Air Products and Chemicals INC.

576

Date 29 January 1975

INTEROFFICE
MEMORANDUM

Subject Photochemical Oxidation of Vinyl Chloride

To Distribution (Location, Organization, or Department)

From J. T. Barr Valley Forge (Location, Organization, or Department)

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In my 9 January report of a visit to EPA in Research Triangle I stated that I had been referred to a Dr. Altschuler for information on Agency studies on vinyl chloride in the atmosphere. I have not been able to reach Dr. Altschuler, but did contact a Dr. Joseph Bufalini of his group.

Dr. Bufalini was not able to cite a reference to the reported 6-hour half-life of vinyl chloride in air given in the Briefing Report dated October 15, 1973.

He did know of the work sponsored by Diamond-Shamrock at Battelle and reported earlier through MCA. This was the smog chamber comparison of VCM with Toluene. (Dr. H. Everson of Diamond-Shamrock was Dr. Altschuler's professor at school.) He did not mention the Dow work that also has been reported.

Some work was done by EPA three years ago in a 335 ft^3 chamber, and more recently in a 9.1 meter glass tube, comparing VCM to ethylene. This work has been submitted to Environmental Science and Technology, and a draft is attached.

He knew of no other studies in progress and felt that none were needed, since it has been shown that VCM is not persistent, and the oxidation products have been identified.

J. T. Barr

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(320)

Environmental Science and Technol

Draft
Do not cite 76

Abstract

Oxidation of Ethylene and Halogenated Hydrocarbons at Low Concentrations

this has been corrected before it was submitted for publication

by

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The photooxidation of several halocarbons in the presence of oxides of nitrogen was investigated. These include, vinyl chloride, 1, 1-dichloroethylene, 1, 2-dichloroethylene, trichloroethylene, tetrachloroethylene, chloroform, and chloroform in the presence of ethylene, and ethylene. The latter compound i.e. ethylene was photooxidized to enable comparisons of the reactivity parameters.

Vinyl chloride in the presence of NO_x and ultra-violet light leads to the formation of formic acid, hydrochloric acid, carbon monoxide, formaldehyde, ozone, and a small quantity of formyl chloride. 1, 1-dichloroethylene reaction lead to the formation of products similar to those found with vinyl chloride. However, phosgene and nitric acid were also observed. 1,2-Dichloroethylene also leads to similar products as those of vinyl chloride with the exception of formaldehyde formation. Larger quantities of HCl are observed for the reaction. This product probably arises from formyl chloride decomposition since this compound quickly thermally decomposes to HCl and CO. The photooxidation of trichloroethylene resulted in the formation of phosgene and formyl chloride as well as the other products (HCl, CO, HNO_3, and HCOOH). The tetrachloroethylene was found to be the least reactive of all the chlorinated ethylenes. The products observed were HCOOH, HCl, CO, $COCl_2$, and O_3. Chloroform was irradiated with ethylene largely because this compound was expected to be very unreactive when photooxidized alone. The products arising from the chloroform-ethylene-NO_x system are CO, formaldehyde, O_3, phosgene, and formic acid.

From these studies, it was found that vinyl chloride is approximately 60 percent as reactive as ethylene in terms of cpd reacted. In terms of NO oxidation, the vinyl chloride is 70 percent as reactive. The ozone produced from a vinyl chloride-NO_x system is approximately one-half that produced with the ethylene-NO_x systems. In terms of O_3 reaction, the rate constant for the vinyl chloride-O_3 reaction is 1/10 that of the ethylene-O_3 reaction. The rate constant for the O_3 - vinyl chloride reaction is 0.3×10^{-3} ppm^{-1} min^{-1}.

OXIDATION OF ETHYLENE AND HALOGENATED HYDROCARBONS

Bruce W. Gay, Jr., Richard C. Noonan, Joseph J. Bufalini

INTRODUCTION

Vinyl chloride has recently received notoriety by being linked to angiosarcoma of the liver, a rare type of cancer in the human liver. Exposures to vinyl chloride are greatest in occupational situations and in the past when vinyl chloride was used as propellent in aerosol products in many home use products. (The use as propellent has since been banned.) Atmospheric emissions are primarily from vinyl chloride and polyvinyl chloride production plants. Vinyl chloride losses have been estimated at approximately 6 percent based primarily on material balance studies of these types of plants. It is estimated that emissions of vinyl chloride currently exceeds 90 million Kg annually. Of these emissions 90 percent are estimated as emanations from polyvinyl chloride plants. Monomer plants are responsible for less than 10 percent. Because of concern with pollutants in the ambient atmosphere and more so because of the health implications of vinyl chloride, the Environmental Protection Agency has initiated a program to make extensive atmospheric vinyl chloride measurements in the vicinity of vinyl chloride - polyvinyl chloride production sources to determine ambient exposure concentrations which might effect the general populous.

The measurements to date suggest that in the majority of cases, samples obtained some distance downwind from plants are below 1 ppm (v/v) vinyl chloride. Although concentrations of vinyl chloride in the atmosphere may be low it is just one of many halogenated compounds emitted into the atmosphere. There is in general a paucity of information on possible environmental effects arising from the degradation of vinyl chloride as well as other halocarbons in general in the atmosphere. The production of halogenated hydrocarbons in the United States alone

totaled more than 16 billion pounds in 1968 (Tariff 1969). Information concerning the degradation products of halogenated compounds is critically needed. The work presented here is concerned primarily with the oxidation of the chlorinated ethylene compounds.

EXPERIMENTAL

The ultraviolet irradiations were carried out in two different chambers. The first chamber was a 335 ft^3 aluminum chamber equipped with polyvinyl fluoride film windows (Korth, et.al., 1964). This chamber was equipped with fluorescent blacklights and sunlight located externally. The kd value for the chamber was 0.4 $min.^{-1}$ (Tuesday 1961). The chamber was preheated with infrared lamps before the start of the irradiations and operated at 32 $\pm$ 1° C at a relative humidity of approximately 33 percent. The gaseous reactants were charged directly into the chamber by calibrated syringes.

Nitrogen dioxide was analyzed colorimetrically (Saltzman, 1954). Nitric oxide was analyzed as nitrogen dioxide after oxidation with dichromate paper (Wilson and Kopczynski, 1968). Oxidant was determined manually by the colorimetric 1 percent neutral potassium iodide method (Byers and Saltzman, 1958). The ethylene and vinyl chloride were analyzed by gas chromatography.

The second chamber was a 9.1 meter long by 0.31 meter inside diameter borosicilate glass tube made up of 6, 1.52 meter sections. Around the tube are fluorescent blacklights with energy maxima at 3660 Å. This photochemical reactor also serves as a long path I.R. cell. An eight mirror optical system is used in order to achieve multiple reflections. The cell is capable of 72 n meters where n is any integer from 1 to 25. The optical path length used for these experiments were 500 meters. The spectrometer is a Digilab FTS® rapid scan Michelson interferometer which is capable of 0.125 cm^{-1} resolution (Hanst et.al., 1973). Liquid nitrogen cooled detectors are used in this system.

The reactants for the experiments are introduced into the long path cell through a manifold from a glass gas handling system that

had two known volume bulbs. By using 0-50 Torr and 0-800 Torr pressure gauges and the known volume bulbs, the calculated quantitities of gases could be introduced. The reactants were used as obtained from the manufacturers without further laboratory pre-purification. It is doubtful that any impurities were present since no unexpected or unidentified bands were present in the infrared with detection limits of less than one-tenth part per million.

RESULTS

The photooxidation of the chloroethylenes is summarized in Table 1. Exact comparisons on the reactivities is not possible since the same hydrocarbon to NO_x ratio was not maintained with each compound. However, since the ratio was approximately constant, the reactivities are at least qualitatively correct. The various runs made on each system will be discussed separately.

Chamber of 335 ft^3 Volume

Ethylene

The photooxidation of ethylene in the presence of NO_x is shown in Figure 1. This hydrocarbon being a major constituent of auto exhaust has been studied extensively. It is shown here primarily for comparative purposes. After 300 minutes irradiation, approximately 67 percent of the ethylene had reacted. The NO_2 maximum occurs at approximately 90 minutes and the O_3 reaches a maximum of 0.82 ppm at 300 minutes. The formaldehyde maximum of 1.06 ppm also occurred at 300 minutes.

Vinyl Chloride

The reaction of vinyl chloride in the presence of NO_x is shown in Figure 2. The conditions for this photooxidation are the same as those for the ethylene. After five hours irradiation, approximately 39 percent of the vinyl chloride had reacted. The NO_2 maximum occurs at 130 minutes. The ozone observed after 330 minutes was 0.44 ppm. The formaldehyde concentration reached a maximum of 0.32 ppm at 140 minutes and leveled off

at this value for the remainder of the run. This suggests that the production rate of formaldehyde is approximately equal to the rate of destruction after 140 minutes of irradiation.

In terms of NO oxidation, the vinyl chloride is approximately 70 percent as reactive as ethylene. In terms of compound reacted, the vinyl chloride is about 60 percent as reactive as ethylene. The ozone produced at the close of the run i.e., 330 minutes, appears to be one-half as great for the vinyl chloride case compared to the ethylene case. However, for the vinyl chloride photooxidation the slope of ozone versus time curve is still positive even at the close of the run. This suggests that with continued irradiation the ozone concentration would build-up to a higher value. At the close of the irradiation, approximately 20 percent of the reacted vinyl chloride appeared as formaldehyde, where as 33 percent of the reacted ethylene appeared as formaldehyde in the ethylene photooxidation. The higher formaldehyde yield from ethylene is to be expected since both ends of the molecule can give rise to formaldehyde.

Long Path Infrared Chamber

Ethylene

The photooxidation of ethylene and NO_2 in the 700 liter LPIR cell is shown in Figure 3. After 240 minutes irradiation approximately 82 percent of the ethylene had reacted. The maximum ozone concentration of 1.23 ppm was formed at about 200 minutes. After 180 minutes irradiation, the formaldehyde concentration became constant with increasing irradiation time.

Vinyl chloride

The data for the irradiation of vinyl chloride in the presence of NO_2 is shown in Figure 4. At 160 min. irradiation time, approximately 40 percent of the vinyl chloride had been reacted compared to 25 percent reacted for the 335 ft^3 chamber. The reaction is more rapid in the LPIR chamber for two reasons: (1) The light intensity used was

greater (kd approximately 0.6 min.$^{-1}$ versus kd = 0.4 min^{-1} for the 335 ft. chamber) and (2) The starting NO_x was exclusively NO_2 which enabled O_3 to build up more quickly. The LPIR chamber system optics for in-situ measurements gave direct product analysis. The products observed were, formic acid, hydrochloric acid, carbon monoxide, formaldehyde, and ozone. Trace amounts of formyl chloride and nitric acid were also detected but were not quantified. The formyl chloride is thermally unstable and decomposes to HCl and CO. A small fraction of a ppm of CO_2 is probably produced but this goes undetected since part of the optical system is exposed to room air which is laden with approximately 350 ppm of CO_2. Weakly absorbing unidentified peaks were observed at 790 cm^{-1} and 1165 cm^{-1}. In an attempt to identify these bands, 3-chloropropene-NO_x was photooxidized to produce the chlorinated PAN. The products from this photooxidation had peaks at 790 and 1165 cm^{-1}. This suggests that a chlorinated peroxyacetyl type compound is produced. The compound produced from these systems had the larger absorption at 790 cm^{-1} than at 1165 cm^{-1} compared to the case of PAN, where the absorption at 1162 cm^{-1} is larger than at 790 cm^{-1}. At the conclusion of the irradiation i.e. 160 minutes, 76 percent of the original carbon could be accounted for as products and 87 percent of the Cl could be accounted for.

1, 1-Dichloroethylene

The 1, 1-dichloroethylene photooxidizes much more quickly than vinyl chloride. After 140 minutes irradiation (Figure 5), approximately 85 percent of the compound has reacted. The products observed were those found for vinyl chloride plus phosgene and a large unidentified peak at 720 cm^{-1}. This latter peak could be chloroacetyl chloride - a product from the ozonolysis of 1, 1-dichloroethylene (Hull et. al., 1972). However, this compound should be unstable in the presence of water vapor.

1, 2 - Dichloroethylene

The photooxidation of 1, 2-dichloroethylene is shown in Figure 6.

The reactivity of this halocarbon is also greater than vinyl chloride but less than 1, 1-dichloroethylene. The products from the photooxidation of this compound are similar to those observed with vinyl chloride with the exception that no formaldehyde is observed. Hydrochloric acid appeared to be the largest product accounting for 45 percent of the chloride consumed.

Trichloroethylene

Trichloroethylene was photooxidized a number of years ago by Kopczynski (1968). This investigator found that this compound reacted faster than ethylene but slower than propylene. This compound was reinvestigated in order to establish the formation of phosgene and formyl chloride as was suggested in Kopczynski's work (Altshuller and Bufalini, 1971). In Figure 7 is shown the photodissociation of trichloroethylene with phosgene as product. Formyl chloride was also observed but its concentration could not be quantified.

Tetrachloroethylene

The photooxidation of tetrachloroethylene completes the study of the reactions of the substituted ethylenes. As can be seen from Figure 8, the reactivity of this compound is quite low. It is the least reactive of the chlorosubstituted ethylenes. Only 0.37 ppm or 7.5 percent of the compound reacted over a period of 3 hours. Formic acid, HCl, CO, $COCl_2$, and a little ozone were produced over the three-hour irradiation. The presence of a small quantity of ozone suggests that nitric oxide inhibition is occuring since the nitrogen dioxide concentration is quite high after 3 hours irradiation.

Vinyl Chloride – Ozone Reaction

Our photooxidation of vinyl chloride in the presence of NO_x suggest that this compound is moderately reactive. Its reactivity appears to be approximately 60 percent that of ethylene. Since it is moderately reactive, the O_3 – vinyl chloride reaction should also be moderately reactive. The results of this investigation are shown in Figure 9. The primary products

of the ozone-vinyl chloride reaction are; CO, CH_2O, HCOOH, and a small quantity of HCl. The rate constant for the reaction assuming a second order mechanism is 0.34×10^{-3} ppm^{-1} min^{-1}. This value is approximately 1/10 that for the ethylene-ozone reaction (3×10^{-1} ppm^{-1} min^{-1}) recommended by Garvin and Hampton (1974). This ratio i.e. k_{vc}/k_e is much greater than that found by Williamson and Cvetanovic (1968) in CCl_4 solution. The stoichiometry of the reaction shown in Figure 9 suggest that more ozone than vinyl chloride is consumed. However, the ozone curve has not been corrected for thermal and heterogenous degradation of ozone. The ozone degraded in the LPIR chamber at a rate of 4.7 percent per hour. If this same correction is used for the ozonolysis run, the amount of O_3 consumed in 3 hours is only approximately 0.5 ppm. Thus, more vinyl chloride than ozone is consumed during the reaction - an observation compatible with other olefin-ozone reactions (Hull et.al. 1972, Bufalini, and Altsbuller, 1965, Wei and Cvetanovic 1963).

Chloroform

The irradiation of 9.85 ppm of chloroform with 1.08 ppm of NO_2 resulted in almost no reaction of chloroform. A 6 percent reaction in 230 min. was observed but there was considerable uncertainty in this value. All other reactivity parameters were very low. With 230 minutes irradiation, .05 ppm of $COCl_2$, 0.2 ppm of HCOOH and 0.08 ppm of CH_2O was produced. No ozone was produced during the irradiation. The slight amount of HCOOH and CH_2O are probably a result of wall contamination.

Chloroform-Ethylene-NO_x-Systems

Since chloroform is unreactive when irradiated alone in the presence of NO_x, it was investigated in the presence of ethylene. In Figure 10 are shown these data. In general, even in the presence of a moderately reactive hydrocarbon, the reactivity of chloroform is quite low. Over a period of 3 hours irradiation, only 17 percent of the chloroform reacted. In contrast, over 54 percent of the ethylene had reacted. Most of the

reaction product produced from chloroform is phosgene with only a trace of formyl chloride and HCl. No CCl_4 was observed in this or the tri and tetra chlorinated ethylene systems. The amount of ozone and CO produced from this system is not significantly different from that produced from the irradiation of ethylene alone under similar conditions. Thus, with ethylene at 1.8 ppm and NO_2 at .8 ppm, 1.24 ppm of O_3 was produced at 3 1/2 hours. The CO level was 1.56 ppm at 4 hours. In the chloroform-ethylene system with 2.21 ppm of ethylene and 1.28 ppm of NO_2, the O_3 produced was 1.24 ppm at 3 1/2 hours and CO is 1.54 ppm.

DISCUSSION

The products arising from the oxidation of chlorinated ethylenes are not unexpected when compared to products arising from ethylene oxidation. The initial attack on the double bond is a result from a combination of reactions. These include; (1) O-atom reaction arising from the NO_2 photolysis [$NO_2 + h\nu \rightarrow NO + O\ (^3P)$], (2) O_3 reaction from $O + O_2\ (M)$, (3) OH reaction from HNO_2 photolysis or from an organic free radical decomposition and (4) HO_2 and RO_2 reactions.

Products observed can arise from fragmentation of the chloro-ethylene molecule after attack from one of the above species. If ozone is taken for example, the following set of reactions would occur with vinyl chloride.

(1) $O_3 + CH_2{=}CHCl \rightarrow H_2CO + O_2\ CHCl$

(2) $\rightarrow HClCO + O_2CH_2$

(3) $O_2CH_2 \rightarrow OH + CHO$

(4) $CHO + O_2 \rightarrow HO_2 + CO$

(5) $HClCO \rightarrow HCl + CO$

(6) $HClCO + H_2O \rightarrow HCOOH + HCl$

This mechanism is not meant to be complete since a large number of reactions can be written with the free radicals arising from the photooxidation. Also, the role of NO_x is not shown and many reactions can be written involving nitrogen containing compounds. Instead, the above reactions as shown only to suggest how some of the products are produced. The formyl chloride can arise from reaction 2. This product has been observed by its spectra but has not been quantified - largely because of its instability. Hisatsune and Heicklen (1973) have shown that formyl chloride gas is thermally unstable with a half-life of approximately 20 minutes. They report that the thermal decomposition products are HCl and CO. Both products have been observed in the photooxidation of the chloroethylenes. The HCl concentration is in every case greater than CO. This observation is compatible with the formation of HCl via reaction (6). Phosgene that has been observed as a product from the 1, 1 dichloro, the trichloro and tetrachloroethylenes, is expected to arise from the same type of reaction that produced formyl chloride i.e.

(7) $O_3 + CCl_2 = CH_2 \rightarrow CCl_2O + O_2CH_2$
$\rightarrow CCl_2O_2 + CH_2O$

No CCl_4 was detected in any of the irradiations involving the chloroethylenes. This observation is not in agreement with the recent findings of Singh et.al. (1974). These investigators report CCl_4 formation from the photooxidation of tetrachloroethylene and suggest that a large fraction of the ambient levels of CCl_4 could arise from the degradation of chlorohydrocarbons.

It is interesting to note that most of the irradiations gave rise to high concentrations of ozone. Also, as shown in the case of the chloroform-ethylene-NO_x reaction, the quantity of ozone produced was not significantly different from that produced from ethylene-NO_x alone. This observation suggest that chlorine atoms are not produced. If chlorine atoms were produced, then the following reactions would lead to ozone destruction:

(8) $Cl + O_3 \rightarrow ClO + O_2$

(9) $ClO + O_3 \rightarrow Cl + 2O_2$

(10) $ClO + CO \rightarrow Cl + CO_2$

This mechanism for ozone destruction has been proposed for upper atmospheric chemistry (Molina and Rowland 1974). However, it is possible that a more complete mechanism for these chamber type conditions, would show no such ozone depletion when applied to lower atmospheric conditions even in the presence of chlorine atoms.

This study has shown that most of the chlorinated ethylenes are of moderate reactivity and are photooxidized to compounds such as formaldehyde, hydrochloric acid, phosgene, formyl chloride, and tentatively chloroacetyl chloride and a chlorinated peroxyacyl type compound. It is, therefore, possible that such products i.e., phosgene, formyl chloride and hydrogen chloride will be produced in the ambient atmosphere under stagnant meterological conditions around the vicinity of sources emitting these halocarbons. It is doubtful, however, that high concentrations of such products could be observed, since these products are usually only a fraction of the original reactant, which are found at low concentrations.

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TABLE 1. REACTIVITY PARAMETERS FOR CHLOROETHYLENES

Halocarbon	HC/NO_x	HC	t(min). O_3 max.	140 Min. Reactivity				
				O_3 ppm	o/oHC reacted	HCl ppm	CO ppm	$COCl_2$ ppm
Vinyl Chloride	3.0	4.63	> 160	0.95	34	1.25	1.20	None
1, 1-Dichloro-ethylene	2.15	4.85	125	2.20	83	1.12	0.87	0.72
1, 2-Dichloro-ethylene	3.0	5.0	>150	2.07	66	2.90	1.75	None
Trichloro-ethylene	2.66	3.45	115	2.07	66	1.45	0.80	0.47
Tetrachloro-ethylene	2.83	5.0	>180	0.07	7.0	0.42	0.27	0.12

List of Figures

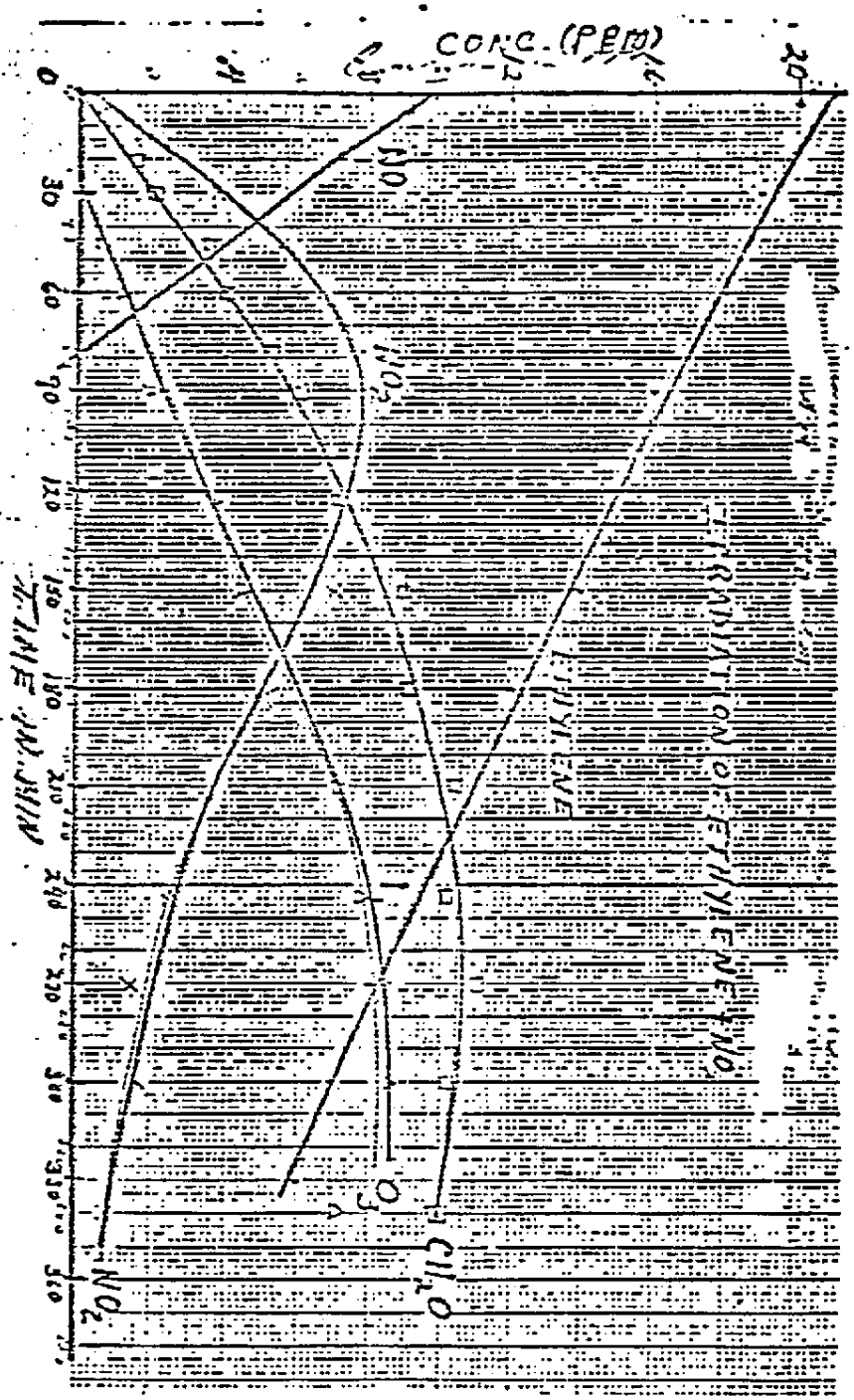
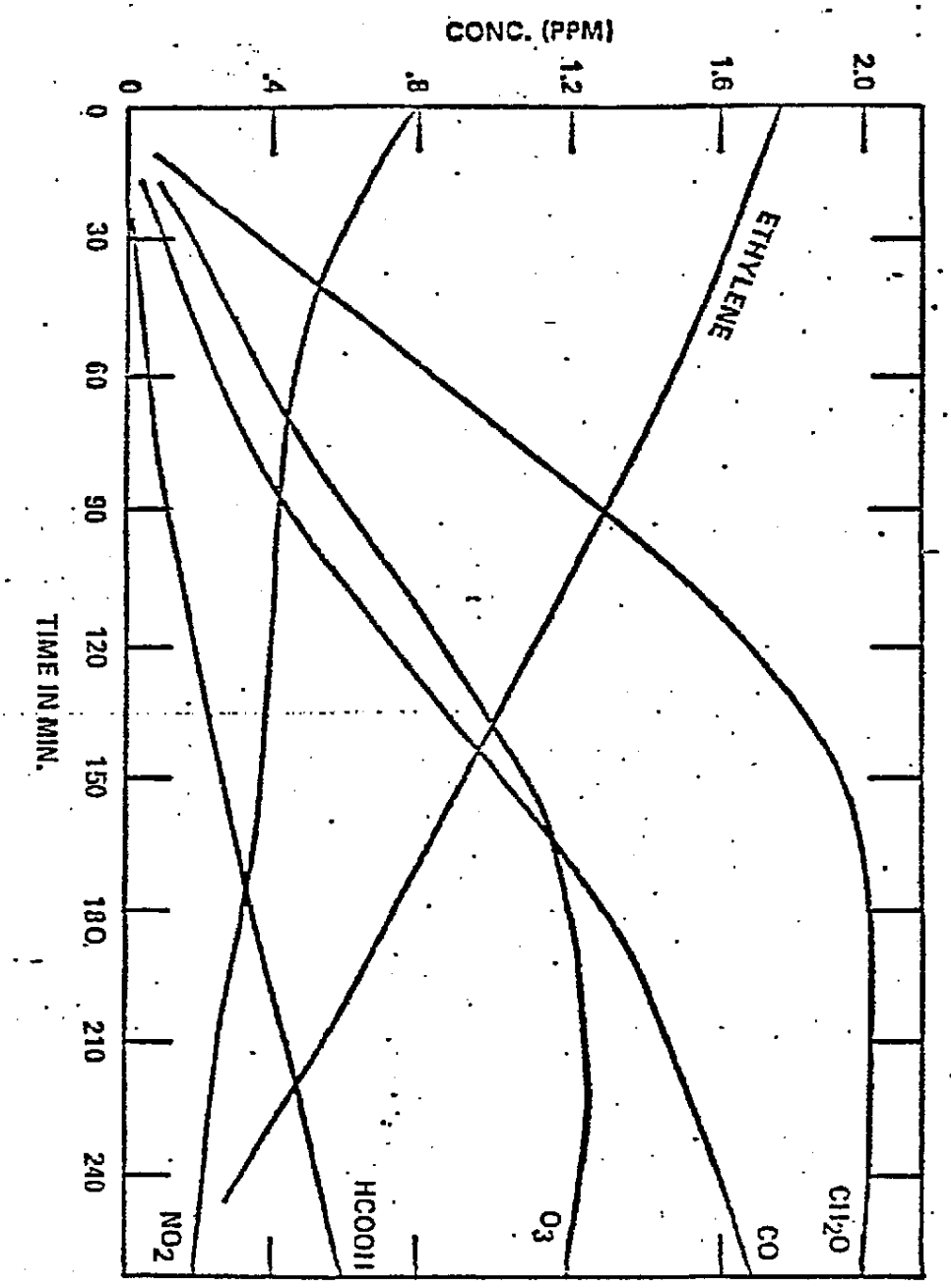
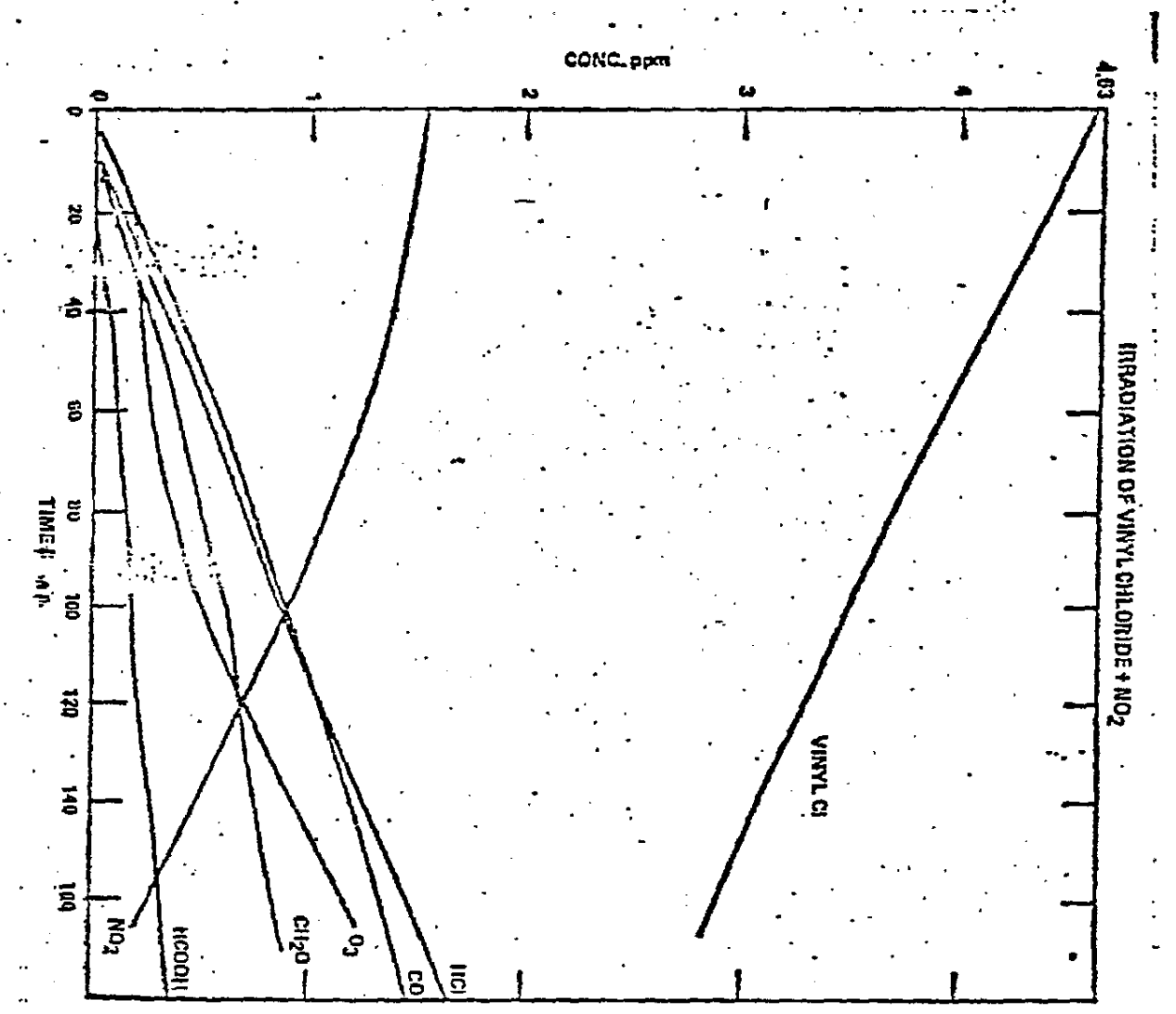


FIG 1

Fig 2


CONC. (PPM)
0
.4
.8
1.2
1.6
2.0
TIME IN MIN.
0
30
60
90
120
150
180
210
240
ETHYLENE
NO_2
HCOOH
O_3
CO
Cl_2O
IRRADIATION OF ETHYLENE + NO_2


CONC. ppm
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1
2
3
4
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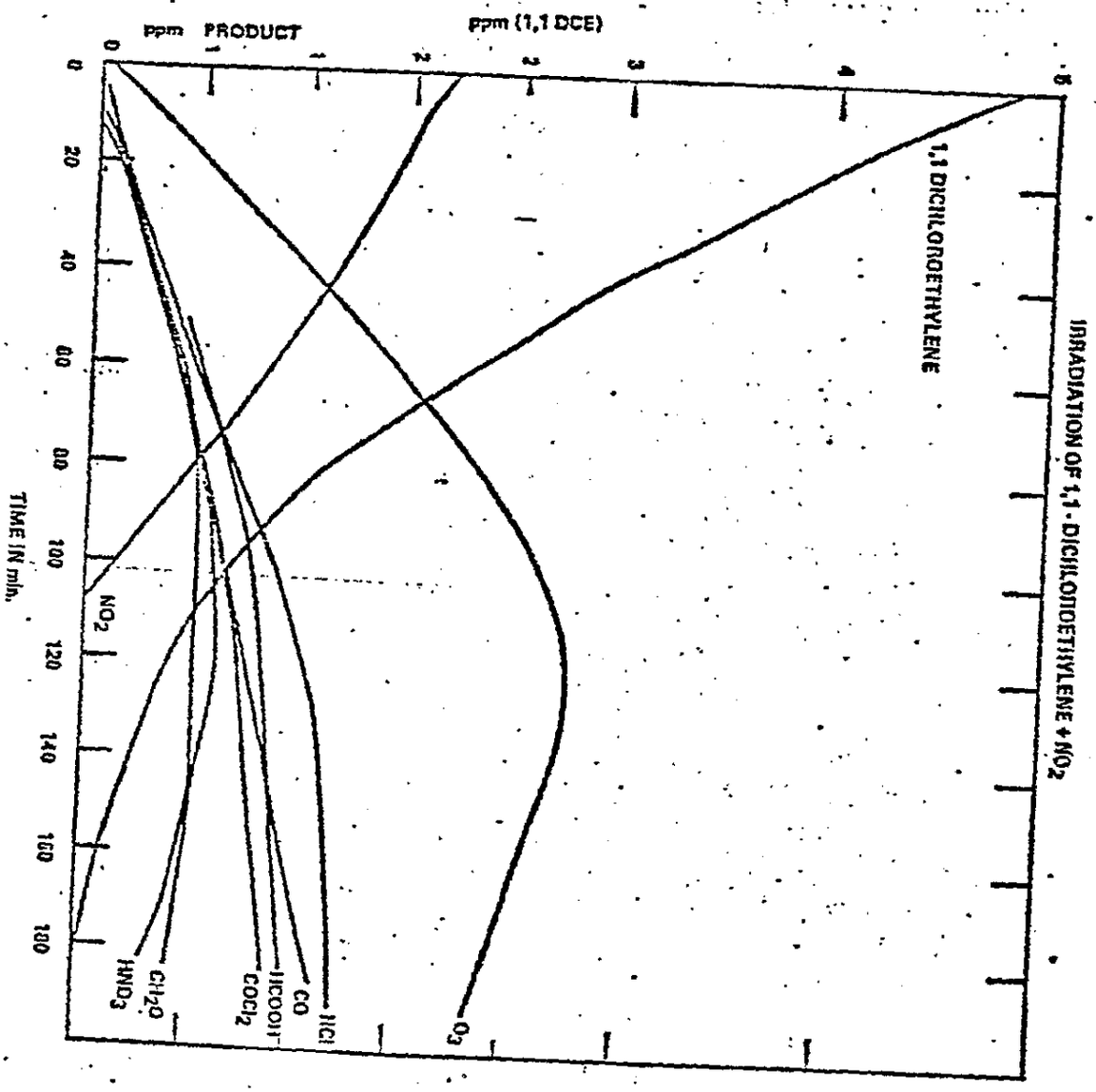
CO
O_3
Cl_2O
HCOCl
NO_2
TIME


Ppm PRODUCT
Ppm (1,1 DCE)
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1
2
3
4
5
0
20
40
60
80
100
120
140
160
180
TIME IN min.
1,1 DICHLOROETHYLENE
IRRADIATION OF 1,1 - DICHLOROETHYLENE + NO_2
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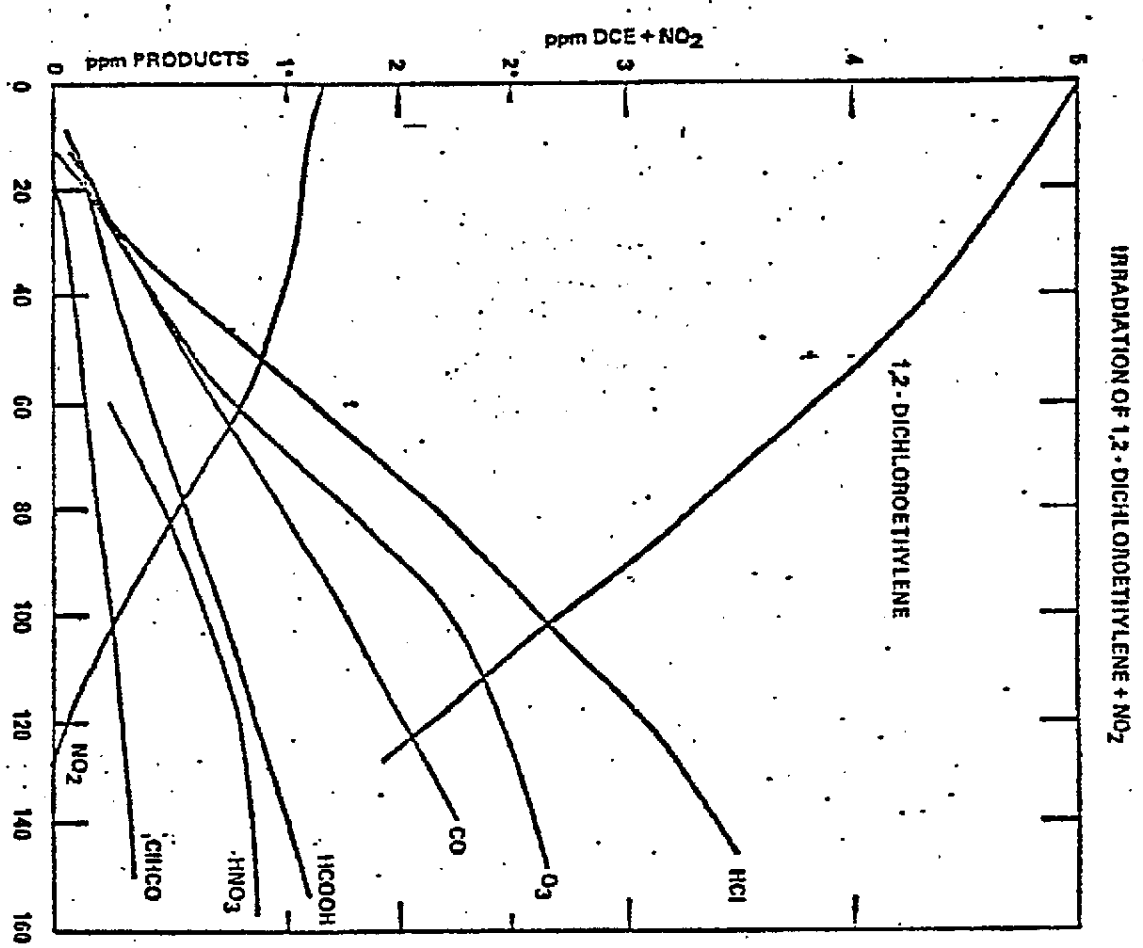
HNO_3
CH_2O
$COCl_2$
HCOOH
CO
HCl
O_3


ppm PRODUCTS
ppm DCE + NO_2
IRRADIATION OF 1,2 - DICHLOROETHYLENE + NO_2
TIME IN min.
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HNO_3
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O_3
HCl
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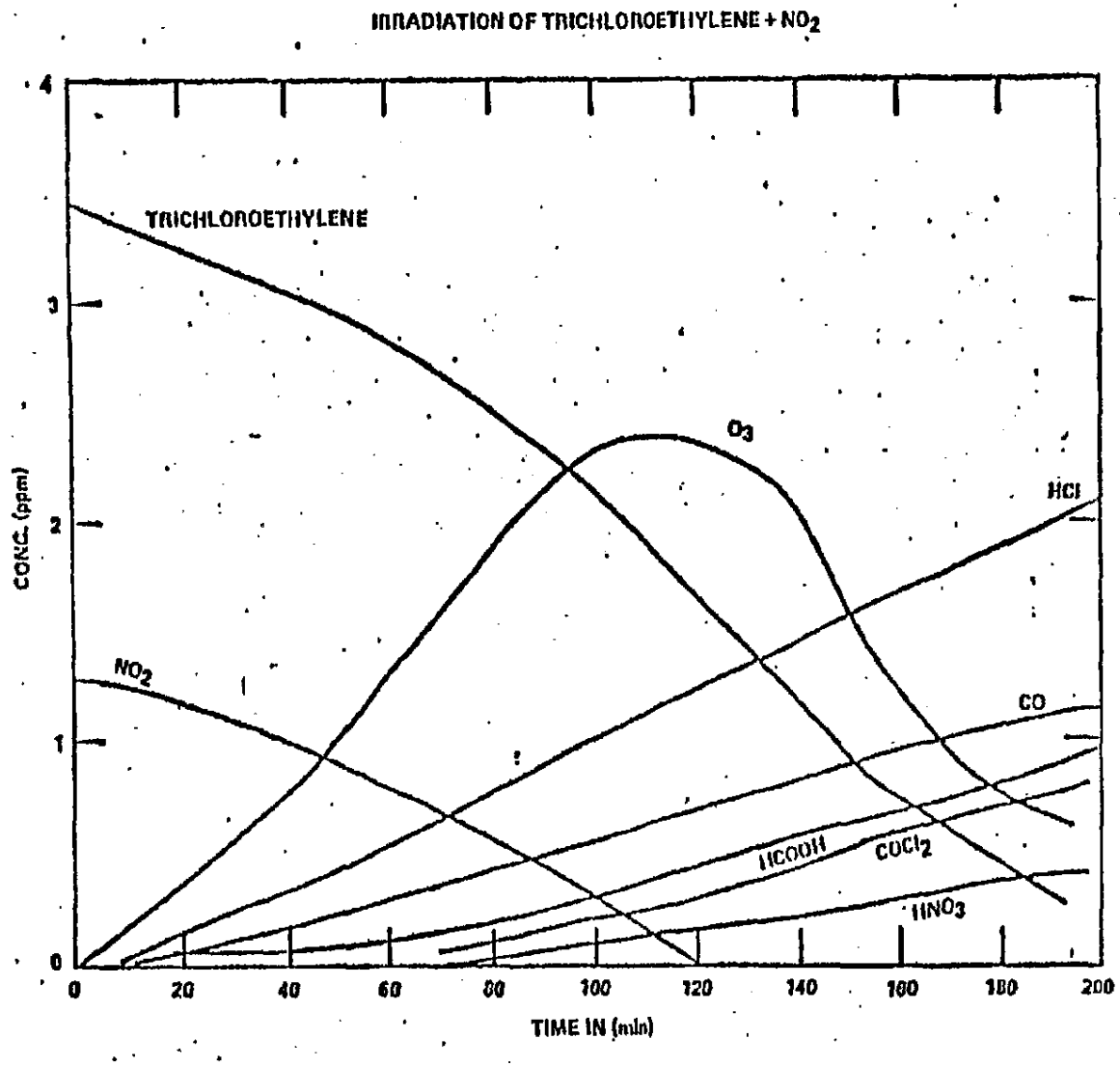
IRRADIATION OF TRICHLOROETHYLENE + NO_2
TRICHLOROETHYLENE
O_3
HCl
NO_2
CO
HCOOH
$COCl_2$
HNO_3
CONC. (ppm)
TIME IN (min)
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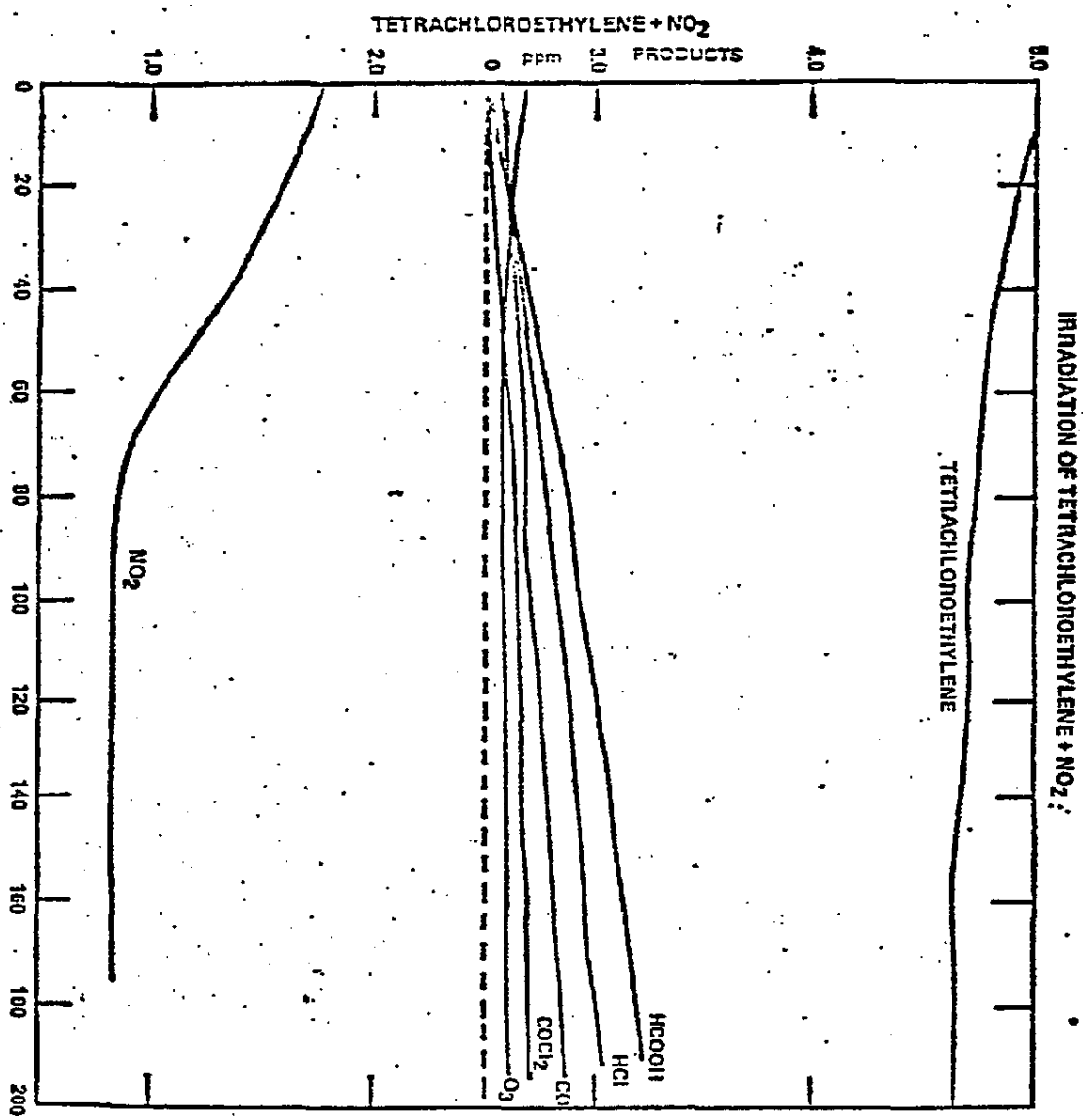
180
200

Fig 7


TETRACHLOROETHYLENE + NO_2
PRODUCTS
ppm
1.0
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3.0
4.0
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0
20
40
60
80
100
120
140
160
180
200
TIME, min.
NO_2
O_3
$COCl_2$
Cl
HCl
HCOOH
TETRACHLOROETHYLENE
IRRADIATION OF TETRACHLOROETHYLENE + NO_2

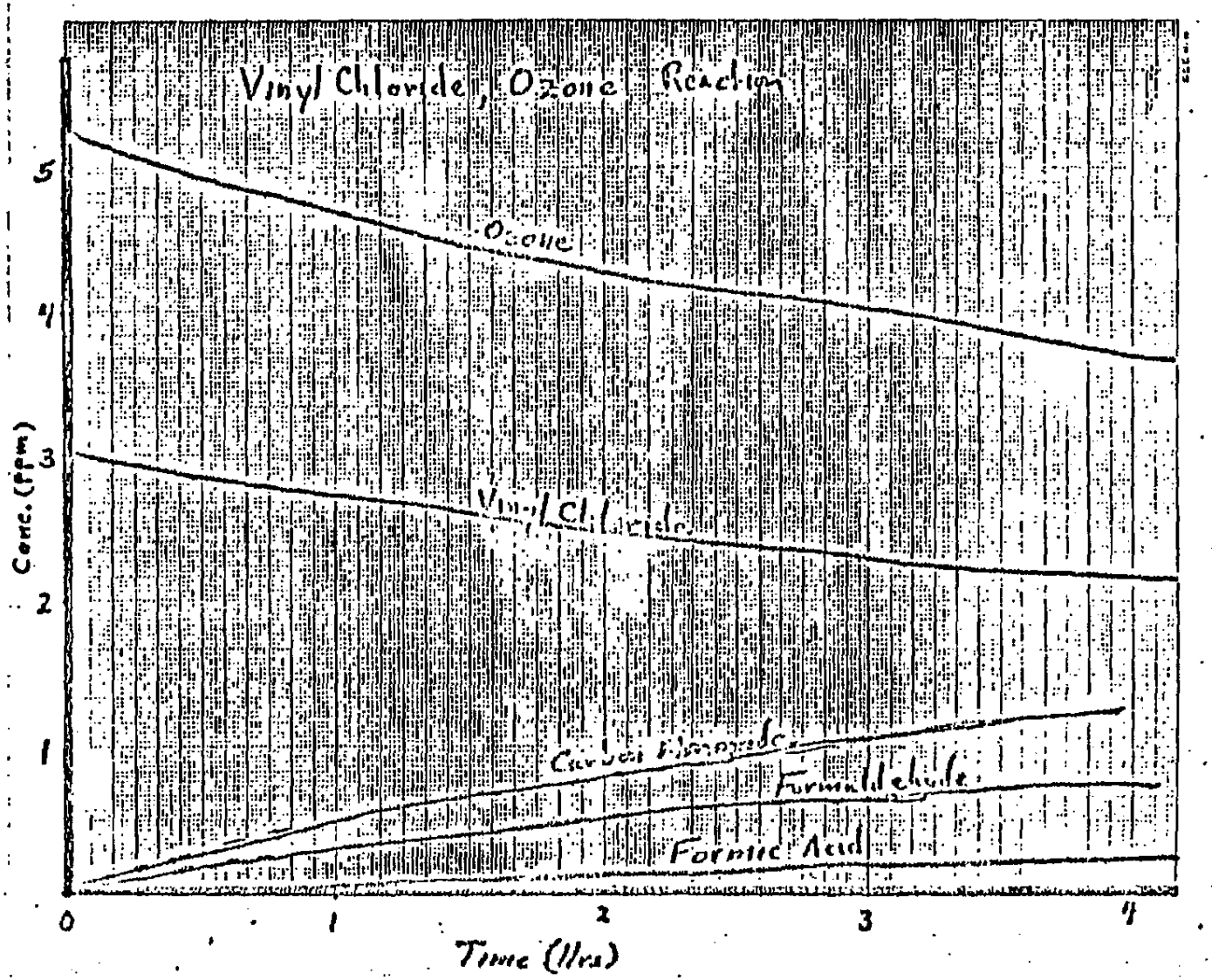
Vinyl Chloride, Ozone Reaction
Ozone
Vinyl Chloride
Carbon Monoxide
Formaldehyde
Formic Acid
Conc. (ppm)
Time (Hrs)
0
1
2
3
4
5

Fig. 10