VAPOR-PHASE PHOTODECOMPOSITION OF CHLOROPICRIN (TRICHLORONITROMETHANE)

K. W. MOILANEN,* D. G. CROSBY, J. R. HUMPHREY and J. W. GILES

Department of Environmental Toxicology, University of California, Davis, CA 95616, U.S.A.

Abstract—Under simulated environmental (atmospheric) conditions, chloropicrin vapor was readily converted in light to phosgene, which remained stable, and nitrosyl chloride which was subsequently photolyzed to nitric oxide and chlorine; a portion of the nitric oxide was oxidized to nitrogen dioxide and dinitrogen tetroxide. The unexpected dependence of the reaction upon oxygen, the initial photoproducts, and the incorporation of ^{18}O when the photolysis occurred in the presence of $^{18}O_2$ suggest an intramolecular rearrangement involving a trioxazole N-oxide.

The atmosphere has become recognized as an important medium in the dispersal of pesticides and other chemicals.[1-3] Many toxic substances are susceptible to photolysis by sunlight,[4-6] and their photodecomposition in the atmosphere offers a potentially significant route for environmental dissipation.

Chloropicrin (trichloronitromethane, **1**) is widely used for the control of soil-borne pests including fungi, nematodes, insects, and weed seeds;[7] more than 10 million pounds of the chemical are used annually in California alone.[8] It also is a powerful irritant which affects all body surfaces; it causes lachrymation, vomiting, bronchitis, and pulmonary edema, and interferes with oxygen transport by its reaction with SH-groups in hemoglobin.[9] This toxicity, coupled with its popularity as a fumigant, makes its fate in the environment a rather important matter, especially if it were to persist in the atmosphere.

Gardner and Fox[10] reported that **1** was slowly converted to phosgene (**2**) and nitrosyl chloride (**3**) when held at its normal boiling point (112°), and Piutta and Mazza[11] found that irradiation of liquid **1** with 254 nm ultraviolet (UV) light resulted in the same products, with the phosgene being further split into carbon monoxide and chlorine. Irradiation of alcohol solutions of **1** resulted in the rapid formation of ammonium chloride;[12] other compounds present during photolysis were oxidized, chlorinated, or nitrated depending upon their nature.[13]

While these data indicate that **1** is reactive photochemically, the conditions employed were far different from those found in the environment. The purpose of the present investigation was to identify the products of the vapor-phase photolysis of chloropicrin under simulated environmental (atmospheric) conditions and to rationalize their formation.

RESULTS AND DISCUSSION

Frequent sampling of **1** vapor in a dark control revealed only the slight decrease in concentration due to sampling during the 70 days of each experiment (Curve A, Fig. 1). The photolysis rate in air (Curve B) indicated that **1** vapor is labile at sunlight wavelengths (>290 nm). At an initial concentration of $14 \mu g/ml$ (2060 ppm), 20 days were required for half of **1** to be photolyzed, and a reddish-yellow color became apparent by the tenth day. The photolysis rate slowed markedly after 20 days, and 25% of **1** remained after 70 days. Analysis on day 10 revealed phosgene (**2**) and nitrosyl chloride **3** (Scheme 1), accounting for the observed color. By day 13, nitric oxide (**4**), nitrogen dioxide (**5**) and dinitrogen tetroxide (**6**)

also were detectable, while chlorine (**7**) appeared in the day 20 analysis. Similar results were obtained with initial chloropicrin concentrations of 206 or 1.4 ppm (1.4 or $0.01 \mu g/ml$, respectively).

The order in which photoproducts appeared and the variation of their concentrations with time (Fig. 2) support the reaction sequence outlined in Scheme 1. **1** initially forms $COCl_2$ and $NOCl$, and the subsequent accumulation of $COCl_2$ indicates its stability under reactor conditions. This observation contrasts with the results of Piutta and Mazza,[11] probably due to their use
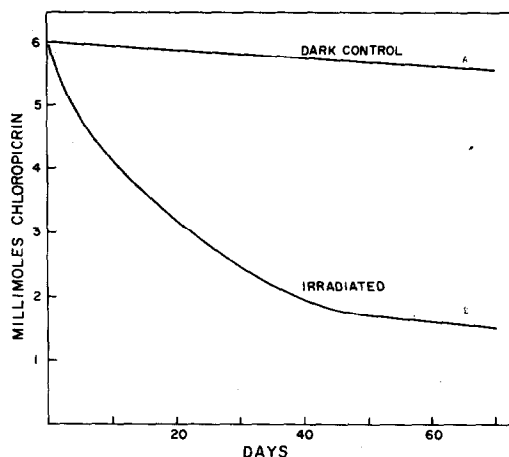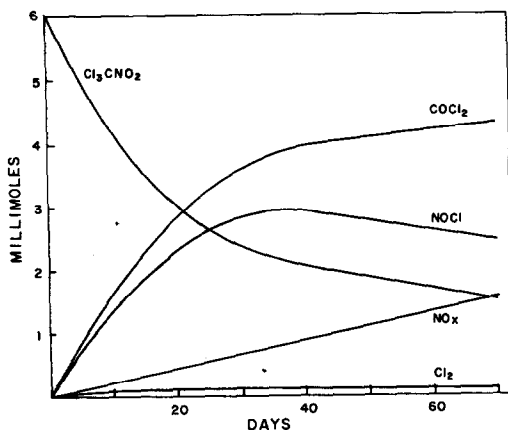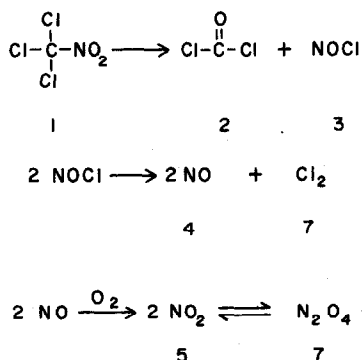

Fig. 1. Photolysis rate of chloropicrin.

Fig. 2. Concentration profiles of photoproducts.

$$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-NO_2 \longrightarrow Cl-\overset{\overset{O}{||}}{C}-Cl \quad + \quad NOCl$$

$$1 \qquad\qquad 2 \qquad\qquad 3$$

$$2\ NOCl \longrightarrow 2\ NO \quad + \quad Cl_2$$

$$4 \qquad\qquad 7$$

$$2\ NO \xrightarrow{O_2} 2\ NO_2 \rightleftharpoons N_2O_4$$

$$5 \qquad\qquad 7$$

Scheme 1. Photoproducts of chloropicrin.

of the more energetic 254 nm light.[14,15] The photolysis of NOCl to NO and Cl_2 is not surprising; Kistiakowsky[16] reported a quantum yield of 2.0 for the process over the entire visible and near-UV region. NO_2 results from air oxidation of NO, with N_2O_4 arising from its familiar dimerization, while Cl_2 results from the combination of chlorine atoms produced in the photolysis of NOCl. The material balance of the photolysis (Table 1) was reasonably good, considering the analytical difficulties caused by the high reactivity of the photoproducts. However, the apparent 84% and 113% recoveries of Cl and N,

Table 1. Material balance from chloropicrin photolysis[a]

| Product	Amount Detected (mmole)	Elements Accounted for		
		C	N	Cl
$COCl_2$	4.3	4.3		8.6
NOCl	2.5		2.5	2.5
N_2O_4	1.0		2.0	
NO_2	.4		.4	
NO	.2		.2	
Cl_2	0.1			0.2
Total (mmoles)		4.3	5.1	11.3
(%)		96	113	84

[a]Initial chloropicrin 6.0 mmoles, final chloropicrin 1.5 mmoles after 70 d.

respectively, could be due to the formation of (undetected) ClO_2 which would shift them toward 100%. The decrease in the photolysis rate of 1 after 20 days may be explained both by dilution and by the absorption of light by the products, as all but NO absorb strongly above 290 nm.[17-20] Additional free-radical reactions also may be involved, since NO and NO_2 have unpaired electrons[20] and Cl_2 is efficiently cleaved to Cl atoms by UV light above 290 nm.[21]

The initial photoproducts $COCl_2$ and NOCl which account exactly for the atoms of 1, the observed rate, and the occurrence of the reaction even in highly dilute vapor suggest a unimolecular decomposition mechanism. 1 might undergo an n-Π* transition to the diradical 8,[22,23] followed by Nesmeyanov rearrangement to 9,[24] ring-closure to the oxazirane N-oxide 10, and decomposition to $COCl_2$ and NOCl (Path A, Scheme 2). Relatively stable oxaziranes have been synthesized,[25] and their proposed N-oxides indeed decompose spontaneously to the expected carbonyl and nitroso compounds.[26]

However, in a nitrogen atmosphere, 1 was found to be stable to UV irradiation, indicating that oxygen is required for photodecomposition and suggesting that triplet oxygen might combine with 9 (Path B, Scheme 2) to form a peroxyl radical and the trioxazole N-oxide 11 which decomposes to $COCl_2$, NOCl, and molecular oxygen (Scheme 3a). This form of trioxazole, a well-characterized product of olefin ozonolysis,[27,28] has been invoked as the intermediate in the reaction of 1,1-dichloroethylene with ozone in which phosgene was formed spontaneously and quantitatively (Scheme 3b).[29] The open form of the 5-membered trioxazole N-oxide ring was the proposed intermediate in the ozonolysis of nitrones to corresponding carbonyl and nitroso compounds (Scheme 3c),[30] and formation of the same products from heterocyclic N-oxides[31] and nitronates[32] suggests that the process may be a general one (Scheme 3d).

The photolysis of 1 next was conducted in an oxygen-18 enriched atmosphere; if oxygen adds to 9 to produce 11 the $COCl_2$ resulting from subsequent decomposition should have an ^{18}O label (Scheme 4), while carbonyl oxygen derived from 1 should contain no label. The mass spectra of unlabelled and (theoretical) ^{18}O-labelled $COCl_2$ (Fig. 3) show distinct differences near the base peak and parent peak cluster; the mass spectrum of $COCl_2$ resulting from the photolysis of 1 in an at-
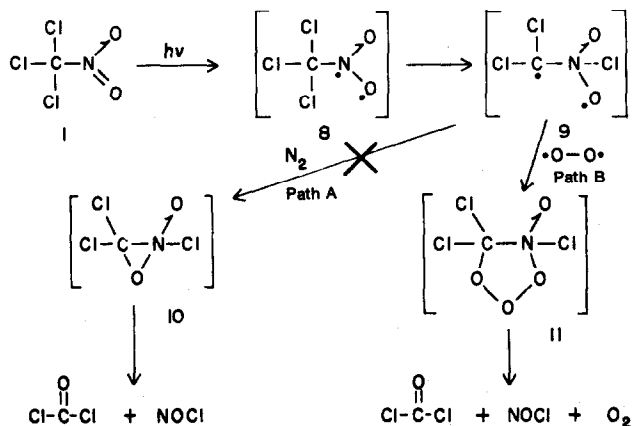
Scheme 2. Proposed mechanism for chloropicrin photolysis.
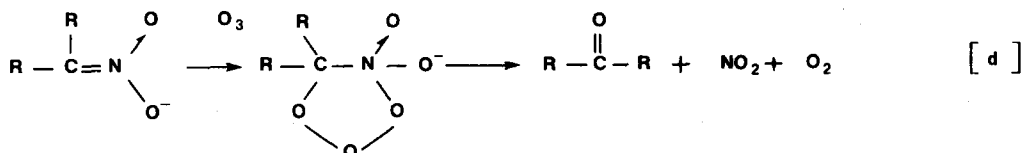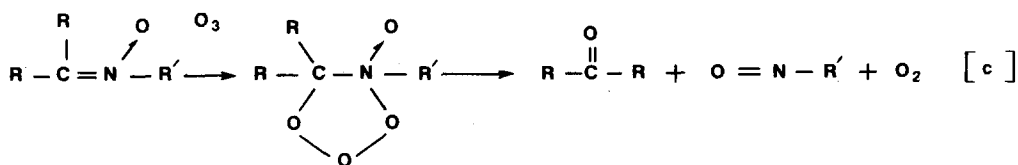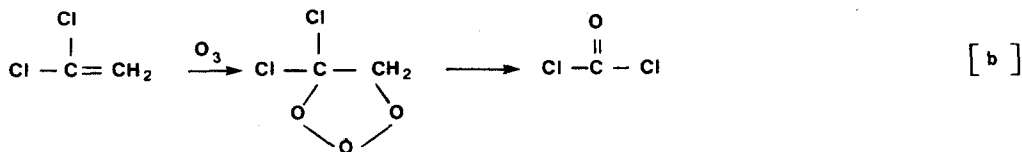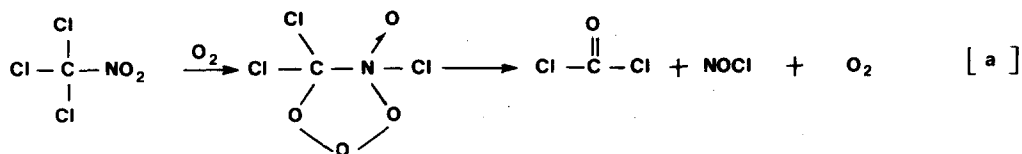
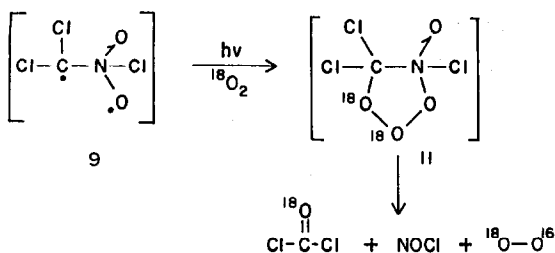Scheme 3. Trioxazole intermediates in oxidation mechanisms.
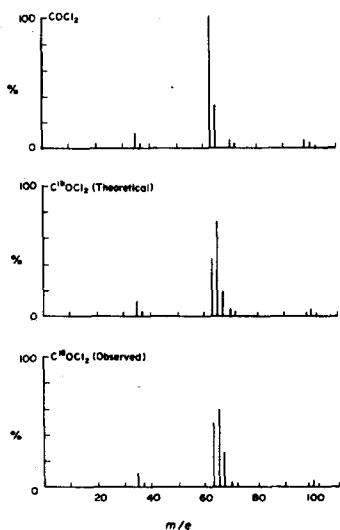
Fig. 3. Mass spectra of $COCl_2$ and $C^{18}OCl_2$.

mosphere containing 56.9 atom-percent ^{18}O, also shown in Fig. 2, clearly exhibited the isotope distribution expected from incorporation of an atom of ^{18}O. The small discrepancy between the theoretical and observed spectra can be ascribed to progressive dilution of the oxygen-18 by oxygen-16 generated in the photolysis so

that at detectable $COCl_2$ levels the air-enrichment would be only about 45 atom-percent.

An alternate mechanism (Scheme 5) could provide the labelled $COCl_2$ by reaction of oxygen with a CCl_3 radical formed by C–N cleavage of 1: irradiation of nitroalkanes witha mercury arc is known to result in alkyl radicals and NO_2.[33,34] Irradiation of 1 vapor at high concentration (200 $\mu g/ml$) in air produced no hexachloroethane, and 1 again was recovered quantitatively when oxygen was excluded; the formation of trichloromethyl radicals and NO_2 may require the higher energy provided by 254 nm light.[33,34] The same evidence also precludes generation of a Cl atom as the initial step. Another photochemical reaction of nitroalkanes, the elimination of the oximino-radical (NOH),[35] also would account for the observed products, but it too should be independent of external oxygen.

The results indicate that chloropicrin vapor will be efficiently photolyzed in the atmosphere. The initial products would be subject to rapid dissipation, $COCl_2$ eventually to be hydrolyzed to carbon dioxide and hydrogen chloride while NOCl would provide the recognized atmospheric contaminants NO, N_2O_4 and Cl_2. However, while any inadvertently released 1 would undergo complete tropospheric mineralization and could not reside intact in the atmosphere for any appreciable period of time, the possible localized generation of phosgene or nitrogen oxides from chloropicrin photolysis requires further consideration.

Scheme 4. Photolysis of chloropicrin in ^{18}O.

$$Cl_3CNO_2 \longrightarrow Cl_3C + NO_2$$

$$2Cl_3C \longrightarrow Cl_3CCCl_3$$

$$Cl_3C + O_2 \longrightarrow Cl_2CO + ClO$$
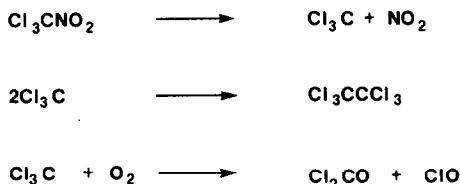
Scheme 5. Photochemical reactions of chloropicrin in 254 nm light.

EXPERIMENTAL

Chemicals. Chloropicrin (99%, Dow Chemical Co.) and hexachloroethane (98%, Aldrich Chemical Co.) were used without further purification. Chlorine, nitric oxide, nitrosyl chloride, and phosgene (Matheson Gas Products, Research Grade) were used as received. Air oxidation of nitric oxide produced a standard of nitrogen dioxide, while dimerization of the latter provided dinitrogen tetroxide. ^{18}O enriched oxygen (56.9 atom-% ^{18}O) was obtained from ICN Isotope and Nuclear Division (Irvine, California).

Photolysis. The photoreactor used for the vapor-phase photolyses[4] minimized possible wall reactions.[5] Typically, the 72-l. reaction chamber was charged with 0.6 ml (1.0 g) of liquid chloropicrin which evaporated to produce a concentration of 2060 ppm (14 μg/ml) in air. Experiments also were run at 206 ppm and 1.4 ppm. A 275-W RS Sunlamp (General Electric Co.) was the light source, and irradiation was allowed to continue for 70 days at 25–30°. Samples were withdrawn at regular intervals with a gas-tight syringe and analyzed by glc and gsc. Another experiment was conducted under identical conditions except that the reactor was purged with N_2, and the absence of O_2 was confirmed by gsc on a Mol Sieve 5A column providing a sensitivity of 100 ppm. The photolysis of chloropicrin vapor also was conducted in an ^{18}O enriched oxygen atmosphere (56.9 atom-%), and a dark control was included in yet another flask.

Analysis. Glc employed a Varian Aerograph Model 200 instrument equipped with a thermal conductivity detector and a 150 cm × 0.3 cm i.d. stainless steel column containing 2% OV-1 on 60/80 mesh, acid-washed, DMCS-treated Chromosorb G (System A). The initial column temp. was 50°, final column temperature 250°, program rate 10°/min, injector 240°, detector 275°C, and helium carrier gas at 100 ml/min.

Gsc utilized the same instrument, the column containing Porapak Q, 100/120 mesh (Waters Associates Inc., Framington, MA) (System B). The initial column temp. was 30°, final column temp. 200°, program rate 10°/min, injector 240°, detector 275°, and He carrier gas at 40 ml/min. Similar columns contained 30/60 mesh silica gel (System C), column temp. 140°, injector 240°, detector 275°, and He carrier gas at 80 ml/min, or Mol Sieve 5A, 60/80 mesh (System D), column temp. 30°, injector temp. 50°C, detector temp. 200° and He carrier gas at 20 ml/min.

Combined GC–MS employed a Finnigan Model 3000 Peak Identifier equipped with System A, initial column temp. was 50°, final column temp. 250°, program rate 10°/min, with He carrier gas at 16 ml/min. A similar glass column contained Porapak Q, 100/120 mesh, with an initial column temp. of 100°C, final column temp. of 220°C, program rate 10°/min, and He carrier gas at 16 ml/min. GC–MS was used to confirm the identity of the photoproducts by comparison with authentic standards.

Table 2. GLC and GSC conditions

Compound	GLC or GSC System	Retention Time (min)
$COCl_2$	B	3.25 (180°C)
NOCl	B	1.67 (30°C)
	D	6.75 (35°C)
NO	B	1.42 (0°C)
NO_2	B	3.58 (5°C)
N_2O_4	B	2.50 (5°C)
Cl_2	C	2.83 (75°C)
O_2	D	1.67 (35°C)
N_2	D	3.33 (35°C)
Cl_3CNO_2	A	2.58 (70°C)
C_2Cl_6	A	4.25 (75°C)

Table 2 summarizes the columns and temps used for analysis of each photoproduct. The photoproducts were quantitated by comparing peak areas with those of known amounts of standards.

REFERENCES

[1] C. A. Wheatley, *Environmental Pollution by Pesticides* (Edited by C. A. Edwards), p. 365. Plenum Press, London (1973).
[2] J. T. Middleton, *Research in Pesticides* (Edited by C. O. Chichester), p. 191. Academic Press, New York (1965).
[3] W. F. Spencer and M. M. Cliath, *Environmental Dynamics of Pesticides* (Edited by R. Haque and V. H. Freed), p. 61. Plenum Press, New York (1975).
[4] D. G. Crosby and K. W. Moilanen, *Arch. Environ. Contam. Toxicol.* 2, 62 (1974).
[5] D. G. Crosby and K. W. Moilanen, *Chemosphere* 4, 167 (1977).
[6] K. W. Moilanen, D. G. Crosby, C. J. Soderquist and A. S. Wong, *Environmental Dynamics of Pesticides* (Edited by R. Haque and V. H. Freed), p. 61. Plenum Press, New York (1975).
[7] E. G. Sharrelle, *The Nature and Uses of Modern Fungicides*, pp. 186–189. Burgess, Minneapolis, Minn. (1960).
[8] *Pesticide Use Report.* California Department of Food and Agriculture, 1973.
[9] N. I. Sax, *Dangerous Properties of Industrial Materials*, Reinhold, New York (1968).
[10] J. A. Gardner and F. W. Fox, *J. Chem. Soc.* 115, 1189 (1919).
[11] A. Piutti and F. P. Mazza, *Gazz. Chim. Ital.* 57, 610.
[12] G. L. Ciamician and P. Silber, *Ibid.* 16, (1886).
[13] A. Piutti, *Atti Congr. Naz. Chim Pura Applicata* 437 (1923).
[14] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.* 62, 454 (1940).
[15] M. H. J. Wijnen, *Ibid.* 83, 3014 (1961).
[16] G. B. Kistiakowsky, *J. Am. Chem. Soc.* 52, 102 (1930).
[17] C. F. Goodeve and S. Katz, *Proc. Roy. Soc A* 172, 432 (1939).
[18] T. C. Hall, Jr. and F. E. Blacet, *J. Chem. Phys.* 20, 1745 (1952).
[19] G. E. Gibson and N. S. Bayliss, *Phys. Rev.* 44, 188 (1933) 2nd Edn.
[20] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd Edn, pp. 342–345. Interscience, New York (1966).
[21] J. G. Calvert and J. N. Pitts, *Photochemistry*, p. 226. Wiley, New York (1966).
[22] H. A. Morrison, *The Chemistry of the Nitro and Nitroso Groups*, Part I, (Edited by H. Feuer). Wiley, New York (1969).

[24]R. Kh. Freidlina, *Adv. in Free Radical Chem.* (Edited by G. H. Williams). Vol. 1, Chap. 6, pp. 231–248. Logos, London (1965).

[25]W. D. Emmons, *J. Am. Chem. Soc.* **79**, 5739, 6522, (1957).

[26]G. G. Spence, E. C. Taylor and O. Buchardt, *Chem. Rev.* **70**, 231 (1970).

[27]P. S. Bailey, J. A. Thompson and B. A. Shoulders, *J. Am. Chem. Soc.* **88**, 4098 (1966).

[28]R. Criegee, *Chimia* **2222**, 392 (1968).

[29]L. J. Durham and F. L. Greenwood, *J. Agr. Chem.* **33**, 1929 (1968).

[30]R. E. Erickson and T. M. Myszkiewicz, *J. Org. Chem.* 4326 (1965).

[31]E. J. Moriconi and F. A. Spano, *J. Am. Chem. Soc.* **86**, 38 (1964).

[32]J. E. McMurry, J. Melton and H. Padgett, *J. Org. Chem.* **39**, 259 (1974).

[33]J. Mason, *J. Chem. Soc.* 3904 (1957).

[34]J. Sander and R. N. Haszeldine, *Ibid.* 696 (1954).

[35]E. Hirschlaff and R. G. W. Norrish, *Ibid.* 1580 (1936).