-CCl_2$ (Table I) are marketed, it was of interest to determine if these grades showed different reactivities under simulated atmospheric conditions. The reactivity differences were small; the formulations with lower stabiliser concentrations were more reactive. Table II shows that there is essentially no difference between the reactivities of uninhibited CH_2CCl_2 and the most highly stabilised **CHLOROCHEM[®] VO**. All formulations showed very little or no reaction (Dilling et al., 1974).

The photochemical reactivities of a number of chlorinated compounds, standard hydrocarbons (Dilling et al., 1974) and other organic compounds were investigated in combination with other organic materials which had a wide range of reactivities, as shown in Table III.

$CHCl-CCl_2$ was studied more extensively than the other compounds. In all combinations, except those which involved $CHCl-CCl_2$ with CCl_2-CCl_2 and with CH_2CCl_2 , the photochemical reactivity of $CHCl-CCl_2$ decreased compared with the reactivity of $CHCl-CCl_2$ in the absence of other organic compounds. In the extreme case with $MeOCCl_2CHCl_2$ the reactivity of $CHCl-CCl_2$ was reduced about three-fold. In a mixture of $CHCl-CCl_2$ and $g-C_6H_{12}$, the reactivity of $CHCl-CCl_2$ was about one-half that of $g-C_6H_{12}$ in the mixture, and was somewhat less than that of $g-C_6H_{12}$ in the absence of $CHCl-CCl_2$. These results are qualitatively consistent with the generation of chlorine atoms as reactive intermediates. $g-C_6H_{12}$ is about five times more reactive toward chlorine atoms than is $CHCl-CCl_2$ (Poutama and Hinman, 1964).

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Table I. Photochemical Reactivity of Various Formulations of $\text{CHCl}_2\text{-CCl}_2$

Stabilizers	Formulation (concn of stabilizers in ppm)		
	III-III ^a	Baker Analyzed	Millbrodt III-III ^a
T-butyl oxide ($\text{C-CH}_2\text{CH}_2\text{O}$)	2,000	1,000	--
Diphenylpicrylhydrazyl [$\text{C-CH}(\text{CH}_2\text{Cl})(\text{CH}_2\text{O})$]	1,100	600	--
Di-<i>n</i>-butyl sebacate (sebac)	500	250	--
Di-<i>n</i>-butyl crotonate ($\text{C-CH}_2\text{CH}=\text{CH}_2$)	250	120	--
Di-<i>n</i>-butyl pivalate ($\text{C-C}_4\text{H}_9\text{CO}_2$)	125	75	--
Di-<i>n</i>-propylamine (1-Pr_2NH)	20	30	20
Total	3,975	2,075	20

Time (hr) for 50% disappearance
 of $\text{CHCl}_2\text{-CCl}_2$ ^a

4.4 4.1 3.5 3.5

^aInitial concentrations: 10 ppm $\text{CHCl}_2\text{-CCl}_2$, 5 ppm HO, 35% relative humidity.

Table II. Photochemical Reactivity of Various Formulations of CH_2Cl_2

Stabilizers	Formulation (concn of stabilizers in per cent)		
	CHLOROXONE [®] V6	Technical	Unstabilized
Phenone [$\text{C}_6\text{H}_5\text{C}(\text{C}_2\text{H}_5)_2\text{O}$]	4.0	--	--
Nitroethane (CH_3NO_2)	0.5	--	--
$\text{C}_2\text{H}_5\text{NO}_2$	0.5	--	--
$\text{C}_2\text{H}_5\text{NO}_2$	0.0025	--	--
n-Butyl alcohol (n-BuOH)	--	0.25	--
Total	5.0025	0.25	0.0
Time (hr) for indicated % disappearance of CH_2Cl_2	20.9 (> 5%)	16.7 (< 5%)	23.5 (< 5%)

^aInitial concentrations: 10 ppm CH_2Cl_2 , 5 ppm NO, 2% relative humidity.

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It should also be noted that in nearly all cases, the photochemical reactivity of the other organic material was substantially increased over that of the reactivity in the absence of $\text{CHCl}_2\text{-CCl}_2$. In no case was there a reduction in reactivity. The reactivities of $\text{p-CH}_3\text{C}_6\text{H}_4\text{O}$, $\text{CCl}_2\text{-CCl}_2$, p-BuOH , and trans- MeCH-CHMe changed the most dramatically, while EtOAc , i-BuOH , $\text{CH}_2\text{-CH}_2$, and $\text{p-C}_6\text{H}_{10}$ changed only slightly. Thus, in an atmosphere which contains a wide variety of reactive materials, it cannot be determined which organic material(s) are the most reactive simply by investigating only single component systems, particularly where $\text{CHCl}_2\text{-CCl}_2$ is involved.

In general, the reactivities of CH_2OCl_2 , CH_2Cl_2 , and $\text{CCl}_2\text{-CCl}_2$, in combination with materials other than $\text{CHCl}_2\text{-CCl}_2$, were not appreciably affected. In only two cases, the combinations of CH_2Cl_2 with $\text{p-C}_6\text{H}_{10}$ and CH_2OCl_2 with $\text{CH}_2\text{-CH}_2$, was there the possibility of some interaction. However, in both cases the reactivity of only one of the compounds was affected whereas the other remained nearly unchanged. However the reactivities of the chlorinated solvents are still very low compared with the reactivity of a "slow reactor" such as $\text{p-C}_6\text{H}_{10}$ alone. Although $\text{CCl}_2\text{-CCl}_2$ was not affected appreciably by $\text{p-C}_6\text{H}_{10}$, $\text{CH}_2\text{-CH}_2$, or trans- MeCH-CHMe , it was considerably more reactive when $\text{CHCl}_2\text{-CCl}_2$ was present.

Since the photochemical reactivity of $\text{CHCl}_2\text{-CCl}_2$ was significantly reduced by the presence of a wide variety of organic materials, it was of interest to determine if other olefinic materials would behave similarly. $\text{CH}_2\text{-CH}_2$, which is normally moderately reactive, shows a slightly reduced photochemical reactivity in combination with a wide variety of materials (Table III). The reactivity of the other organic materials in conjunction with $\text{CH}_2\text{-CH}_2$ generally increased, particularly in the case of p-BuOH . The photochemical reactivity of trans- MeCH-CHMe , which is very reactive by itself, was only slightly changed by the presence of other organic materials, with the exception of $\text{CHCl}_2\text{-CCl}_2$.

The reactivity of some competitive materials did change, e.g., *p*-BuOK and *g*-C₆H₁₀ increased in reactivity, while CHCl-CCl₂ decreased markedly in reactivity.

When the chlorinated ethylenes were involved in competition experiments with *g*-C₆H₁₂, some significant changes were observed. In all cases excepting CCl₂-CCl₂, the photochemical reactivity of *g*-C₆H₁₂ increased while that of the chlorinated ethylenes decreased. *cis*-CHCl-CHCl was more than four times less reactive than it was in the absence of *g*-C₆H₁₂.

A "real" atmospheric environment was simulated by adding CHCl-CCl₂ to the reactor which contained several other materials which had varying reactivities (Table IV). It was again observed that many of the reactivities changed in the presence of other organic compounds. CHCl-CCl₂, in particular, was reduced in reactivity by more than a factor of three. It is also interesting to note that the reactivities of *g*-C₆H₁₂ and *trans*-MeCH-CHMe were nearly identical to those found in the experiment where these two materials were the only organic compounds present (Table III).

The ratio of CHCl-CCl₂ to other organic materials reasonably can be expected, under real atmospheric situations, to range from very high (at a CHCl-CCl₂ emission point) to near zero (some distance downwind from the emission point). In order to demonstrate what might happen to the photochemical reactivity of CHCl-CCl₂ under these conditions, *g*-C₆H₁₂ (an unreactive compound) was chosen as a model organic contaminant in an atmosphere which contained CHCl-CCl₂. By holding the NO concentration constant, it was found that the half-life of CHCl-CCl₂ increased from 3.5 hours (only CHCl-CCl₂ present) to more than 20 hours [ratio of CHCl-CCl₂ to *g*-C₆H₁₂ 0.2 (Table V)]. A half-life of 20 hours or more indicates that CHCl-CCl₂ would be much less reactive than *g*-C₆H₁₂ ($t_{1/2}$ = 6.9 hours). In contrast, the photochemical reactivity of *g*-C₆H₁₂ increased markedly, from a half-life of 6.9 hours to < 1 hour, as the concentration of *g*-C₆H₁₂ decreased.

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Table IV. Photochemical Reactivity of $\text{CHCl}_2\text{-CCl}_2$ in Combination with Several Organic Materials

Compound ^b	Time (hr) for 50% disappearance of compound ^a	
	In mixture	In absence of other organic material ^c
$\text{g-CH}_2\text{CH}_2\text{O}$	12.9	15.0
$\text{CHCl}_2\text{-CCl}_2$	11.1	3.5
$\text{CH}_2\text{-CH}_2$	3.5	2.9
$\text{g-C}_6\text{H}_5$	0.35	0.87
<u>trans-1,2-CH=CH₂</u>	0.35	0.30

^aAll reactions carried out with 35% relative humidity. ^bEach compound initially present at 10 ppm (total 50 ppm organic compounds); NO initial concentration 25 ppm. ^cInitial concentrations: 10 ppm organic compound, 5 ppm NO.

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Table V. Effect of Organic Compound Ratio of Photochemical Reactivities of $\text{CHCl}_2\text{-CCl}_2$ and $\text{g-C}_6\text{H}_{12}$

Initial concentration, ppm ^a		Ratio [$\text{CHCl}_2\text{-CCl}_2$] [$\text{g-C}_6\text{H}_{12}$]	Initial NO concentration, ppm	Time (hr) for 50% disappearance	
$\text{CHCl}_2\text{-CCl}_2$	$\text{g-C}_6\text{H}_{12}$			$\text{CHCl}_2\text{-CCl}_2$	$\text{g-C}_6\text{H}_{12}$
10	0	=	5	3.5	--
10	0.01	1000	5	3.3	--
10	0.1	100	5	2.7	~0.9
10	0.2	50	5	3.5	1.3
10	2	5	5	5.6	2.2
10	10	1	5	>16	5.5
2	10	0.2	5	>20	6.7
0	10	0	5	--	6.9
10	2	5	10	6.6	2.8
10	10	1	10	8.7	4.9

^aAll reactions carried out with 35% relative humidity.

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The photochemical reactivity of each component in the $\text{CHCl}_2\text{-CCl}_2$ - $\text{p-C}_6\text{H}_4$ system also was dependent on the NO concentration, but the effect was dependent on the relative amounts of the two organic components. In the 10:2 ratio ($\text{CHCl}_2\text{-CCl}_2$: $\text{p-C}_6\text{H}_4$) experiments, the reactivity of each organic component decreased as the NO concentration was changed from 5 ppm to 10 ppm. The opposite effect was observed when the initial ratio of organic compounds was 10:10. In the latter case, at the 5 ppm NO level, $\text{CHCl}_2\text{-CCl}_2$ appeared to cease reacting, which suggested that all the NO or NO_2 had been consumed.

In a series of experiments similar to those described in the preceding paragraph, $\text{p-CH}_2\text{CH}_2\text{O}$, which has a very low reactivity in the absence of other organic compounds, was used as a competitive material with $\text{CHCl}_2\text{-CCl}_2$ at various ratios. Similar to the results described above, a trend was observed where the photochemical reactivity of $\text{CHCl}_2\text{-CCl}_2$ decreased as its concentration decreased, and the photochemical reactivity of $\text{p-CH}_2\text{CH}_2\text{O}$ increased as its concentration decreased (Table VI).

The conclusions from these competitive experiments can be summarized as follows. In the presence of other organic materials, the photochemical reactivity of $\text{CHCl}_2\text{-CCl}_2$ changed, as did the reactivities of the other organic materials when they were combined with $\text{CHCl}_2\text{-CCl}_2$. The photochemical reactivity of $\text{CHCl}_2\text{-CCl}_2$ decreased by as much as three times when mixed with $\text{MnOCH}_2\text{CH}_2\text{O}$, while the photochemical reactivity of the competitive reactant generally increased, in some cases by as much as a factor of two (e.g., with $\text{p-CH}_2\text{CH}_2\text{O}$, trans- $\text{MeCH-CH}_2\text{O}$, and p-BuOH). If the ratio of $\text{CHCl}_2\text{-CCl}_2$ to the organic materials (e.g., $\text{p-C}_6\text{H}_4$) was < 1 , $\text{CHCl}_2\text{-CCl}_2$ became quite unreactive and the reactivity of the organic material was not significantly affected. It follows that in a real atmosphere where the ratio of organic contaminants to $\text{CHCl}_2\text{-CCl}_2$ is quite large,

Table VI. Effect of Organic Compound Ratio on Photochemical Reactivities of $\text{CHCl}_2\text{-CCl}_2$ and $\text{p-CH}_2\text{C}_6\text{H}_4\text{O}$

Initial concentration, ppm ^a		$\frac{[\text{CHCl}_2\text{-CCl}_2]}{[\text{p-CH}_2\text{C}_6\text{H}_4\text{O}]}$	Initial NO concentration, ppm	Time (hr) for 50% disappearance, ca	
$\text{CHCl}_2\text{-CCl}_2$	$\text{p-CH}_2\text{C}_6\text{H}_4\text{O}$			$\text{CHCl}_2\text{-CCl}_2$	$\text{p-CH}_2\text{C}_6\text{H}_4\text{O}$
10	0	∞	5	3.5	--
10	2	5	5	4.2	4.1
10	10	1	10	7.0	6.4
0	10	0	5	--	14.9 ^b (47%) [15.1 ^c]

^aAll reactions carried out with 35% relative humidity. ^bTime required for 47% disappearance of $\text{p-CH}_2\text{C}_6\text{H}_4\text{O}$. ^cEstimated value for 50% disappearance of compound.

the photochemical smog symptoms resulting from $\text{CHCl}_2\text{-CCl}_2$ probably would be quite small. If the ratio of $\text{CHCl}_2\text{-CCl}_2$ to the other organic materials (e.g., $\text{g-C}_6\text{H}_{12}$) was ≥ 1 , $\text{CHCl}_2\text{-CCl}_2$ appeared to behave as a catalyst and increased the rate of decomposition of the organic materials. $\text{CH}_2\text{-CHCl}$, $\text{CH}_2\text{-CCl}_2$, and cis-CHCl-CHCl behaved like $\text{CHCl}_2\text{-CCl}_2$. Of the compounds studied only $\text{CHCl}_2\text{-CCl}_2$ increased the photochemical reactivity of $\text{CCl}_2\text{-CCl}_2$. The other organic materials examined did not alter its reactivity significantly. The photochemical reactivities of CH_2Cl_2 and CH_3CCl_3 were not affected significantly by the presence of any other organic materials. The photochemical reactivities of $\text{CH}_2\text{-CH}_2$, trans-MeCH-CHMe , $\text{g-C}_6\text{H}_{10}$, and $\text{g-C}_6\text{H}_{12}$ generally were less affected by other organic materials, excluding the chlorinated ethylenes, than was the reactivity of $\text{CHCl}_2\text{-CCl}_2$. There was some indication of leveling effects (Bafalini and Altshuler, 1967) when only hydrocarbons were involved. When $\text{CHCl}_2\text{-CCl}_2$ was one of the components in the combination experiments, the leveling effect was not important, whereas other catalytic effects may be.

The above results which showed that, for example, $\text{g-C}_6\text{H}_{12}$ was less reactive than $\text{CHCl}_2\text{-CCl}_2$ in individual experiments, whereas in experiments with both $\text{CHCl}_2\text{-CCl}_2$ and $\text{g-C}_6\text{H}_{12}$ present, the reactivities were reversed, with $\text{g-C}_6\text{H}_{12}$ being more reactive. This change in reactivity indicated that a reactive species which was formed from $\text{CHCl}_2\text{-CCl}_2$, reacted more rapidly with $\text{g-C}_6\text{H}_{12}$ than with $\text{CHCl}_2\text{-CCl}_2$. An attempt was made to identify this reactive species. This involved the use of NO , NO_2 , O_3 , and other potentially reactive species with $\text{CHCl}_2\text{-CCl}_2$ and other organic materials in individual and competition experiments.

Previous work (Dilling et al., 1974) showed that with slow reacting materials, both NO and NO_2 gave similar results, while with very reactive materials, such as trans-MeCH-CHMe and $\text{g-C}_6\text{H}_{10}$, NO_2 produced an increased reactivity over that observed when NO was used (Table VII). Other data, shown in Table VII, indicate that O_3 is much more reactive than is NO or NO_2 .

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Table VII. Photochemical Reactivity of Organic Materials with NO, NO₂,
and O₃

Compound ^a	Time (hr) for 50% disappearance ^b			Relative reactivity		
	NO ^{c,d}	NO ₂ ^{d,e}	O ₃ ^f	NO	NO ₂	O ₃
g-CH ₂ CH ₂ O	14.9 ^g (47%) [13.9] ^h	15.8	0.83	0.23	0.19	0.51
g-C ₆ H ₁₂	6.9	7.5	1.0	0.51	0.38	0.42
CHCl-CCl ₂	3.5	2.9 ⁱ	0.42	1.0	1.0	1.0
CH ₂ =CH ₂	2.9	2.5 ⁱ	--	1.2	1.2	--
g-C ₆ H ₁₀	0.87	0.19	--	4.0	15.1	--
trans-4eCH-CH ₂ e	0.30	0.17	--	11.7	16.9	--

^aAll compounds at 10 ppm initially. ^bAll reactions carried out with 37% relative humidity. ^cAll initial concentrations 5 ppm. ^dData from Dilling et. al. (1974). ^eAll initial concentrations 5 ppm except as noted. ^fInitial concentration 15 ppm. ^gTime required for 47% disappearance of g-CH₂CH₂O. ^hEstimated value for 50% disappearance of compound. ⁱInitial NO₂ concentration 16.8 ppm.

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Table VII shows that the relative reactivity of α -CH₂CH₂O is greater with O₃ than with NO or NO₂. The differences in the relative reactivities can be partially explained on the basis that all of the reactions do not involve the same type and quantity of reactive intermediates. For example, some organic materials can cause a faster oxidation of NO to NO₂ than do others, and some organic materials produce O₃ at a faster rate than do others. Consequently if O₃ is one of the key reactive intermediates, then its concentration will be important in determining how reactive a material is in the reactor as well as in the real atmosphere.

The simultaneous use of slow and fast reacting organic materials in competitive photochemical reactions should eliminate some of the differences in relative reactivity caused by different "initiators" such as NO, NO₂ or O₃. Also, this type of system would approximate a real atmosphere more closely. In these competitive experiments the ratios of the photochemical reactivities of the compound pairs were very similar even though the absolute reactivities varied as the "initiator" was varied from NO to NO₂ to O₃ (Table VIII). O₃ appeared to have a slightly greater leveling effect than did NO or NO₂. Since these ratios in the competitive experiments are more nearly alike than those in the individual experiments, this method is suggested as a better way to evaluate how a certain organic material would behave in the real atmosphere. Also, NO, NO₂ and O₃ could be used interchangeably or in combination.

Comparison of the data in Tables VII and VIII further suggests that CHCl-CCl₂ caused the formation of some reactive species other than O₃ in the photochemical reactions. Whether NO, NO₂, or O₃ was used as the "initiator", CHCl-CCl₂ was more reactive than α -CH₂CH₂O and α -C₆H₁₂, whereas in competitive experiments, CHCl-CCl₂ was less reactive. If O₃ were the only important reactive species, one would expect similar ratios of reactivities from individual and combination experiments. This unknown reactive species appeared to be highly reactive toward CHCl-CCl₂ in individual

Table VIII. Photochemical Reactivity of Organic Materials in Competition

Experiments which Involve NO, NO₂, and O₃

Compound pair	Time (hr) for 50% disappearance of compound in combination			Reactivity Ratio		
	NO ^a	NO ₂ ^a	O ₃ ^a	NO	NO ₂	O ₃
<i>g</i> -C ₆ H ₁₂	4.9	5.0	0.73	1.8	2.1	1.2
CHCl-CHCl	8.7	10.5	0.87			
<i>g</i> -CH ₂ CH ₂ O	6.4	8.0	0.5	1.1	1.3	1.0
CHCl-CCl ₂	7.0	10.5	0.5			
<i>trans</i> -MeCH-CHMe	0.37	0.13	--	1.0	1.1	--
<i>g</i> -C ₆ H ₁₀	0.37	0.15	--			

^aInitial concentration 10 ppm each. ^bAll reactions carried out with 35% relative humidity. ^cInitial concentration 10 ppm.

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experiments, but more reactive towards $g-C_6H_{12}$ when the latter was present. This led us to consider possible products from the photochemical oxidation of $CHCl-CCl_2$ such as phosgene ($COCl_2$), chlorine (Cl_2), chloral (CCl_3CHO) (Jeffrey, 1967), dichloroacetyl chloride ($CHCl_2COCl$), etc. (Dilling and Tefertiller, 1974). These materials could lead to free radicals such as chlorine atoms, tri-chloromethyl radicals ($\cdot CCl_3$), and acyl radicals ($\dot{R}C=O$), etc., under the reaction conditions. Table IX shows the photochemical reactivity of $CHCl-CCl_2$ with a number of these possible products and also with acetaldehyde ($MeCHO$) and bromotrchloromethane ($CBrCl_3$).

CCl_3CHO increased significantly the reactivity of $CHCl-CCl_2$ in comparison with the effect of NO or NO_2 . Chloral would be expected to lead to two types of radicals, trichloroacetyl ($CCl_3\dot{C}=O$) and $\cdot CCl_3$. $MeCHO$ was used to determine if the acetyl radical ($Me\dot{C}=O$) (Altshuller et al., 1967) would lead to similar results. $MeCHO$ decreased the reactivity of $CHCl-CCl_2$ with NO . $CBrCl_3$ which produces $\cdot CCl_3$ radicals, did not enhance the reactivity of $CHCl-CCl_2$ whereas $CBrCl_3$ in combination with NO , did appear to increase the reactivity of $CHCl-CCl_2$. From these experiments, it is not clear why CCl_3CHO was so active.

Chlorine atoms also are potential intermediates in the photochemical oxidation of $CHCl-CCl_2$. Indeed, $CHCl-CCl_2$ was found to be extremely reactive in a photochemical reaction with Cl_2 , even more reactive than with O_3 . NO in combination with Cl_2 also increased the reactivity of $CHCl-CCl_2$.

Although $COCl_2$ was a product from the photochemical oxidation of $CHCl-CCl_2$ (Dilling and Tefertiller, 1974), and the photolysis of $COCl_2$ would be expected to give chlorine atoms, $COCl_2$ by itself did not increase the reactivity of $CHCl-CCl_2$. A combination of $COCl_2$ and NO did increase the reactivity of $CHCl-CCl_2$ significantly. Formation of chlorine atoms more slowly from $COCl_2$ than from Cl_2 could explain this difference in reactivity.

Table IX. Photochemical Reactivity of $\text{CHCl}_2\text{-CCl}_2$ with Possible Photooxidation Products and Other Co-reactants

Co-reactants (concentration in ppm) ^a	Time (hr) for 50% disappearance of $\text{CHCl}_2\text{-CCl}_2$ unless otherwise indicated
NO (5)	3.5
NO_2 (16.8)	2.9
CCl_3CHO (2)	3.2
CCl_3CHO (5)	0.93
CCl_3CHO (10)	0.45
MeCHO (10)	4.7 (19%) [15.7] ^b
MeCHO (10) + NO (5)	6.4 (30%) [10.7] ^b
CH_2Cl_2 (10)	5.0
CH_2Cl_2 (10) + NO (10)	1.3
Cl_2 (1)	1.8 (28%) [3.1] ^b
Cl_2 (1) + NO (5)	0.43
Cl_2 (2)	0.18
Cl_2 (5)	<0.08 (85%) [<0.05] ^b
Cl_2 (10)	<0.11 (100%) [<0.05] ^b
COCl_2 (5)	5.8
COCl_2 (5) + NO (5)	2.3

^aInitial concentration of $\text{CHCl}_2\text{-CCl}_2$ was 10 ppm in each case. All reactions carried out with 35% relative humidity. ^bEstimated value for 50% disappearance of $\text{CHCl}_2\text{-CCl}_2$.

Using a quite unreactive organic material such as \underline{g} -CH₂CH₂O, CCl₃CHO by itself or in combination with NO or NO₂ significantly increased the reactivity of \underline{g} -CH₂CH₂O (Table X). To a lesser extent, both CHCl₂COCl with NO and CHCl-CCl₂ with NO increased the reactivity of \underline{g} -CH₂CH₂O.

Table XI shows data for the reactivity of various organic materials with NO, MeCNO, MeCHO with NO, and CCl₃CHO. MeCHO was chosen since it is a very common product in an oxidizing atmosphere. MeCHO was not as effective an "initiator" as was NO in the photo-chemical reactions. In the presence of MeCHO and NO, highly reactive compounds, such as \underline{g} -C₆H₁₀ and trans-MeCH=CH₂, became more reactive than in the presence of NO alone. Slower reacting materials, such as \underline{g} -C₆H₁₂ and CHCl-CCl₂, became less reactive. MeCHO seems to be an inhibitor in these latter cases. Table XI also shows the reactivity of organic compounds with CCl₃CHO. In combination with compounds which react slowly in the presence of NO, CCl₃CHO increased the compound's reactivity while with materials which react rapidly in the presence of NO, CCl₃CHO caused a rate retardation.

Since Cl₂ greatly increased the reactivity of CHCl-CCl₂ (Table IX), it was of interest to determine how Cl₂ would behave in the presence of more than one compound. Table XII shows three combinations with all compounds showing very high reactivities. Especially noteworthy is the combination of CHCl-CCl₂ and CCl₂-CCl₂ with Cl₂. Based on the known reactivities of CH₂=CH₂, CHCl-CCl₂, and CCl₂-CCl₂ with Cl₂ and with chlorine atoms (Chilts et al., 1963) it is obvious that there are reactive species other than chlorine atoms involved in the destruction of these olefins. Interestingly the reactivity of CCl₂-CCl₂ increased markedly in the presence of CHCl-CCl₂, over that observed in the presence of CH₂=CH₂, just as the reactivity of CCl₂-CCl₂ increased in the presence of CHCl-CCl₂ and NO compared with the reactivity observed in the presence of NO alone (Table (II)).

Table XI. Photochemical Reactivity of Organic Materials with NO, MeCHO, and CCl₃CHO

Compound ^a	Time (hr) for 50% disappearance of compound unless otherwise indicated ^b			
	NO ^c	MeCHO ^d	MeCHO ^e + NO ^c	CCl ₃ CHO ^d
g-CH ₂ CH ₂ O	14.9 (47%) [15.9] ^f	--	--	3.3
g-C ₆ H ₁₂	6.9	14.0 (21%) [33.3] ^f	15.2 (37%) [21.7] ^f	3.4
CHCl-CCl ₂	3.5	4.7 (19%) [15.6] ^f	6.1 (20%) [15.3] ^f	0.45
CH ₂ =CH ₂	2.9	--	6.4 (31%) ^g [10.3] ^f	3.1
g-C ₆ H ₁₀	0.87	4.4 (18%) [12.2] ^f	0.90 0.67 ^g	1.8
g-CH ₂ -MeCH-CH ₂	0.30	2.4 (19%) [6.3] ^f	0.22	2.3

^aAll compounds at 10 ppm initially. ^bAll reactions run with 35% relative humidity. ^cAll initial concentrations 5 ppm. ^dAll initial concentrations 10 ppm. ^eAll initial concentrations 10 ppm except as noted. ^fEstimated value for 50% disappearance of compound. ^gInitial concentration of MeCHO 5 ppm.

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Table XII. Photochemical Reactivity of Organic Materials in Competition
Experiments Which Involve Cl₂

Compound pair ^a	Time (hr) for 90% disappearance (unless otherwise indicated) of compound in combination ^b
CHCl-CCl ₂	<0.12 (100%)
CCl ₂ -CCl ₂	<0.12 (100%)
CH ₂ =CH ₂	0.37
CCl ₂ -CCl ₂	1.5 (46%) [1.7] ^c
CH ₂ =CH ₂	0.57
CHCl-CCl ₂	0.57 (49%) [0.58] ^c

^aInitial concentration 10 ppm each. ^bAll reactions carried out with 35% relative humidity. Initial Cl₂ concentration 5 ppm. ^cEstimated value for 90% disappearance of compound.

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Other possible reactive species in these photochemical reactions are singlet oxygen (Pitts et al., 1969; Kumler et al., 1969; Coomber et al., 1970; Hamming, 1970; Kumler et al., 1970; Altshuller and Bufalini, 1971), oxychlorine radicals such as $\text{ClO}\cdot$ and $\text{ClOO}\cdot$ (Kiriyushin and Poluaktov, 1968; Johnston et al., 1969; Pierrard, 1969; Altshuller and Bufalini, 1971), and hydroxyl radicals (Stedman et al., 1970).

In conclusion, we have found that the relative photochemical reactivities of slow reacting organic materials are similar whether NO or NO_2 is added to the reactor in individual experiments. Replacing NO with NO_2 significantly affected the reactivities of fast reacting compounds. Use of O_3 as the "initiator" also leads to relative reactivities which are different from those observed with NO or NO_2 . If more than one organic material is investigated in competitive experiments, the relative photochemical reactivities of these materials with NO , NO_2 , or O_3 are quite similar. Since a real atmosphere generally contains a mixture of organic pollutants, these results suggest that competitive experiments which involve more than one organic material (preferably several materials) are necessary in order to more accurately assess the relative photochemical reactivities of various organic materials. Our results also suggest that the key reactive intermediate(s) in these photochemical reactions is not NO , NO_2 , or O_3 , but rather some other species which is formed during these reactions. The competitive experiments especially indicate that a common reactive intermediate, oxygen atoms possibly (Altshuller and Bufalini, 1965), is formed irregardless of whether NO , NO_2 or O_3 is used as the "initiator". Chlorine atoms may be reactive intermediates when CHCl-CCl_2 is photolyzed in the presence of NO , NO_2 or O_3 . Cl_2 is more reactive than O_3 with CHCl-CCl_2 in photochemical reactions. Photolysis of CHCl-CCl_2 and $\text{OCl}_2\text{-CCl}_2$ together in the presence of Cl_2 , leads to very rapid destruction of both olefins.

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Literature Cited

- Altshuler, A. P., Bufalini, J. J., Photochem. Photobiol., 4, 97-146 (1965);
- Altshuler, A. P., Bufalini, J. J., Environ. Sci. Technol., 2, 39-64 (1971).
- Altshuler, A. P., Klosterman, D. L., Leach, P. W., Hindawi, I. J., Sigsby, J. E., Jr., Int. J. Air Water Pollut., 10, 81-98 (1966).
- Altshuler, A. P., Cohen, I. R., Parcell, T. C., Science, 156, 937-9 (1967).
- Bufalini, J. J., Altshuler, A. P., Environ. Sci. Technol., 1, 133-8 (1967).
- Myers, D. H., Saltzman, B. E., "Causes Chemistry and Technology," Advances in Chemistry Series, No. 21, pp 93-101, American Chemical Society, Washington, D.C., 1959.
- Chilts, G., Goldfinger, P., Hymbrechts, G., Martens, G., Verbeke, G., Chem. Rev., 63, 355-72 (1963).
- Coomer, J. W., Herbert, E. M., Kummer, W. A., Marsh, D. G., Pitts, J. N., Jr., Environ. Sci. Technol., 4, 1141-5 (1970).
- Dilling, W. L., Tefertiller, W. B., ibid., 8, 0000-00 (1974).
- Dilling, W. L., Tefertiller, W. B., Bredeveg, C. J., ibid., 8, 0000-00 (1974).
- Farber, H. A., "Chlorinated Solvents and the Environment," paper presented at AAFCC Symposium, Atlanta, Ga., January 10-11, 1973; Textile Solvent Technology - Update '73, pp 6-12.
- Hanning, W. J., Environ. Sci. Technol., 4, 1147-8 (1970).
- Jeffrey, G. C., Dow Chemical Co., Freeport, Texas, private communication, 1967.
- Johnston, H. S., Morris, E. D., Jr., Van den Bogernde, J., J. Amer. Chem. Soc., 91, 7712-27 (1969).
- Kiryushin, Y. A., Poluaktov, J. A., Dokl. Akad. Nauk SSSR, 180, 1194-6 (1968) (Russian); Chem. Abstr., 62, 6664g (1968).
- Kumler, R. H., Bortner, M. H., Baurer, T., Environ. Sci. Technol., 3, 848-50 (1969).
- Kumler, R. H., Bortner, M. H., Baurer, T., ibid., 4, 1142-50 (1970).
- Murray, A. J., ibid., J. P., Anal. Chim. Acta, 62, 261-70 (1973a).

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Murray, A. J., Riley, J. P., Nature, 242, 37-8 (1973b).

Pierrard, J. M., Environ. Sci. Technol., 3, 48-51 (1969).

Stedman, D. H., Morris, E. D., Jr., Daby, E. E., Niki, H., Weinstock, E.,

"The Role of OH Radicals in Photochemical Smog Reactions," paper

presented at 160th American Chemical Society National Meeting, Chicago, Ill.

September 13-18, 1970; Abstracts of Papers, WATER 26.

Tuesday, C. S., Arch. Environ. Health, 7, 188-201 (1963).

Wilson, K. W., "Photoreactivity of Trichloroethylene," Summary Report for
Manufacturing Chemists Association on SRI Project PSC-6687, Stanford
Research Institute, South Pasadena, Calif., September 1969.

Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical
Reactivity of Organic Solvents," Technical Report to Manufacturing Chemist.
Association, Stanford Research Institute, South Pasadena, Calif., September
1969.

Pitts, J. N., Jr., Khan, A. U., Smith, E. B., Wayne, R. P., ibid., 3, 241-7 (1969).

Foutsma, M. L., Minman, R. L., J. Amer. Chem. Soc., 86, 3807-14 (1964).

Organic Photochemistry. XV.¹ Environmental Fate and Effect of Chlorinated Solvents. IV.² Product Studies on the Simulated Atmospheric Photolyses of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, and Tetrachloroethylene

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Abstract

In order to determine the products formed from four important chlorinated solvents in the atmosphere, laboratory studies were carried out under simulated atmospheric conditions in a flow reactor. Under sea level conditions, which included nitrogen dioxide and water vapor in air with ultraviolet radiation ($\lambda > 295$ nm) followed by trapping the products with the water, trichloroethylene gave dichloroacetic acid (40%) and hydrogen chloride (52%); tetrachloroethylene gave trichloroacetic acid (36%), hydrogen chloride (16%), and chlorine (5%). Phosgene was detected as an intermediate from

¹Part XIV: (Dilling and Bredeweg, 1974).

²Part III: (Dilling and Bredeweg, 1974).

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both chlorinated olefins while trichloroacetyl chloride, chlorine, and carbon dioxide were also detected from tetrachloroethylene. Under high altitude conditions, which involved dry air and short wavelength light ($\lambda 254$ nm principally), methylene chloride gave hydrogen chloride (9%), chlorine (16%), chloric acid (8%), and perchloric acid ($\geq 30\%$); 1,1,1-trichloroethane gave hydrogen chloride (20%), chlorine (39%), chloric acid (3%), perchloric acid ($\geq 24\%$), acetic acid (10%), and a trace of chloroacetic acid.

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The fate and effect of chlorinated solvents which may be discharged to the environment (Murray and Riley, 1973a; Murray and Riley, 1973b; Farber, 1973) are important from an ecological standpoint. In preceding papers of this series (Dilling et al., 1974; Dilling and Bredeweg, 1974) the reactivities (rates of disappearance) of the four most widely used chlorinated solvents, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), were determined under simulated atmospheric conditions. The two olefinic solvents, $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$, underwent reaction under simulated sea level atmospheric conditions which included ultraviolet radiation of wavelength greater than 290 nm, nitric acid (NO) or nitrogen dioxide (NO_2), and water vapor in air (Dilling et al., 1974). CH_2Cl_2 and CH_3CCl_3 were unreactive under these simulated sea level conditions, but did react rapidly under simulated high altitude atmospheric conditions which included short wavelength ultraviolet radiation (primarily 254 nm) in air (Dilling et al., 1974). Having determined that these four compounds do decompose under certain simulated atmospheric conditions, another important consideration is, into what products are these materials transformed under these conditions. The experiments reported in this paper were carried out under conditions as near as possible to those found in the environment. However, higher concentrations of the compounds in air than would normally be found in the environment were required, in order to collect enough material in a reasonable length of time for reliable product identification.

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No data have been reported on the products from either CH_2Cl_2 or CH_2CCl_2 , under simulated atmospheric conditions. However, one can postulate in some cases what the products might be, based on other chemical studies of these materials. Liquid CH_2Cl_2 was unreactive toward oxygen (O_2) even at 290° (Carlisle and Levine, 1932a; Hardie, 1964a), and produced only trace amounts of hydrogen chloride (HCl) (Archer, 1970). Photolysis of liquid CH_2CCl_2 in the presence of air gave chloroacetyl chloride (CH_2ClCOCl), chloroacetic acid ($\text{CH}_2\text{ClCO}_2\text{H}$) (Archer and Harter, 1964), and HCl (Scott, 1961). COCl_2 was reported as a product from CH_2CCl_2 , when oxidized by the atmosphere at an elevated temperature (Hardie, 1964b).

The products formed from $\text{CHCl}=\text{CCl}_2$, under simulated atmospheric conditions were reported to be phosgene (COCl_2), carbon monoxide (CO), and dichloroacetyl chloride (CHCl_2COCl) (Wilson et al., 1968). It has been suggested that formyl chloride (HCOCl) is probably a product (Altshuller and Bufalini, 1971). No formaldehyde (HCHO) was formed (Wilson et al., 1969; Altshuller and Bufalini, 1971), and the amount of total aldehydes formed probably was no more than the background (i.e. with no $\text{CHCl}=\text{CCl}_2$ present) (Hamming, 1967). Vapor phase photooxidation of $\text{CHCl}=\text{CCl}_2$, with short wavelength light gave CHCl_2COCl and COCl_2 (Dahlberg, 1969). Liquid phase photooxidation gave CHCl_2COCl , trichloroethylene^{oxide} ($\text{C}_2\text{-CHClCCl}_2\text{O}$), CO , HCl , COCl_2 , chlorine (Cl_2), formic acid (HCO_2H), and glyoxylic acid (HOOCO_2H) in varying amounts under different conditions (Carlisle and Levine, 1932b; Müller and Ehrmann, 1936; Kirkbride, 1942; Gilbert, 1960; Shepherd, 1962; Yasnitskii et al., 1965; Howard and Montgomery, 1967; Yasnitskii et al., 1967). Photooxidation

of CHCl_2COCl gave CO and COCl_2 , via radical intermediates which initiated the oxidation of chloroethylenes (Yasnitskii et al., 1966). Vapor phase oxidation of $\text{CHCl}=\text{CCl}_2$ gave carbon dioxide (CO_2) and HCl (Hardie, 1964c). The oxidation of liquid $\text{CHCl}=\text{CCl}_2$ with air or O_2 gave CHCl_2COCl , $g\text{-CHClCOCl}_2\text{O}$, COCl_2 , CO , HCl , chloral (CCl_2CHO), and various peroxides (Erdmann, 1912; Mugdan and Wimmer, 1929; Carlisle and Levine, 1932b; Mugdan and Wimmer, 1934; McKinney et al., 1955; Shepherd, 1962; Hardie, 1964c; Shell Internationale, 1966; Howard and Montgomery, 1967; Jeffrey, 1967; Mayo and Honda, 1968; Archer, 1970). $\text{CHCl}=\text{CCl}_2$ reacted with ozone (O_3) to give HCl , COCl_2 , CO , CH_2ClCOCl , and an "oxide of chlorine" (Erdmann, 1912).

The only product data reported for $\text{CCl}_2=\text{CCl}_2$ under simulated atmospheric conditions was that there was no significant increase in the total amount of aldehydes formed compared with a blank run (Hamming, 1967). The vapor phase photooxidation of $\text{CCl}_2=\text{CCl}_2$ with O_2 or air gave trichloroacetyl chloride (CCl_3COCl) and COCl_2 (Calfee and Wallace, 1956; Bertrand et al., 1971; Dahlberg et al., 1972). The mechanism probably involved the intermediacy of the chloroxy radical ($\text{ClO}\cdot$) (Kiriyushin and Poluektov, 1968). The liquid phase photooxidation of $\text{CCl}_2=\text{CCl}_2$ with O_2 gave CCl_2COCl , COCl_2 , HCl , and various peroxides (Besson, 1895; Kirkbride, 1941; Rushmer and Smith, 1947; Yasnitskii et al., 1963a; Hardie, 1964d). Photolysis of CCl_2COCl with O_2 gave COCl_2 and CO via free radicals which were able to initiate the oxidation of chloroethylenes

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(Yasnitskii et al., 1966). Photooxidation of $\text{CCl}_2=\text{CCl}_2$ in the presence of water gave trichloroacetic acid ($\text{CCl}_2\text{CO}_2\text{H}$) (Bailey and Hickson, 1941; Yasnitskii et al., 1963b; Yasnitskii et al., 1970). Oxidation of liquid $\text{CCl}_2=\text{CCl}_2$ with O_2 gave CCl_2COCl , tetra-chloroethylene oxide ($\text{g-CCl}_2\text{CCl}_2\text{O}$), COCl_2 , and HCl (Müller and Ehrmann, 1936; Shepherd, 1962; Jeffrey, 1967; Archer, 1970), although it has been reported that $\text{CCl}_2=\text{CCl}_2$ was stable toward O_2 in the dark (Hardie, 1964d). O_2 reacted slowly with liquid $\text{CCl}_2=\text{CCl}_2$ to give CCl_2COCl and COCl_2 (Besson, 1894; Swarts, 1898; Hardie, 1964d).

Experimental

Flow Reactor. The reaction vessel and associated gas handling equipment are shown in Figure 1.

For the experiments with $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$, dry cylinder air and a dry air- NO_2 mixture from Matheson Gas Products were passed through 1/4 inch Nupro In-line check valves, 1/4 inch Nupro needle valves and Brooks 1A-15-1 rotameters. Two of the air streams were passed through liquid bubbling tubes with sintered glass gas dispersion tubes. One tube contained water at -25° , and the other contained the chlorinated solvent at a lower temperature (CH_2Cl_2 , -78° ; CH_2CCl_2 , -25° ; $\text{CHCl}=\text{CCl}_2$, -32° ; $\text{CCl}_2=\text{CCl}_2$, -15°). The low temperature was necessary in order to obtain the desired concentration of the chlorinated compound in the air stream.

The low temperature was maintained by circulating CH_2Cl_2 from a refrigeration unit through a jacketed vessel which surrounded the lower part of the bubbling tube except for CH_2Cl_2 where dry ice was used. The concentrations of chlorinated sol-

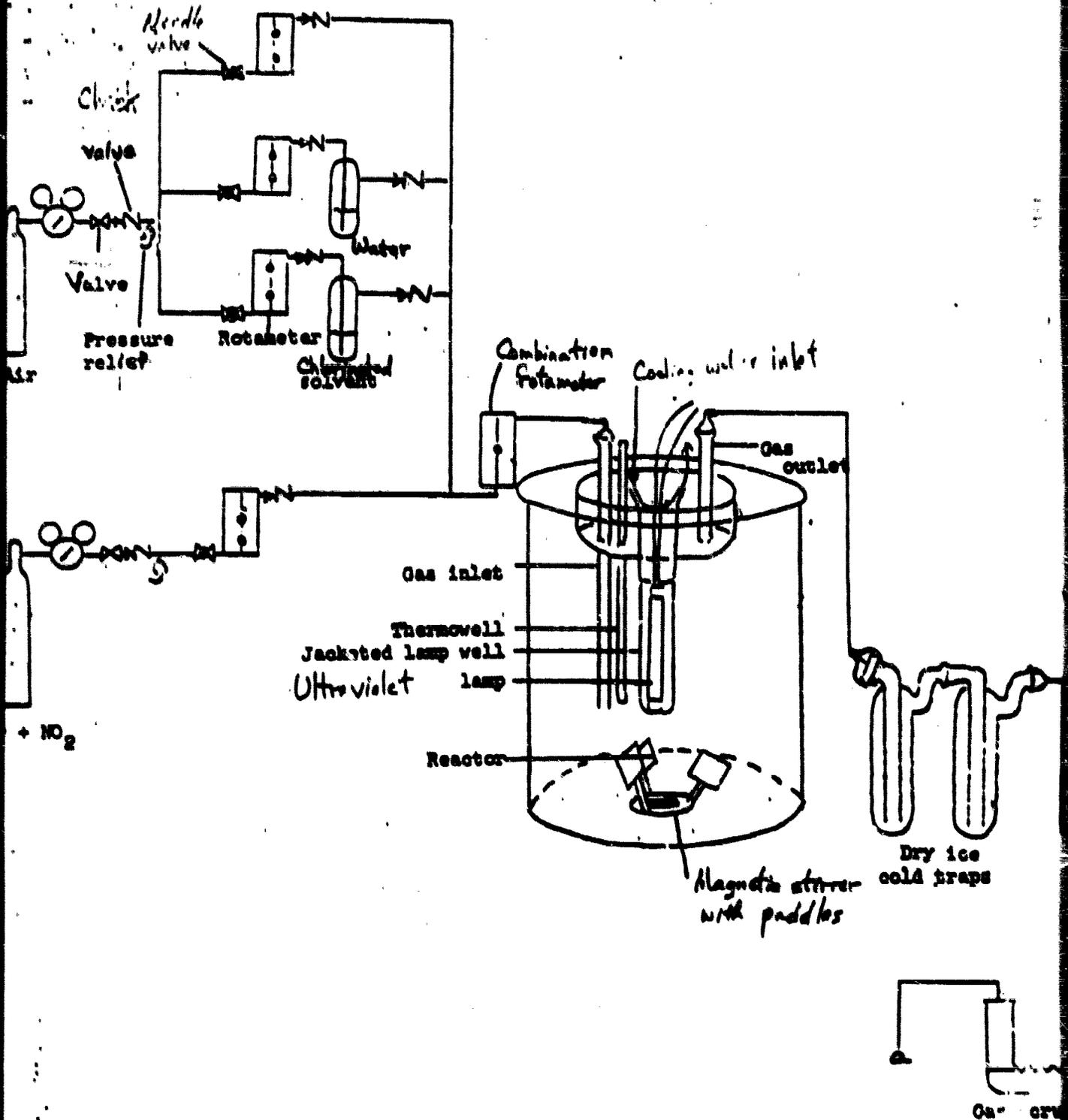


Figure 1. Photochemical flow reactor (in some cases an additional condition
 and (a) another condition may be added to the system)

vents in the air streams were determined by weight loss of the bubbling tube and weight gain of the dry ice trap in blank runs. The air stream, which was passed through the water, was essentially saturated with water as determined by a control experiment. The four air streams which contained NO_2 , the chlorinated solvent, water, and air alone in the desired proportions were each passed through check valves and combined. For the reactions with CH_2Cl_2 and CH_2ClCl , the NO_2 and water were omitted. The combined gas streams were passed through a Brooks 2-15-3 rotameter and into the reactor. The flow meters were calibrated with the actual gas mixtures used in the reactions.

The gas mixture was introduced near the bottom of the reactor and dispersed by means of a magnetically driven large Teflon paddle stirrer. The reactor was a large flat bottomed cylindrical vessel with a volume of 26 liters. The top edge of the vessel was ground flat. A flat glass plate was mounted on the top, sealed with Silicone or Apieson grease, and secured with spring clips. The reactor temperature was maintained at $25 \pm 1^\circ$ by wrapping the sides of the aluminum foil covered vessel with flat sided rubber tubing through which water from a refrigerated bath was circulated.

The radiation source for the reactions of $\text{CHCl}_2\text{-CCl}_2$ and $\text{CCl}_2\text{-CCl}_2$ was a Hanovia 450 watt medium pressure mercury arc lamp. The lamp was placed in a water cooled Pyrex well which transmitted only wavelengths greater than 295 nm as determined by measuring the

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emission spectrum with a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. The lamp intensity is estimated to be .50 times that of sunlight in the 295-400 nm region, based on the manufacturer's specifications. The radiation source for the CH_2Cl_2 and CH_2ClCl reactions was a 10 watt Hanovia low pressure mercury arc lamp which has been described previously (Dilling et al., 1974).

For the reactions of $\text{CHCl}_2\text{-CCl}_2$ and $\text{CCl}_2\text{-CCl}_2$, the exit gas mixture from the reactor was passed through two dry ice traps, the first of which was of about one liter capacity. The second trap had a capacity of ~350 ml. Most of the condensable products and water were collected in the first trap. The noncondensable gases were then passed through a low back pressure gas scrubber which contained standard sodium hydroxide solution. For the reactions of CH_2Cl_2 and CH_2ClCl , the exit gas stream was passed through two 350 ml dry ice traps, then through the gas scrubber, and finally through a one liter dry ice trap. In some cases a second caustic gas scrubber was also used.

All connections between the various parts of the system were constructed from 1/4 inch stainless steel or Teflon tubing and Swagelok fittings.

Simulated Sea Level Atmospheric Photolysis of $\text{CHCl}_2\text{-CCl}_2$.
Water (75 ml) and $\text{CHCl}_2\text{-CCl}_2$ (50 ml) were placed in their respective bubbling tubes (Figure 1). The air flow rates were as fol-

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flows: 25 cc/minute through the $\text{CHCl}_3\text{-CCl}_4$, which was 175 ppm $\text{CHCl}_3\text{-CCl}_4$ (molar or volume basis) after mixing with the other gas streams, 140 cc/minute through the water which was 35% relative humidity after mixing with the other gas streams, and 235 cc/minute of the air- NO_2 mixture [90 ppm NO_2 , as determined by a modified Saltzman procedure (Dilling et al., 1974)] which was 50 ppm NO_2 after mixing with the other gas streams. The total flow rate was 400 cc/minute which corresponded to a 63 minutes residence time in the reactor. Into the gas scrubber was placed 100 ml of 1.000 N NaOH and 115 ml of water. Dry ice-ethanol was used to cool the cold traps.

The reaction was run for 166 hr during which time 3,980 liters (calculated from flow rates) of air (slightly above atmospheric pressure), 29.53 g of water, and 3.67 g (27.9 μmoles) of $\text{CHCl}_3\text{-CCl}_4$ had passed through the reactor. No deposit was detected on the lamp well, the reactor surface, or the gas lines. Nearly all of the condensable material was found in the first cold trap. A total of 35.75 g of material (one phase) was obtained.

After they melted, the aqueous solutions from the cold traps were transferred to a 50 ml volumetric flask with rinsing and were made up to volume with water. A 5.0 ml aliquot was removed, acidified with nitric acid (HNO_3) and titrated potentiometrically for chloride ion (Cl^-) with 0.100 N AgNO_3 on a Precision-Dow Recordomatic Titrator. The 20.67 ml of titrant required corresponded to 20.7 μmoles of Cl^- in the original 50 ml of solution.

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Another 5.0 ml aliquet of the aqueous reaction solution was removed and titrated for acidity with 1.000 N NaOH on a Sargent-Welch Recording Titrator, Model DG. The 4.09 ml of titrant required to reach pH 7 corresponded to 40.9 μ moles of strong acid (H^+) in the original 50 ml of solution.

After another 2 ml of the aqueous reaction mixture was removed (for gc analysis, etc.), the remaining 38 ml of solution was extracted continuously with 200 ml of ether for 77 hr. The ether extract was evaporated under vacuum to ~5 ml. After a small amount of water was separated, 4.842 g of the ether solution remained. Gc analysis (2 ft x 1/4 inch column packed with 1.5% LAC 446 and 2% H_3PO_4 on 60-80 mesh Chromosorb MAW, column temp 127°, injection port temp 140°, detector block temp 300°, He flow rate 50 cc/minute) of this ether solution showed a single product, t_R 4.3 minutes, which had the same retention time as an authentic sample of dichloroacetic acid ($CHCl_2CO_2H$). To a 1.640 g portion of the ether solution was added 85.0 mg of 1-chloronaphthalene ($1-C_{10}H_7Cl$) as an internal gc standard, t_R 1.2 minutes. Gc analyses of this solution showed the presence of 0.559 g of $CHCl_2CO_2H$ which corresponded to 2.17 g (61% yield based on carbon) of $CHCl_2CO_2H$ in the original 50 ml of aqueous solution. The 33.8 mg atoms of chlorine which are contained in this amount of $CHCl_2CO_2H$ represents 40% of the chlorine present in the $CHCl_2CCl_3$ used. A portion of the ether extract was evaporated. The mass spectrum of the residue indicated the sample to be almost entirely $CHCl_2CO_2H$ by

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comparison with the spectrum of an authentic sample. Minor amounts of other compound(s) may have been present.

GC analysis of the original aqueous solution showed only $\text{CHCl}_3\text{CO}_2\text{H}$. GC analyses of the ether extract on longer columns (from which $\text{CHCl}_3\text{CO}_2\text{H}$ was not eluted) showed traces of two short retention time components which were not identified.

The sodium hydroxide solution in the scrubber was transferred to a 250 ml volumetric flask with rinsing and made up to volume with water. A 10.0 ml aliquot was acidified with nitric acid (HNO_3) and titrated for Cl^- ; 9.11 ml of 0.100 N AgNO_3 was required. This corresponded to 22.8 mmoles of Cl^- in the total scrubber solution. The excess base in a 25.0 ml aliquot of the scrubber solution was titrated with 1.000 N hydrochloric acid. Three breaking points were observed at 5.61 ml (pH = 10.4), 5.95 ml (pH = 8.2), and 6.88 ml (pH = 4.8). The 6.88 ml of titrant corresponded to the absorption of 31.2 mmoles ^{of H^+} which had been picked up by the caustic scrubbing solution. Titration of sodium carbonate and sodium bicarbonate solutions indicated that the extra breaking points noted above were not due to the presence of carbon dioxide.

The total Cl^- in the traps and scrubber was 43.5 mmoles which corresponded to 52% of the theoretical amount of chlorine in the $\text{CHCl}_3\text{CO}_2\text{H}$ used. The total H^+ in the traps and scrubber was 72.1 mmoles.

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Simulated Sea Level Atmospheric Photolysis of $\text{CCl}_2=\text{CCl}_2$.

Water (75 ml) and $\text{CCl}_2=\text{CCl}_2$ (50 ml) were placed in their respective bubbling tubes. The gas flow rates were set at 25 cc/minute through the $\text{CCl}_2=\text{CCl}_2$, 140 cc/minute through the water, 28 cc/minute of an air- NO_2 mixture (1000 ppm NO_2), and 207 cc/minute of diluent air. The total gas flow rate was 400 cc/minute and consisted of 142 ppm $\text{CCl}_2=\text{CCl}_2$, 35% relative humidity, and 70 ppm NO_2 in air. The residence time in the reactor was 65 minutes. Into the gas scrubber were placed 150 ml of 1.000 N NaOH and 100 ml of water.

The reaction was run for 167 hr. During this time, 4.21 g of $\text{CCl}_2=\text{CCl}_2$ (25.4 μmoles $\text{CCl}_2=\text{CCl}_2$, 191.6 mg atoms chlorine) and 27.73 g of water had passed through the reactor. The NO_2 concentration in the gas stream was determined after the termination of the photoreaction by filling a large gas bulb with the gas mixture which was used throughout the reaction and analysing the contents by the modified Saltzman technique.

The reactor was rinsed with water until the rinses were neutral. This solution contained 5.3 μmoles of H^+ and no Cl^- . Gas analysis showed the presence of 5.66 μmoles of $\text{CCl}_2\text{CO}_2\text{H}$, which corresponds to 17.0 mg atoms of chlorine.

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A total of 28.87 g of acidic liquid was collected in the two cold traps. Contained in this liquid were 5.63 mmoles of Cl^- and 13.00 mmoles of H^+ . A continuous ether extraction was run for approximately 105 hr on a portion of the cold-trap solution. G c analysis showed the presence of 5.43 mmoles of $\text{CCl}_3\text{CO}_2\text{H}$ in the ether extract, which corresponded to 16.3 mg atoms of chlorine. No other products were detected. Infrared analysis confirmed the presence of $\text{CCl}_3\text{CO}_2\text{H}$ in the ether extract, and also indicated another unidentified product. Mass spectroscopic analysis showed only $\text{CCl}_3\text{CO}_2\text{H}$.

Cl^- titration of the trap solution which remained after ether extraction showed the presence of 5.65 mmoles, which indicated that all of the Cl^- remained in the solution after ether extraction. Base titration showed 5.20 mmoles of H^+ in the solution. Thus, all the acid, with the exception of the HCl , had been extracted from the trap solution.

Analysis of the solution from the gas scrubber showed the presence of 27.50 mmoles of Cl^- and 16.50 mmoles of hypochlorite ion (OCl^-) which was determined by the iodide-thiosulfate method (Furman, 1962). A portion of the scrubber solution was acidified to pH 1 and continuously extracted with ether for approximately 70 hr. G c analysis of the ether extract showed 1.25 mmoles of $\text{CCl}_3\text{CO}_2\text{H}$ present in the total scrubber solution, which corresponded to 3.75 mg atoms of chlorine. Titration of the scrubber

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solution with 1.000 N HCl indicated that 65.50 mmoles of base had been neutralized by acidic products. This was an excess of 20.25 mmoles of H^+ over that which could be accounted for by the chlorinated products.

The overall recovery of products was 33.1 mmoles of Cl^- , 16.5 mmoles of OCl^- , 12.3 mmoles of CCl_2CO_2H which corresponds to 37.0 mg atoms of chlorine, and 83.8 mmoles of H^+ . Assuming the OCl^- arises from Cl_2 , the yields (based on total chlorine present in the $CCl_2=CCl_2$) of products were 33% Cl_2 , 16% HCl, and 36% CCl_2CO_2H .

Simulated High Altitude Atmospheric Photolysis of CH_2Cl_2 .
 CH_2Cl_2 (50 ml) was placed in the bubbling tube, and 290 cc/minute of dry air was passed through. The resulting stream was diluted with more dry air to give a total gas flow of 1200 cc/minute. This gave a concentration of 155 ppm CH_2Cl_2 in air and a residence time of 22 minutes in the reactor. Two gas scrubbers were used in the photoreaction. Into each was placed 250 ml of 1.000 N NaOH.

The reaction was run for 165 hr. At the completion of the reaction, 6.51 g of CH_2Cl_2 (76.7 mmoles, 153.4 mg atoms of chlorine) had passed through the reactor. A small amount of white solid, identified silicon dioxide (SiO_2) by infrared analysis, was deposited throughout the reactor. Infrared analysis also

indicated that there was a small amount of unidentified organic material associated with the SiO_2 . A portion of the Apieson grease which had been used to seal the system and which had turned black during the photoreaction was collected and analysed for total chlorine. While the analyses were poorly reproducible, they averaged around 4 wt %.

A total of 3.13 g of liquid had collected in the two dry ice cold traps. It was possible to recover a very small amount of yellow liquid from the second cold trap. Mass spectroscopic analysis of this liquid indicated the presence of water, HCl , and a large amount of CO_2 . There were several minor unidentified ion-peaks. The two cold traps were rinsed with water until the rinses were neutral. The rinses were made up to volume with water in a 500 ml volumetric flask. Analyses indicated a total of 1 mmole of chlorate (ClO_2^-), which was determined by the ferrous sulfate method (Kolthoff et al., 1961), and 21 mmoles of perchlorate (ClO_4^-), which was determined by the ferrous 1,10-phenanthroline method (Fritz et al., 1964). There was no Cl^- or OCl^- present. Titration with 1.000 N NaOH showed 23.0 mmoles of H^+ in the total cold trap solution.

The reactor and connecting lines were rinsed with water and made up to 1000 ml. Present in the solution were 2 mmoles of ClO_2^- and 22 mmoles of ClO_4^- . No Cl^- or OCl^- was found. Base titration showed 22.6 mmoles of H^+ in the total solution.

The solution from the first gas scrubber contained 18 mmoles of Cl^- , 12 mmoles of OCl^- , and 7.25 mmoles of ClO_2^- . It was not possible to analyze for ClO_2^- in the presence of the ClO_2^- . An attempted acid titration of the solution was not successful. The second gas scrubber contained 7.75 mmoles of Cl^- , 1.25 mmoles of ClO_2^- , and 0.50 mmole of ClO_2^- . There was no OCl^- . Acid titration of the solution, however, indicated that a total of 36.75 mmoles of H^+ was present; only 9.50 mmoles of H^+ could be accounted for by HCl , chloric acid (HClO_3), and perchloric acid (HClO_4). GC and NMR analyses for HCO_2H were negative. The unidentified acid does not contain chlorine, as neutron activation analysis showed only 10.1 mg atoms of chlorine in the solution.

The solution in the last cold trap was made up to 250 ml. It contained 1.75 mmoles of ClO_2^- , 0.5 mmole of ClO_2^- , and 2.4 mmoles of H^+ .

The overall recovery of products was 25.8 mmoles of Cl^- , 12.0 mmoles of OCl^- , 12.0 mmoles of ClO_2^- , ^{> 45.8 mmoles of ClO_2^- and} _{> 84.8 mmoles of H^+ .} Assuming the OCl^- arises from Cl_2 , the yields (based on total chlorine present in the CH_2Cl_2) of products were 16% Cl_2 , 9% HCl , 8% HClO_3 , and >30% HClO_4 .

Simulated High Altitude Atmospheric Photolysis of CH_2Cl_2
 CH_2Cl_2 (50 ml) was placed in the bubbling tube. Dry air (18 cc/minute) was passed through the CH_2Cl_2 , and the resulting CH_2Cl_2 air stream was diluted with more dry air to give a total gas flow

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of 1250 cc/minute. This gave a concentration of 169 ppm CH_2Cl_2 in the air and a residence time of 21 minutes in the reactor. In the single gas scrubber was placed 250 ml of 1.000 N NaOH.

The reaction was run for 167 hr. During this time, 12,525 liters of air and 11.51 g of CH_2Cl_2 (86.3 μmoles , 258.9 mg atoms of chlorine) had passed through the reactor. A small amount (≥ 30 mg) of SiO_2 was collected.

A total of 3.53 g of acidic liquid was found in the first two dry ice cold traps. The reactor and the connecting lines in the system also contained acidic liquid. The two cold traps, reactor, and connecting lines were rinsed with water until the rinses were neutral. The rinses and the 3.53 g of acidic liquid were combined in a 1000 ml volumetric flask and made up to volume with water. An aliquot was titrated with AgNO_3 ; these were 5.4 μmoles of Cl^- in the total solution. A 50 ml aliquot was removed and titrated for H^+ with 1.000 N NaOH. Two breaks were observed, the first at pH 3.95 after the addition of 3.23 ml of titrant, and the second at pH 8.50 after an additional 0.44 ml of titrant had been added. This corresponds to 64.6 meq of strong acid and 8.8 meq of weak acid.

A continuous ether extraction was run on 500 ml of the rinse solution for approximately 150 hr. Subsequent titration of the extracted water indicated that all of the weak acid, but only

12% of the strong acid, had been extracted into the ether. The ether was evaporated to a small volume. Mass spectroscopic analysis confirmed acetic acid (HOAc) as the primary product, with a small amount of $\text{CH}_2\text{ClCO}_2\text{H}$ and another minor unidentified component.

The pH of 200 ml of the extracted water solution was raised to 7.5 with NaOH, and the solution was evaporated to dryness. The resultant white solid was identified by infrared analysis as primarily a hydrate of sodium perchlorate (NaClO_4) by comparison with authentic spectra; a minor amount of a carboxylic acid salt and a nitrate (NO_3^-) or a carbonate (CO_3^{--}) were also indicated to be present. Powder x-ray diffraction analysis confirmed NaClO_4 as the major constituent. Mass spectroscopic analysis showed only CO_2 at 460° . Analysis of the extracted water solution showed the presence of 61.6 μmoles of ClO_4^- in the entire extracted solution.

The NaOH solution from the gas scrubber was made up to volume, with water in a 250 ml volumetric flask. Analyses indicated 95.0 μmoles of Cl^- , 50.0 μmoles of OCl^- , and 6.75 μmoles of ClO_2^- in the total scrubber solution; ClO_4^- could not be determined.

The water which had collected in the last cold trap downstream from the gas scrubber was made up to volume with water in a 250 ml volumetric flask. Titration indicated little or no Cl^- . A 50 ml aliquot was titrated with 1.000 N NaOH. The titration

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started at pH 7.2; a breaking point was observed at pH 9.7 after the addition of 0.53 ml NaOH. This corresponds to 2.65 mmoles of H^+ in the total solution. No ClO_2^- was found, but 2.0 mmoles of ClO_3^- in the total solution was found.

The overall recovery of products was 100.4 mmoles of Cl^- , 50.0 mmoles of OCl^- , 6.8 mmoles of ClO_2^- , ≥ 61.9 mmoles of ClO_3^- , and ≥ 76.1 mmoles of H^+ . Assuming the OCl^- arises from Cl_2 , the yields (based on total chlorine present in the CH_2Cl_2) of products were 39% Cl_2 , 20% HCl , 3% $HClO_2$, and $\geq 24\%$ $HClO_3$.

Static Photolysis of $CCl_2=CCl_2$. The photoreactor, described previously for short-term (<24 hr) sea level simulated photolyses (Dilling et al., 1974), was charged with 100 ppm of $CCl_2=CCl_2$, 50 ppm of NO , and enough water for 55% relative humidity. The reaction mixture was irradiated as described previously (Dilling et al., 1974) for 7 hr at which time 60% of the $CCl_2=CCl_2$ had reacted; 50% of the $CCl_2=CCl_2$ had reacted in 4.8 hr. The contents of the reactor were drawn through a trap which was cooled in liquid nitrogen. Mass spectroscopic analysis of the contents of the trap indicated the presence of CCl_2OCCl_2 (and/or $g-CCl_2CCl_2O$), m/e 145 (CCl_2CO^+), 117 (CCl_2^+), 110 (CCl_2CO^+), 82 (CCl_2^+); $COCl_2$, m/e 98 (M^+), 63 ($COCl^+$); Cl_2 , m/e 70 (M^+), 35 (Cl^+); and CO_2 , m/e 44 (M^+), in addition to $CCl_2=CCl_2$. The chlorine isotopic abundance ratios were consistent with the assigned formulas.

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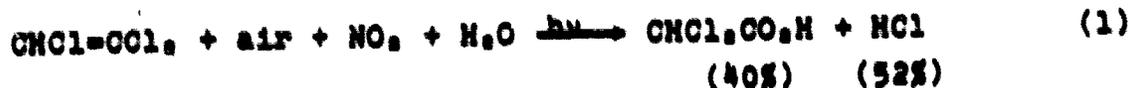
Repetition of this reaction without the water vapor gave essentially the same results.

The preceding reaction was repeated except that the water vapor was omitted. G c analysis (6 ft x 3 mm ID glass column packed with 3.8% UC-W98 on 80-100 mesh Diatoport S, column temperature 60°, electron capture detector) of the gaseous reaction mixture confirmed the presence of COCl_2 by comparison of its retention time with that of an authentic sample.

Static Photolysis of $\text{CHCl}=\text{CCl}_2$: As in the preceding experiment, 100 ppm $\text{CHCl}=\text{CCl}_2$ and 50 ppm of NO_2 in air were irradiated. G c analysis confirmed the presence of COCl_2 .

Results

Vapor phase irradiation of $\text{CHCl}=\text{CCl}_2$ (175 ppm), in a flow reactor, in air which contained NO_2 (50 ppm) and water vapor (35% relative humidity) at 25° with a medium pressure mercury arc lamp ($\lambda > 295 \text{ nm}$) and with a residence time of 65 minutes in the radiation zone gave essentially complete conversion of the $\text{CHCl}=\text{CCl}_2$ to $\text{CHCl}_2\text{CO}_2\text{H}$ and HCl (Equation 1).

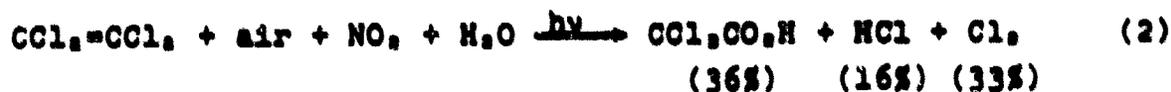


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The conditions of the product collection were such that any hydrolyzable materials would have been isolated as the hydrolysis products. The yields throughout this paper (except for HOAc) are based only on the number of chlorine atoms present in the compounds. The yield of $\text{CHCl}_2\text{CO}_2\text{H}$ was 61% based on the carbon content.

COCl_2 was detected in a gas sample which resulted from the photolysis of $\text{CHCl}=\text{CCl}_2$ (100 ppm) and NO (50 ppm) in air in a static reactor.

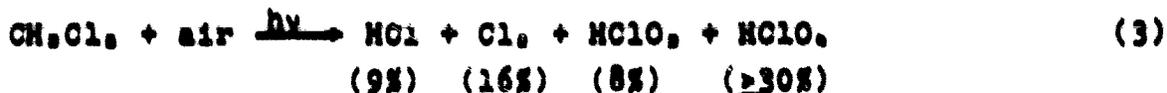
Irradiation ($\lambda > 295 \text{ nm}$) of $\text{CCl}_2=\text{CCl}_2$ (142 ppm) in air which contained NO_2 (70 ppm) and water vapor (35% relative humidity) in the flow reactor (65 minutes residence time) gave $\text{CCl}_2\text{CO}_2\text{H}$, HCl , Cl_2 (or some other product which analyzed as OCl^- and Cl^- in aqueous solution) and unidentified organic products (Equation 2).



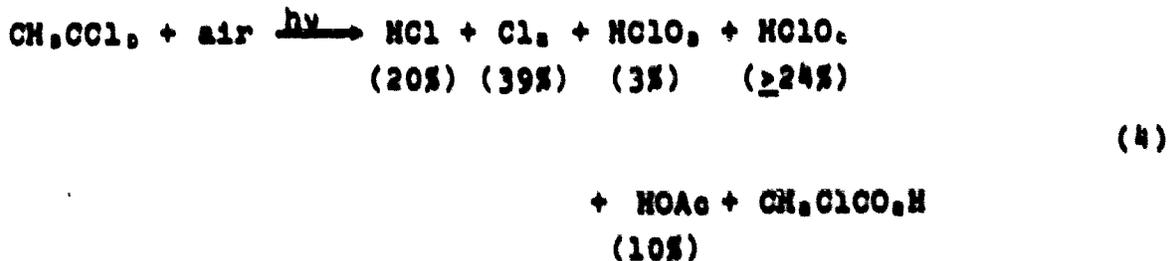
The conversion of the $\text{CCl}_2=\text{CCl}_2$ was essentially complete. The reaction mixture from $\text{CHCl}=\text{CCl}_2$ was not analyzed for OCl^- , but there could not have been more than 8% since 92% of the chlorine was accounted for in the two products shown in Equation 1. There was another strong acid(s), which did not contain chlorine, formed in the photolysis of both $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$.

COCl_2 was detected in the vapor phase from a static photolysis of CCl_4 - CCl_2 (100 ppm), NO (50 ppm), and water vapor (35% relative humidity) in air. Mass spectroscopic analysis of the condensable products from this reaction mixture indicated the presence of CCl_4 , COCl_2 , COCl_2 , Cl_2 , and CO_2 .

Photolysis of CH_2Cl_2 (155 ppm) in dry air under simulated high altitude conditions (λ primarily 254 nm) in the flow reactor at -25° with a residence time of 22 minutes in the radiation zone gave HCl , Cl_2 , HClO_2 , HClO , and traces of unidentified organic products (Equation 3).



Irradiation of CH_2CCl_2 (169 ppm) under simulated high altitude conditions similar to those used for CH_2Cl_2 gave the same four inorganic chlorine products in addition to HOAc and a trace of $\text{CH}_2\text{ClCO}_2\text{H}$ (Equation 4).



The HOAc yield is based on the carbon content. The CH_2Cl_2 and CH_2CCl_2 were completely consumed in the latter two reactions.

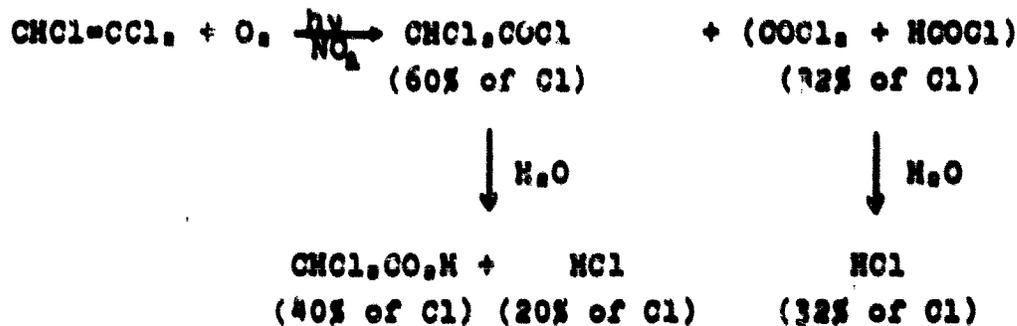
Discussion

The chloroacetic acids produced from $\text{CHCl}_2\text{-CCl}_2$ and $\text{CCl}_2\text{-CCl}_2$, almost certainly arose from hydrolysis of the chloroacetyl chlorides, and the HCl from COCl_2 and possibly HCOCl . These hydrolyses likely occurred in the cold traps where the water and organic products both condensed, and thus were not photoreactions. The detection of COCl_2 , COCl and COCl_2 from the photolysis of $\text{CCl}_2\text{-CCl}_2$, and the reported formation of CHCl_2 , COCl and COCl_2 from $\text{CHCl}_2\text{-CCl}_2$, (Wilson et al., 1968) support this conclusion. COCl_2 is known to hydrolyse very rapidly in the liquid phase ($t_{1/2} \approx 0.1$ sec at 25°) (Manogue, 1958; Ugi and Beck, 1961). CHCl_2 , COCl and CCl_2 , COCl hydrolyse even faster (Ugi and Beck, 1961). HCOCl is unknown, and if formed as a transient intermediate would likely break down to HCl and CO . Thus if these acid chlorides were formed at low concentrations in the atmosphere from $\text{CHCl}_2\text{-CCl}_2$ and $\text{CCl}_2\text{-CCl}_2$, the acid chlorides would be destroyed rapidly on contacting rain or other liquid water bodies. The vapor phase hydrolysis of COCl_2 in the dark was quite slow as shown by injecting COCl_2 into air which contained water vapor and following the COCl_2 rate of disappearance by g.c.

Since one mole of HCl is generated for each mole of CHCl_2 , COCl formed under the simulated atmospheric conditions of this study, $\text{CHCl}_2\text{-CCl}_2$ breaks down to about two parts of CHCl_2 , COCl and one part of other HCl generators (presumably COCl_2 and HCOCl) (Scheme I).

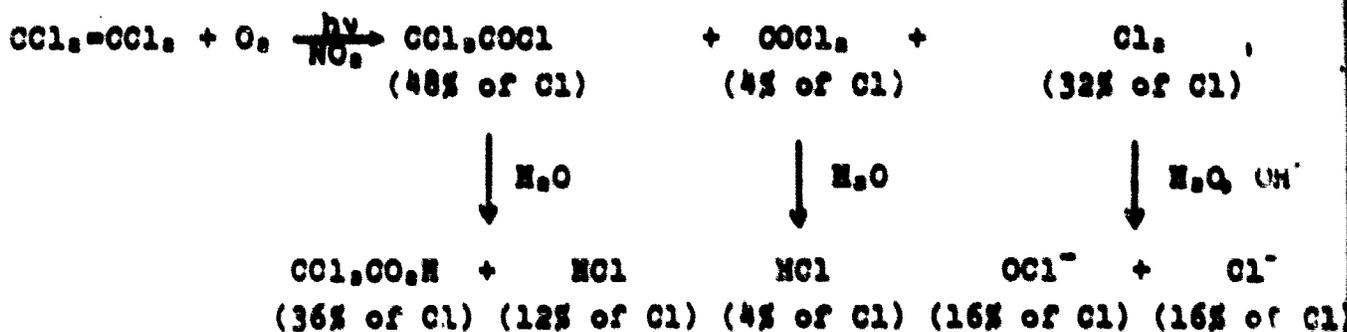
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Scheme I



The major difference between the photolyses of $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$ under similar conditions was the formation of an appreciable amount of Cl_2 from the latter (Scheme II).

Scheme II



Cl_2 was detected both directly, by mass spectroscopy, and indirectly, by thiosulfate titration of the iodine liberated from

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the reaction of potassium iodide with OCl^- which resulted from the reaction of the Cl_2 with aqueous base.

The excess acid ($[\text{H}^+] > [\text{Cl}^-] + [\text{CHCl}_2\text{CO}_2\text{H} \text{ or } \text{CCl}_2\text{CO}_2\text{H}]$) produced in the photolysis of $\text{CHCl}_2\text{COCl}_2$ and $\text{CCl}_2\text{COCl}_2$ is likely HNO_2 , which arose from the reaction of NO_2 , a portion of which probably passed through the photoreactor unchanged, with water in the traps and scrubber (Cotton and Wilkinson, 1966).

The formation of HClO_2 and HClO from CH_2Cl_2 and CH_2CCl_2 in air with short wavelength ultraviolet radiation is indicative of highly oxidising conditions. Ozone is known to be generated rapidly under these conditions (Dilling et al., 1974).

Some of the products identified from the photoreactions under these simulated high altitude conditions were probably formed through the intermediacy of various ^{chlorine} oxides (Sneed et al., 1954; Remy, 1956), which in the presence of water or alkali, gave the oxyacids of chlorine or the salts. The presence of HClO_2 and HClO in the water which accumulated in an empty cold trap downstream from two NaOH scrubbers during the photolysis of CH_2Cl_2 indicates that at least part of the acid is not formed directly during the photolysis. Cl_2 could have formed directly from CH_2Cl_2 or CH_2CCl_2 , from oxidation of HCl , or via the decomposition of a chlorine oxide intermediate. Alternatively, a chlorine oxide itself could have provided the oxidising power observed in the caustic scrubbers (e.g. $\text{Cl}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2 \text{HOCl}$).

All of the products observed in this study were those which probably resulted from reactions which are unimolecular with respect to the chlorinated solvents, i.e. there were no products which require the interaction of two or more organic molecules. Thus, even though the concentrations of the chlorinated solvents may have been considerably higher than those found under many environmentally significant conditions, the products would very likely be the same at lower concentrations.

Acknowledgment

The authors wish to thank Dr. V. A. Stenger for helpful discussions and Dr. C. J. Bredweg and Miss C. G. Mendosa for experimental assistance.

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Literature Cited

- Altshuller, A. P., and Dufalini, J. J., Environ. Sci. Technol., 5, 39-64 (1971).
- Archer, W. L., Dow Chemical Co., Midland, Mich., private communication, 1970.
- Archer, W. L., Harter, M., Dow Chemical Co., Midland, Mich., private communication, 1964.
- Bailey, K. C., Hickson, W. S. E., J. Chem. Soc., 145 (1941).
- Bertrand, L., Exsteen-Meyers, L., Franklin, J. A., Huybrechts, G., Olbregts, J., Int. J. Chem. Kin., 3, 89-96 (1971).
- Besson, M. A., Compt. Rend., 118, 1347-50 (1894).
- Besson, M. A., ibid., 121, 125-8 (1895).
- Calfee, J. D., Wallace, T. A., Jr. (to Allied Chemical and Dye Corp.), U.S. Patent 2,736,695 (February 28, 1956); Chem. Abstr., 50, 10762 (1956).
- Carlisle, P. J., Levine, A. A., Ind. Eng. Chem., 24, 146-7 (1932a).
- Carlisle, P. J., Levine, A. A. ibid., 24, 1164-8 (1932b).
- Cotton, F. A., Wilkinson, G., "Advanced Inorganic Chemistry, A Comprehensive Text," 2nd edn., p 346, Interscience Publishers, New York, N.Y., 1966.
- Dahlberg, J. A., Acta Chem. Scand., 23, 3081-90 (1969).
- Dahlberg, J. A., Moden, A. O., Ostlund, C. A. G. (to Uddeholms Aktiebolag), Ger. Patent Offen. 2,118,540 (January 20, 1972); Chem. Abstr., 76, 72044 (1972).
- Dilling, W. L., Bredeweg, C. J., Environ. Sci. Technol., 8, 0000-00 (1974).
- Dilling, W. L., Tefertiller, N. B., Bredeweg, C. J., ibid., 8, 0000-00 (1974).
- Erdmann, E., J. Prakt. Chem., 85, 78-89 (1912).
- Farber, H. A., "Chlorinated Solvents and the Environment," paper presented at AAPCC Symposium, Atlanta, Ga., January 10-11, 1973; Textile Solvent Technology - Update '73, pp 6-12.

000154

Fritz, J. S., Abbink, J. E., Campbell, P. A., Anal. Chem., 36, 2123-5 (1964).

Furman, N. H., Ed., "Standard Methods of Chemical Analysis," 6th edn., Vol. 1, p 336, D. Van Nostrand Co., Inc., Princeton, N.J., 1962.

Gilbert, R. E., Dow Chemical Co., Freeport, Texas, private communication, 1960.

Haming, W. J., "Photochemical Reactivity of Solvents," paper presented at Aeronautic and Space Engineering and Manufacturing Meeting, Society of Automotive Engineers, Los Angeles, Calif., October 2-6, 1967.

Hardie, D. W. F., "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd edn., Vol. 5, pp 111-9, Interscience Publishers, New York, N.Y., 1964a.

Hardie, D. W. F., op. cit., pp 154-7, 1964b.

Hardie, D. W. F., op. cit., pp 183-95, 1964c.

Hardie, D. W. F., op. cit., pp 195-203, 1964d.

Howard, W. L., Montgomery, W. C., Dow Chemical Co., Freeport, Texas, private communication, 1967.

Jeffrey, G. C., Dow Chemical Co., Freeport, Texas, private communication, 1967.

Kirkbride, F. W. (to Imperial Chemical Industries Ltd.), Brit. Patent 534,732 (March 17, 1941); Chem. Abstr., 36, 1330 (1942).

Kirkbride, F. W. (to Imperial Chemical Industries Ltd.), U.S. Patent 2,292,129 (August 4, 1942); Chem. Abstr., 37, 656 (1943).

Kiryushin, Y. A., Poluektov, V. A., Dokl. Akad. Nauk SSSR, 180, 1154-6 (1968) (Russian); Chem. Abstr., 69, 66642 (1968).

Kolthoff, I. M., Elving, P. J., Sandell, E. B., "Treatise on Analytical Chemistry," Part II, Vol. 7, p 408, Interscience Publishers, New York, N.Y., 1961.

Manogue, W. H., Disc. Abstr., 18, 984 (1958).

Mayo, F. R., Honda, M., Am. Chem. Soc., Div. Petrol. Chem., Preprints, 13, No. 2, 05-010 (1968).

McKinney, L. L., Uhing, E. H., White, J. L., Picken, J. C., Jr., J. Agr. Food Chem., 3, 413-9 (1955).

000155

Mugdan, M., Wimmer, J. (to Consortium für Elektrochemische Industrie, G.m.b.H.), Ger. Patent 531,579 (December 8, 1929); Chem. Abstr., 26, 1302 (1932).

Mugdan, M., Wimmer, J. (to Consortium für Electrochemische Industrie G.m.b.H.), U.S. Patent 1,976,265 (October 9, 1934); Chem. Abstr., 28, 7263 (1934).

Müller, E., Ehrmann, K., Chem. Ber., 69, 2207-10 (1936) (German).

Murray, A. J., Riley, J. P., Anal. Chim. Acta., 55, 261-70 (1973).

Murray, A. J., Riley, J. P., Nature, 242, 37-8 (1973b).

Remy, H., "Treatise on Inorganic Chemistry," J. S. Anderson, Translator, Vol. I, pp 801-10, Elsevier Publishing Co., New York, N.Y., 1956.

Rushmer, A., Smith, W. W. (to Imperial Chemical Industries Ltd.), U.S. Patent 2,427,624 (September 16, 1947); Chem. Abstr., 42, 199 (1948).

Scott, D. J., Dow Chemical Co., Midland, Mich., private communication, 1961.

Shell Internationale Research Maatschappij N.V., Neth. Patent Appl. 6,606,933 (November 22, 1966); Chem. Abstr., 66, 75698 (1967).

Shepherd, C. B., "Chlorine, Its Manufacture, Properties, and Uses," J. S. Seance, Ed., pp 375-428, Reinhold Publishing Corp., New York, N.Y., 1962.

Sneed, M. C., Maynard, J. L., Brasted, R. C., "Comprehensive Inorganic Chemistry," Vol. 3, pp 131-45, D. Van Nostrand, Co., Inc., New York, N.Y., 1954.

Swarts, F., Bull. Acad. Roy. Sci. Belg., 36, 532-52 (1898) (French).

Ugi, I., Beck, F., Chem. Ber., 94, 1839-50 (1961).

Wilson, K. W., Doyle, G. J., Hansen, D. A., "Photochemical Reactivity of Trichloroethylene," Interim Report for Manufacturing Chemists Association on SRI Project PSC-6687, Stanford Research Institute, South Pasadena, Calif., December 1968.

Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical Reactivity of Organic Solvents," Technical Report to Manufacturing Chemists Association, Stanford Research Institute, South Pasadena, Calif., September 1969.

Yasnitskii, B. G., Dol'berg, E. B., Kovalenko, G. I., Med. Prom. SSSR, 17, 37-8 (1963a)(Russian); Chem. Abstr., 59, 11235 (1963).

Yasnitskii, B. G., Dol'berg, E. B., Kovalenko, G. I., U.S.S.R. Patent 156,548 (August 28, 1963b); Chem. Abstr., 60, 6752 (1964).

Yasnitskii, B. G., Kovalenko, G. I., Dol'berg, E. B., Dokl. Akad. Nauk SSSR, 164, 831-4 (1965)(Russian); Chem. Abstr., 61, 1942 (1966).

Yasnitskii, B. G., Dol'berg, E. B., Kovalenko, G. I., Zh. Org. Khim., 3, 2101-8 (1966)(Russian); J. Org. Chem. USSR, 3, 2060-6 (1966).

Yasnitskii, B. G., Kovalenko, G. I., Dol'berg, E. B., ibid., 3, 470-6 (1967)(Russian); J. Org. Chem. USSR, 3, 451-6 (1967).

Yasnitskii, B. G., Dol'berg, E. B., Kovalenko, G. I., Metody Poluch. Khim. Reaktivov Prom., No. 21, 106-8 (1970)(Russian); Chem. Abstr., 76, 85321 (1972).

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Organic Photochemistry. XVI.¹ Environmental Fate and Effect of Chlorinated Solvents. V.² Total Oxidant Formation from Simulated Atmospheric Photolyses of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Vinyl Chloride

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Abstract

In order to estimate the amount of oxidant (ozone, etc.) generated in the presence of several chlorinated solvents in the atmosphere, laboratory studies were carried out under simulated atmospheric conditions which included ultraviolet radiation ($\lambda > 290$ nm), nitrogen dioxide, and water vapor in air in a small

¹Part XV: (Dilling and Tefertiller, 1974).

²Part IV: (Dilling and Tefertiller, 1974).

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reactor (~10 liters). The oxidant was measured by titration of the iodine liberated on passing the reaction mixture through a neutral buffered potassium iodide solution. Trichloroethylene and vinyl chloride caused the formation of significant amounts of oxidant. Tetrachloroethylene caused only a small amount of oxidant to be formed at short irradiation times and little or no oxidant at longer times. Methylene chloride and 1,1,1-trichloroethane contribute little or nothing to the formation of oxidant.

The fate and effect of chlorinated solvents which may be discharged to the environment (Murray and Riley, 1973a; Murray and Riley, 1973b; Farber, 1973) are important from an ecological standpoint. In preceding papers of this series (Dilling et al., 1974; Dilling and Brodeur, 1974; Dilling and Tefertiller, 1974) the reactivities of, and products from, the four most widely used chlorinated solvents, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), were determined under simulated atmospheric conditions. $\text{CHCl}=\text{CCl}_2$ was moderately reactive, and $\text{CCl}_2=\text{CCl}_2$ was slightly reactive under simulated sea level atmospheric conditions which included ultraviolet radiation of wavelength greater than 290 nm, nitric oxide (NO) or nitrogen dioxide (NO_2), and water vapor in air. CH_2Cl_2 and CH_3CCl_3 were unreactive under these conditions. Vinyl chloride ($\text{CH}_2=\text{CHCl}$), a large volume monomer, was nearly as reactive as $\text{CHCl}=\text{CCl}_2$ (Dilling et al., 1974).

An important criterion of the adverse effect of compounds on the environment is the amount of oxidants, principally ozone (O_3), peroxyacetyl nitrate (MeCO_2NO_2), and NO_2 (Pitts, 1969), which are generated due to the presence of the compound in a photolyzing air mass (Leighton, 1961; Altshuler and Bufalini, 1965; Altshuler and Bufalini, 1971). The objectives of the

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present work were to determine the amounts of total oxidant generated due to the presence of the four chlorinated solvents and $\text{CH}_2=\text{CHCl}$, and also to develop a simple method, which utilized a small (~10 liter) photoreactor, by which total oxidant formation could be conveniently determined.

As far as we are aware, no data have been reported on oxidant formation due to the presence of CH_2Cl_2 or $\text{CH}_2=\text{CHCl}$ other than a preliminary report of our data for CH_2Cl_2 (Farber, 1973). CH_2Cl_2 was found to contribute, in a minor way, to oxidant formation (0.11 ppm O_3 under conditions where $\text{CHCl}=\text{CCl}_2$ produced 0.45 ppm O_3) (Fuller, 1968; Farber, 1973).

In general, most workers have found that $\text{CHCl}=\text{CCl}_2$, under simulated atmospheric conditions, had a medium capacity for producing oxidant as compared with other common solvents or atmospheric pollutants (Horton and Bolse, 1958; Brunelle, et al., 1966; Hamming, 1967; Fuller, 1968; Wilson, 1969; Wilson, et al., 1969b; Altshuller and Bufalini, 1971; Farber, 1973). The agreement of results between different workers was not very good. Some claimed that $\text{CHCl}=\text{CCl}_2$ produced oxidant more slowly than did ethylene ($\text{CH}_2=\text{CH}_2$) (Wilson, 1969; Wilson et al., 1969a) while others claimed a rate comparable to that of $\text{CH}_2=\text{CH}_2$ but less than that of propylene ($\text{MeCH}=\text{CH}_2$) (Altshuller and Bufalini, 1971). Still another group claimed a stable ozone concentration

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of ozone (Schuck and Doyle, 1959). The maximum concentration of oxidant formed with $\text{CHCl}=\text{CCl}_2$ was higher than that with $\text{CH}_2=\text{CH}_2$ (Wilson, 1969; Altshuller and Bufalini, 1971), and about the same as that with $\text{MeCH}=\text{CH}_2$ (Altshuller and Bufalini, 1971). The oxidant dosage with $\text{CHCl}=\text{CCl}_2$ was about the same as with $\text{CH}_2=\text{CH}_2$, but less than with $\text{MeCH}=\text{CH}_2$ (Altshuller and Bufalini, 1971). Another report indicated that the amount of O_3 formed in the presence of $\text{CHCl}=\text{CCl}_2$ was at least as great as that produced by automobile exhaust (Hamming, 1967). The amount of oxidant formed decreased sharply as the $\text{CHCl}=\text{CCl}_2:\text{NO}$ ratio fell (Wilson, 1969; Wilson et al., 1969b). Addition of $\text{CHCl}=\text{CCl}_2$ to $\text{MeCH}=\text{CH}_2$ caused a slight increase in the amount of oxidant formed compared to that formed with $\text{MeCH}=\text{CH}_2$ alone (Wilson, 1969; Wilson et al., 1969b). Injection of a high concentration of $\text{CHCl}=\text{CCl}_2$ into a reactive photolyzing air mass showed no increase in oxidant level over that without added $\text{CHCl}=\text{CCl}_2$ (Wilson, 1969; Wilson et al., 1969b).

According to most workers, oxidant or O_3 was either not generated (Brunelle et al., 1966; Hamming, 1967) or only a very small amount was generated (Schuck and Doyle, 1959; Fuller, 1968; Farber, 1973) in the presence of $\text{CCl}_2=\text{CCl}_2$ under simulated atmospheric conditions. One report (Horton and Bolse, 1958) indicated that more oxidant was produced in the presence of $\text{CCl}_2=\text{CCl}_2$ than in the presence of $\text{CH}_2=\text{CH}_2$, $\text{MeCH}=\text{CH}_2$, or toluene (PhMe).

EXPERIMENTAL

Reactor. The photoreactor (9.58 liters capacity), described previously for short term (<24 hr) sea level simulated photolyses (Dilling et al., 1974), was used after slight modification. An exit port was added at the end opposite the sample port so that the contents of the reactor could be swept out with a gas stream. The temperature of the reactor was maintained at 24-25° by means of a Water constant temperature bath.

Materials. High purity dry air and prepurified nitrogen from Matheson were used as received.

Cylinder NO_2 from Matheson was purified by condensing gas from the cylinder in a wet ice cooled trap, freezing the liquid NO_2 (N_2O_4) in dry ice and degassing to 0.01 mm Hg. The sample was thawed by warming to 0°, refrozen and again degassed. This procedure was repeated two more times to insure that all air and other noncondensable impurities had been removed. The purified NO_2 was transferred to a 1 liter sample bulb equipped with a stopcock on one end and a piece of gage-glass tubing on the other end to which was attached a rubber septum secured with Swagelok fittings. This flask was evacuated, loaded with a known pressure of purified NO_2 and brought to atmospheric pressure with air. Samples were withdrawn by syringe from this

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sample bulb and injected into the photoreactor. The NO_2 was not purified for the reactions with PhMe , CH_2Cl_2 , and $\text{CHCl}=\text{CCl}_2$. This difference may account for the apparent oxidant abscissa displacements in Figures 3 and 4 as compared with Figures 2, 5 and 6.

CH_2Cl_2 , "Distilled in Glass", from Burdick and Jackson Laboratories was used as received. Uninhibited CH_2Cl_2 and $\text{CHCl}=\text{CCl}_2$ were redistilled. $\text{CCl}_2=\text{CCl}_2$ (Dow Per[®]) was washed with aqueous HCl and distilled, bp 121° , prior to use. Cylinder $\text{CH}_2=\text{CHCl}$ from Matheson was placed in a black Teflon gas bag from which the $\text{CH}_2=\text{CHCl}$ was withdrawn by a syringe for injection into the photoreactor. Mass spectroscopic analysis of the $\text{CH}_2=\text{CHCl}$ showed a purity of 99.2%. PhMe was redistilled. All of the organic materials were subjected to careful analysis by gas chromatography (gc), mass spectrometry and ultraviolet analyses. No impurities were detected except as noted.

Neutral buffered potassium iodide (KI) solution (Salzman, 1965) was prepared by dissolving successively 13.61 g of potassium dihydrogen phosphate, 14.20 g of anhydrous disodium hydrogen phosphate, and 10.00 g of KI in 500 ml of water. This mixture was diluted to a volume of 1.00 liter to give a 1% KI solution that was 0.1 M in each of the phosphate salts. This solution was transferred to a brown bottle, stoppered, and stored in the dark for 24 hr before use.

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Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, 10.0 ml of 0.1000 N solution) from Curtin Scientific Co. was standardized against potassium iodate in the conventional manner and diluted to 1.00 liter with distilled water to give a solution which was 0.00100 N.

Analyses. The disappearance of the organic compounds was monitored by periodically withdrawing samples by syringe from the reactor for gas analyses. CH_2Cl_2 and $\text{CCl}_2=\text{CCl}_2$ were determined with a thermal conductivity gas equipped with a 10 ft x 1/4 inch column packed with 20% Apieson L using a helium flow rate of 40 cc/minute at 75° and 150° respectively. CH_2CCl_2 , $\text{CHCl}=\text{CCl}_2$ and PhMe were determined with a flame ionization gas equipped with a 3 ft x 1/4 inch column packed with 20% Porapak Q at 175°. $\text{CH}_2=\text{CHCl}$ was determined with an electron capture gas equipped with a 10 ft x 1/8 inch column packed with 20% N,N-bis-2-cyanoethyl-feramide on 80-100 mesh Chromosorb W at 80°.

The total oxidant was determined by flushing the entire reactor contents through a gas-absorbing tower (Smith, et al., 1964) which contained 25 ml of the 1% KI solution. The reactor was flushed with nitrogen at a rate of 1 liter/minute for 30-45 minutes. This time period should remove 95.7-99.0% of the reactor contents according to the equation $C = C_0 e^{-(f/v)t}$, where C is the concentration at time t, C_0 is the initial concentration, f is the flow rate, and v is the reactor volume.

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Attempts to flush the reactor contents with smaller quantities of KI and (or) higher flow rates gave consistently low oxidant values, as determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$. The validity of the method was tested by generating small quantities of O_2 with an electric discharge in a flask, and removing two aliquots by syringe. One was injected into the photoreactor and flushed through a KI solution as described; the other was slowly bubbled directly through an equivalent volume of KI solution. Titration of each solution (several runs) indicated that over 95% of the O_2 in the reactor was accounted for. After the reactor contents had been flushed into the KI solution, the gas tower was rinsed with 15-20 ml of water, 0.75 ml of soluble starch solution was added, and the resulting solution was titrated with 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$. The concentration of oxidant was calculated from the equation, ppm oxidant (as O_2) = 1.276 x ml of 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$. It was necessary to flush the entire reactor in order to have sufficient quantities of O_2 for analysis.

Example of a Typical Photolysis. To the evacuated chamber was added 1.8 μl of CH_2Cl_2 , 1.0 cc of a NO_2 (120 mm Hg pressure) -air (640 mm) mixture, and 95 μl of water to give concentrations of 50 ppm (molar or volume basis) CH_2Cl_2 and 12 ppm NO_2 at 43% relative humidity, after the reactor was filled to atmospheric pressure with air. The contents of the reactor were irradiated

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for 15 hr. The results of CH_2Cl_2 and oxidant analyses are shown in Figure 3. The reaction was repeated several times for different lengths of time to obtain the other oxidant values shown in Figure 3.

Results and Discussion

Many workers have reported that O_3 did not appear in simulated atmospheric photolyses until the NO had been converted to NO_2 (Leighton, 1961; Altshuler and Bufalini, 1965; Pitts, 1969). It is also clear that nearly the same maximum O_3 concentration is attained irregardless of whether NO or NO_2 is part of the starting mixture. In order to avoid this "induction period" and to thereby shorten the analysis time, NO_2 was used in all of our experiments. The concentration of the organic compound used was usually 50 ppm; this concentration was necessary in order to facilitate monitoring of the chlorinated organic compound in some cases. Some experiments were also carried out with ~12 ppm of the chlorinated compounds. A ratio of 4:1 for organic compound: NO_2 was used for all experiments. The range for most of the earlier work was from 2:1 to 8:1.

The precision with which the oxidant could be measured in these experiments suffered from several factors. The

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major one was the fact that each datum point came from a separate experiment. Other factors were the difficulty of introducing NO_2 reproducibly and the large volume of air which was flushed through the absorbing reagent. An estimate of the precision in the oxidant measurement is about $\pm 10-15\%$. While this precision is not as good as one might wish, the data obtained still give adequate representation of oxidant formation, particularly when one is concerned with relative values of various compounds.

In order to validate the method for total oxidant determination, FhMe was subjected to the procedure. This compound had been studied earlier (Levy and Miller, 1970) and was found to lead to moderate quantities of O_3 at a relatively rapid rate. The photolysis of 16 ppm FhMe was carried out in the presence of 4 ppm NO_2 . Figure 1 shows the results of this irradiation. The maximum oxidant concentration (0.8 ppm) was reached after 4 hours irradiation. Levy and Miller (1970) reported a maximum O_3 concentration of 0.44 ppm after 3.3 hours when the initial concentrations were 4 ppm FhMe and 2 ppm NO . In a previous paper of this series (Dilling et al., 1974) a half-life of 6.8 hours was reported for FhMe (10 ppm) when irradiated in the presence of NO (5 ppm); the data in Figure 1 indicate a half life of ~3.5 hours. Bearing in mind

the differences in starting concentrations, light intensities, and differences in reaction times for NO versus NO₂, the agreement in the data seems satisfactory.

Data for the photolysis of CH₂Cl₂ are shown in Figure 2. There was no disappearance of CH₂Cl₂ within experimental error, in agreement with our previous report (Dilling et al., 1974). The oxidant levels were essentially identical with a blank run in which the CH₂Cl₂ was omitted. NO₂ at an initial concentration of 13 ppm in the blank, gave an oxidant level of 3.5 ppm at 0 (Salzman, 1965); this level fell off rapidly to ~0.8 ppm in ~3 hours. Under the conditions of these experiments this level (0.8 ppm) remained relatively constant for at least 15 hours of continued irradiation. Photolysis of an NO₂ blank which started at 2.7 ppm resulted in a total oxidant decrease from 0.7 ppm to 0.3 ppm in 4 hours.

The value for total oxidant obviously includes both O₃ and NO₂ as well as any other oxidizing species which might be produced by photolysis during the course of the experiment. In the early stages of irradiation the oxidant is almost entirely NO₂. However in the later stages of the reaction, where O₃ may be the predominant oxidant, the O₃ concentration cannot be obtained by subtracting the NO₂ (blank) curve from the total oxidant curve because the addition of an organic material can

Practically alter the ($\text{NO}_2 + \text{O}_3 \xrightleftharpoons{h\nu} \text{NO} + \text{O}_3$) equilibrium (Altshuller and Bufalini, 1965).

The photolysis of CH_2CCl_2 was studied at two concentrations, 50 ppm and 10 ppm. The results are illustrated in Figure 3. There was relatively little disappearance of the CH_2CCl_2 . The data at 10 ppm indicate that the oxidant level decreased rapidly until it approached zero. The lowest oxidant level that could be measured was about 0.05 ppm. The curve for the 50 ppm reaction again rapidly decreased, but asymptotically approached ~0.1 ppm, which is very low, considering the high initial concentration of CH_2CCl_2 .

$\text{CHCl}_2\text{-CCl}_2$ produced much more oxidant (Figure 4) than did CH_2Cl_2 and CH_2CCl_2 in the early stages of the photolysis. The formation of a significant amount of oxidant from $\text{CHCl}_2\text{-CCl}_2$ is in agreement with most of the references cited above. The rapidity with which oxidant forms is perhaps surprising. That it is real, however, is borne out by the fact that several of the points in Figure 4 were obtained in duplicate. Again, however, some of the oxidant may be due to a slower decrease in the NO_2 concentration.

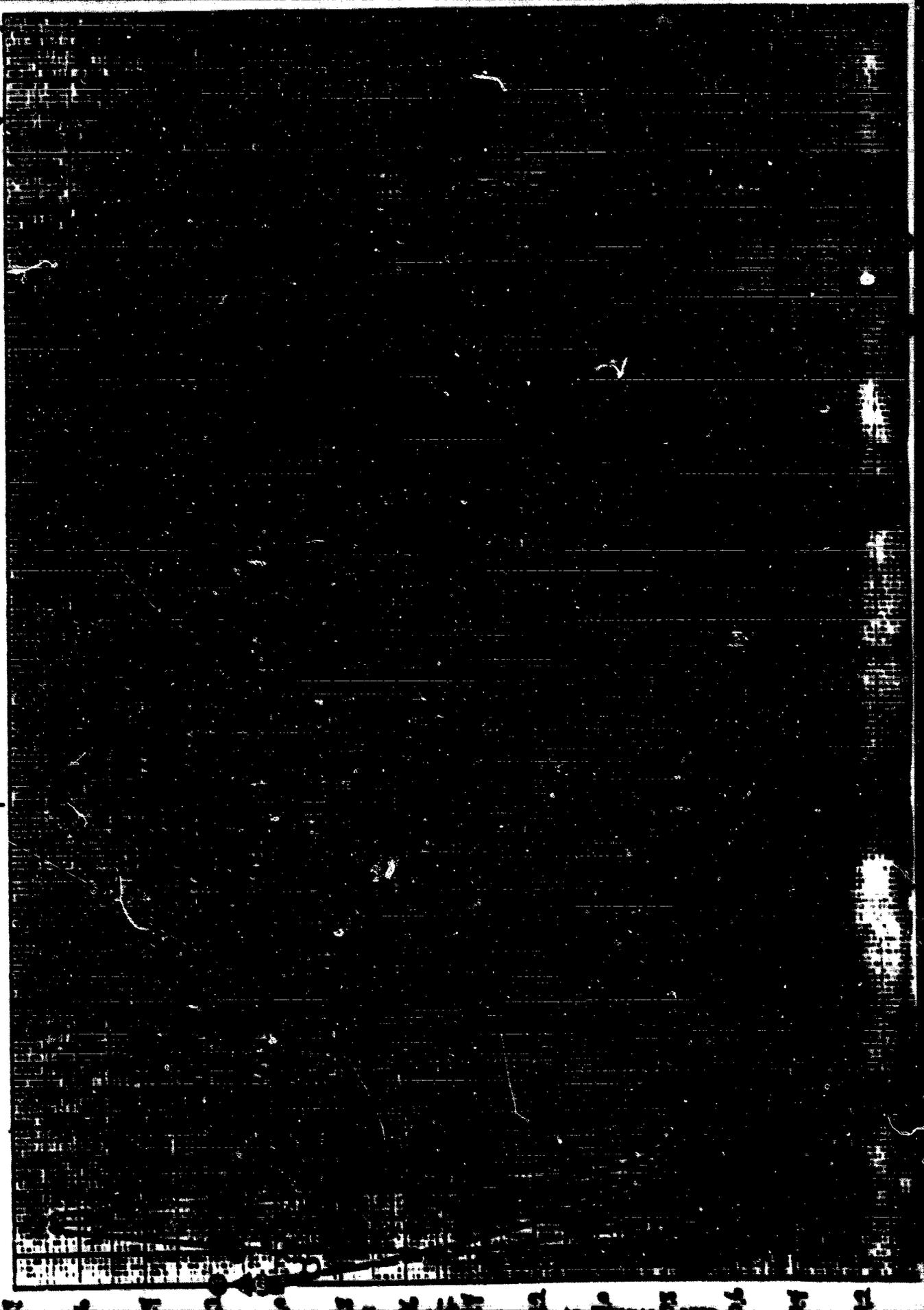
$\text{CCl}_2\text{-CCl}_2$ was found to be rather reactive from the standpoint of disappearance of organic; the concentration dropped from 50 ppm to <3 ppm in 4 hours. In this respect it is quite

Concentration of Ozone (ppm)

Concentration of Ozone (ppm as O₃)

DATE: 10/10/2000
TIME: 10:00 AM
STATION: 10000000

THE UNIVERSITY OF MICHIGAN LIBRARY



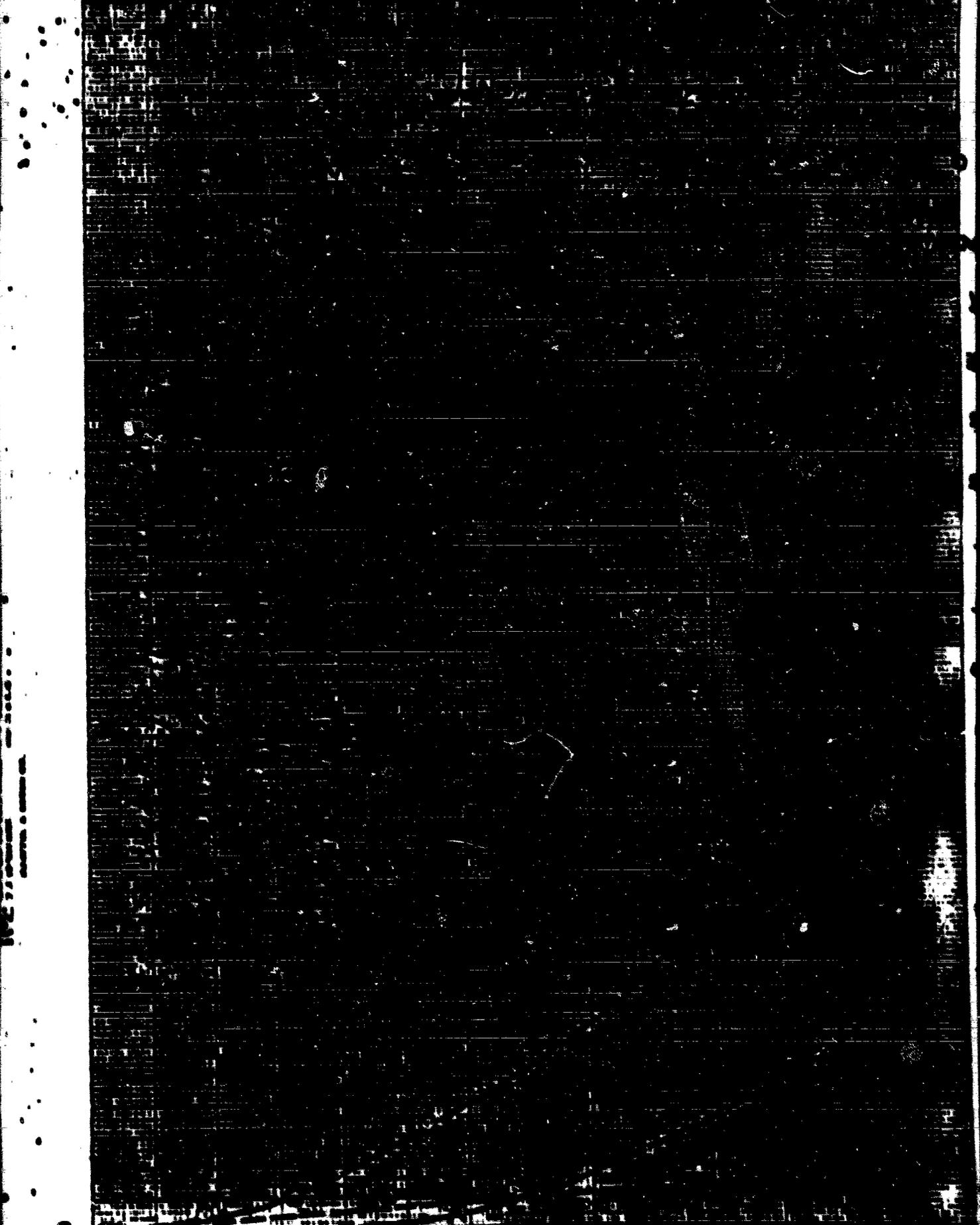
7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30

similar to $\text{CHCl}-\text{CCl}_2$. However, $\text{CCl}_2-\text{CCl}_2$ is rather dramatically different from $\text{CHCl}-\text{CCl}_2$ with respect to oxidant formation. A comparison of the curves in Figure 5 shows that photolysis of $\text{CCl}_2-\text{CCl}_2$ led to slight oxidant formation initially but that the final oxidant level reached after 15 hours of irradiation was lower than that for the blank. This same behavior was also observed in experiments at lower concentrations (13 ppm $\text{CCl}_2-\text{CCl}_2$, 2.8 ppm NO_2). The total oxidant in the presence of $\text{CCl}_2-\text{CCl}_2$ decreased from 0.7 ppm to 0.2 ppm in 4.4 hours; the final oxidant concentration in the blank was 0.5 ppm.

Oxidant formation in the presence of CH_2-CHCl (Figure 6) was comparable to that in the presence of $\text{CHCl}-\text{CCl}_2$. The rate of CH_2-CHCl disappearance was similar to that of $\text{CCl}_2-\text{CCl}_2$ in the initial stages, but became slower as time increased.

In summary, the relative oxidant forming potentials of the five chlorinated compounds studied are as follows:

$\text{CHCl}-\text{CCl}_2 \approx \text{CH}_2-\text{CHCl} > \text{CCl}_2-\text{CCl}_2 > \text{CH}_2\text{Cl}_2 \approx \text{CH}_3\text{CCl}_2$.



100-100000-100000
100-100000-100000

21 22 23 24 25 26 27 28

Literature Cited

- Altshuller, A. P., Bufalini, J. J., Photochem. Photobiol., 4,
97-146 (1965).
- Altshuller, A. P., Bufalini, J. J., Environ. Sci. Technol., 5,
39-64 (1971).
- Brunelle, M. F., Dickinson, J. E., Hamming, W. J., "Effectiveness
of Organic Solvents in Photochemical Smog Formation", Final
Report for Air Pollution Control District, County of Los
Angeles, Calif., July 1966.
- Dilling, W. L., Bredweg, C. J., Environ. Sci. Technol., 8,
0000-00 (1974).
- Dilling, W. L., Tefertiller, N. B., ibid., 8, 0000-00 (1974).
- Dilling, W. L., Tefertiller, N. B., Bredweg, C. J., ibid.,
8, 0000-00 (1974).
- Farber, H. A., "Chlorinated Solvents and the Environment",
paper presented at AAPCC Symposium, Atlanta, Ga., January
10-11, 1973; Textile Solvent Technology - Update '73, pp 6-12.
- Fuller, L. J., "Hearing on Petition to Exempt Trichloroethylene
from Rule 66 of the Los Angeles County Air Pollution Control
District", presented before the Los Angeles County Air
Pollution Control Board, Calif., April 2, 1968.

66178

- Hamming, W. J., "Photochemical Reactivity of Solvents",
paper presented at Aeronautic and Space Engineering and
Manufacturing Meeting, Society of Automotive Engineers,
Los Angeles, Calif., October 2-6, 1967.
- Horton, E. E., Jr., Bolse, C. C., "Eye Irritation from Solar
Radiation of Organic Compounds and Nitrogen Dioxide",
Report No. 23, Air Pollution Foundation, San Marino,
Calif., April 1958.
- Leighton, P. A., "Photochemistry of Air Pollution", pp 2-3,
254-74, Academic Press, New York, N.Y., 1961.
- Levy, A., Miller, S. E., "A Final Technical Report on the
Role of Solvents in Photochemical-Smog Formation", National
Paint, Varnish and Lacquer Association, Inc., Washington,
D.C., 1970.
- Murray, A. J., Riley, J. P., Anal. Chim. Acta, 65, 261-70
(1973a).
- Murray, A. J., Riley, J. P., Nature, 242, 37-8 (1973b).
- Pitts, J. N., Jr., "Advances in Environmental Sciences", Vol. 1,
J. N. Pitts, Jr., and R. L. Metcalf, Eds., pp 289-337, Wiley-
Interscience, New York, N.Y., 1969.
- Saltzman, B. E., in "Selected Methods for Measurement of Air
Pollutants", Public Health Service Pamphlet No. 999-AP-11,
pp D-1 - D-5, U. S. Department of Health, Education and
Welfare, Cincinnati, Ohio, 1965.

000179

Schuck, E. A., Doyle, G. J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide", Report No. 29, Air Pollution Foundation, San Marino, Calif., October 1959.

Smith, G. N., Ludwig, P. D., Wright, K. C., Bauriedel, W. R., J. Agr. Food Chem., 12, 172-5 (1964).

Wilson, K. W., "Photoactivity of Trichloroethylene", Summary Report for Manufacturing Chemists Association on SRI Project PSC-6687, Stanford Research Institute, South Pasadena, Calif., September 1969.

Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical Reactivity of Organic Solvents", Technical Report to Manufacturing Chemists Association, Stanford Research Institute, South Pasadena, Calif., September 1969b.

Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., Am. Chem. Soc., Div. of Org. Coat. and Plast. Chem. Preprints, 29, No. 2, 445-9 (1969a).