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RADIOLYSIS OF CHLOROFORM IN THE INTENSE
RADIATION PULSE FROM A NUCLEAR EXPLOSION

by

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ABSTRACT

Air-free chloroform was irradiated at an average dose rate of 5×10^{12} rad/sec in the radiation flux produced by an underground nuclear explosion. The major products and their yields relative to C_2HCl_5 are: sym- $C_2H_2Cl_4$, 1.2; C_2Cl_6 , 0.31; sym- C_3HCl_5 , 0.21; C_2Cl_4 , 0.08; and CH_2Cl_2 , 0.07. Interpreted on the basis of a free radical mechanism, these yields indicate that some species is competing with $CHCl_3$ for the radiolytically produced chlorine atoms — a phenomenon not observed at lower intensities.

Radiation intensity is a useful parameter for studying mechanisms in radiation chemistry. The maximum intensity previously obtainable was 10^{11} rad/sec from particle accelerators. However, we have used the intense burst of radiation from an underground nuclear explosion to obtain dose rates of nearly 10^{13} rad/sec and to study the radiation chemistry of a variety of simple chemical systems. For preliminary study, chloroform was chosen because intensity effects on the yields of the radiolytic products have been reported for its irradiation at lower dose rates (1,2). The results of our study not only support the mechanism proposed at lower intensities by Werner and Firestone (3), but also indicate that at our higher dose rates CHCl_3 is no longer successful in scavenging all the radiolytically produced chlorine atoms (one of the primary dissociation products).

These irradiation experiments were performed in conjunction with an underground nuclear test at the USAEC test site in Nevada. The chloroform samples were sealed under vacuum in "Pyrex"* tubes (8-mm OD x 5 cm), and these along with several LiF thermoluminescent dosimeters were sealed in wax into a steel secondary cylinder, which was designed to provide protection against mechanical shock and soft electromagnetic radiations. This assembly was then positioned so that the radiation from the detonation passed through the length of the cylinder. The distance from the sample cylinder to the device was great enough to negate any effects caused by the heat generated from the explosion.

* Trademark of Corning Glass Works, Corning, N. Y.

The CHCl_3 irradiated in this experiment was purified by washing several times with water, distilling under an inert atmosphere, and drying with a Linde 5A molecular sieve. Samples were then prepared by vacuum distilling the CHCl_3 into the irradiation vessels where it was degassed by several freezing-pumping-thawing cycles. The only impurities detected in the unirradiated samples by gas-liquid chromatography were: cis- $\text{C}_2\text{H}_2\text{Cl}_2$ (4.9×10^{-2} mole %), 1,1- $\text{C}_2\text{H}_4\text{Cl}_2$ (2.5×10^{-2} mole %), and CCl_4 (8×10^{-3} mole %). Mechanistic considerations indicate that these impurities at these concentrations should not significantly affect the important reactions in the CHCl_3 . The presence of CCl_4 prevented the determination of the radiolytic yield of this compound.

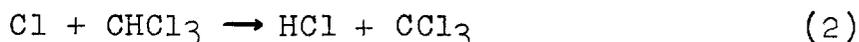
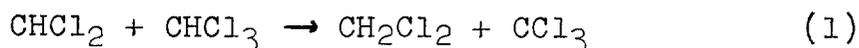
After the detonation and recovery, analysis of the dosimeters indicated that the absorbed dose decreased smoothly along the length of the cylinder; but adjacent dosimeters gave results that differed as much as 40%, indicating a nonuniform cross-sectional distribution. This, along with other difficulties introduced by the complex nature of the radiation pulse (4), prevented an accurate estimation of the dose received by the CHCl_3 , and thus prevented the determination of the 100-ev yields of the products. The average dose rate determined from the dosimeters was 5×10^{12} rad/sec.

The yields of the major products found in the irradiated CHCl_3 relative to that for C_2HCl_5 are given in Table I. In several samples, the yields of some of the organic products were below the minimum limit of sensitivity of the analytical

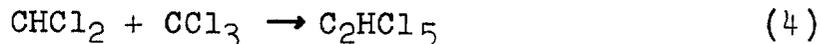
method. This was also true for Cl_2 and HCl , the major inorganic products (3). $\text{Sym-C}_3\text{H}_3\text{Cl}_5$ has not been observed at such high relative yields at lower intensities (1,3); we believe that this compound was formed by reaction of the $\text{C}_2\text{H}_2\text{Cl}_2$ impurity present in our samples.

To compare these data with results contained at lower intensities, at which 100-ev yields were determined (1,2), the number of molecules of each product formed per molecule of CHCl_3 decomposed was calculated. The number of molecules of CHCl_3 decomposed was determined by summing the yields of all the organic products after each had been multiplied by the number of carbon atoms in that specific product. At all intensities, $\text{sym-C}_2\text{H}_2\text{Cl}_4$, C_2HCl_5 , C_2Cl_6 , and CH_2Cl_2 accounted for >94% of the decomposed CHCl_3 molecules. These results are presented in Figure 1. The relative yields at 10^{10} rad/sec were obtained in experiments using an electron accelerator capable of generating 20-microsecond-X-ray pulses; these results will be reported in more detail in a future publication (5).

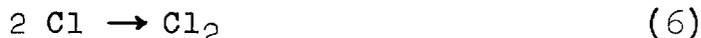
The mechanism of the radiolytic decomposition of CHCl_3 at lower intensities has been developed by Firestone and his colleagues (1,3). In this mechanism, the primary radical species formed by charge neutralization, dissociative electron attachment, and dissociative neutral excitation processes are CHCl_2 radicals and Cl atoms. These species then produce CCl_3 radicals by reactions with the solvent:



Combination reactions of chlorinated methyl radicals then produce the two-carbon products:



Increasing the radiation intensity increases the instantaneous or steady-state concentration of CHCl_2 radicals, and thus reaction (3) is favored over reaction (1); the number of CCl_3 radicals formed decreases and thereby the rate of reaction (5) diminishes. Recently, Abramson and Firestone (1) described this effect quantitatively by calculating the intensity dependence of the 100-ev yields at dose rates $<10^3$ rad/sec using steady-state equations for CHCl_2 and CCl_3 radicals, and the fact that all chlorine atoms disappear via reaction (2). We have found that the yields at 10^{10} rad/sec agree favorably with predictions from their calculations (5); this indicates that their mechanism is still applicable at this high dose rate. At 5×10^{12} rad/sec, however, the yields of C_2Cl_6 and C_2HCl_5 decrease significantly, and $\text{C}_2\text{H}_2\text{Cl}_4$ becomes the major product; this indicates a further decrease in the yield of CCl_3 radicals. Since reaction (1) is unimportant as a source of CCl_3 radicals (as indicated by the low yield of CH_2Cl_2), some process must compete with reaction (2) — the other source of CCl_3 radicals. A likely possibility is the recombination reaction (6), which would be favored by the large radical density produced by the radiation pulse from a nuclear explosion.



Work is continuing on the use of radiation from nuclear explosions for studying the radiation chemistry of both aqueous and organic systems.

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REFERENCES AND NOTES

1. F. P. Abramson and R. F. Firestone, J. Phys. Chem. 70, 35 (1966).
2. J. B. Gardner and B. G. Harper, Paper No. 53, Radiation Research Society Annual Meeting, San Francisco, 1960.
The results of this study are summarized in Reference 1.
3. H. R. Werner and R. F. Firestone, J. Phys. Chem. 69, 840 (1965).
4. The Effects of Nuclear Weapons, S. Glasstone, Ed., USAEC, Washington, D. C., 1962.
5. N. E. Bibler, in preparation.
6. The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission. This work is being sponsored by the Division of Peaceful Nuclear Explosives.

TABLE 1

Yields of the Major Organic Products Relative
to C_2HCl_5 in the Radiolysis of $CHCl_3$ at 5×10^{12} rad/sec

<u>Sample</u>	<u>CH₂Cl₂</u>	<u>C₂Cl₄</u>	<u>C₂H₂Cl₄</u>	<u>C₂Cl₆</u>	<u>C₃H₃Cl₅</u>
1	0.09	0.07	1.3	0.27	0.24
2	0.06	0.07	1.5	0.26	0.23
3	0.06	0.10	1.2	0.30	0.22
4	a	a	1.1	0.36	b
5	a	a	1.0	0.35	0.15
6	a	a	1.2	0.30	b
7	a	a	1.1	0.36	a
8	a	a	a	0.26	a

a not detected.

b detected, but not determined.

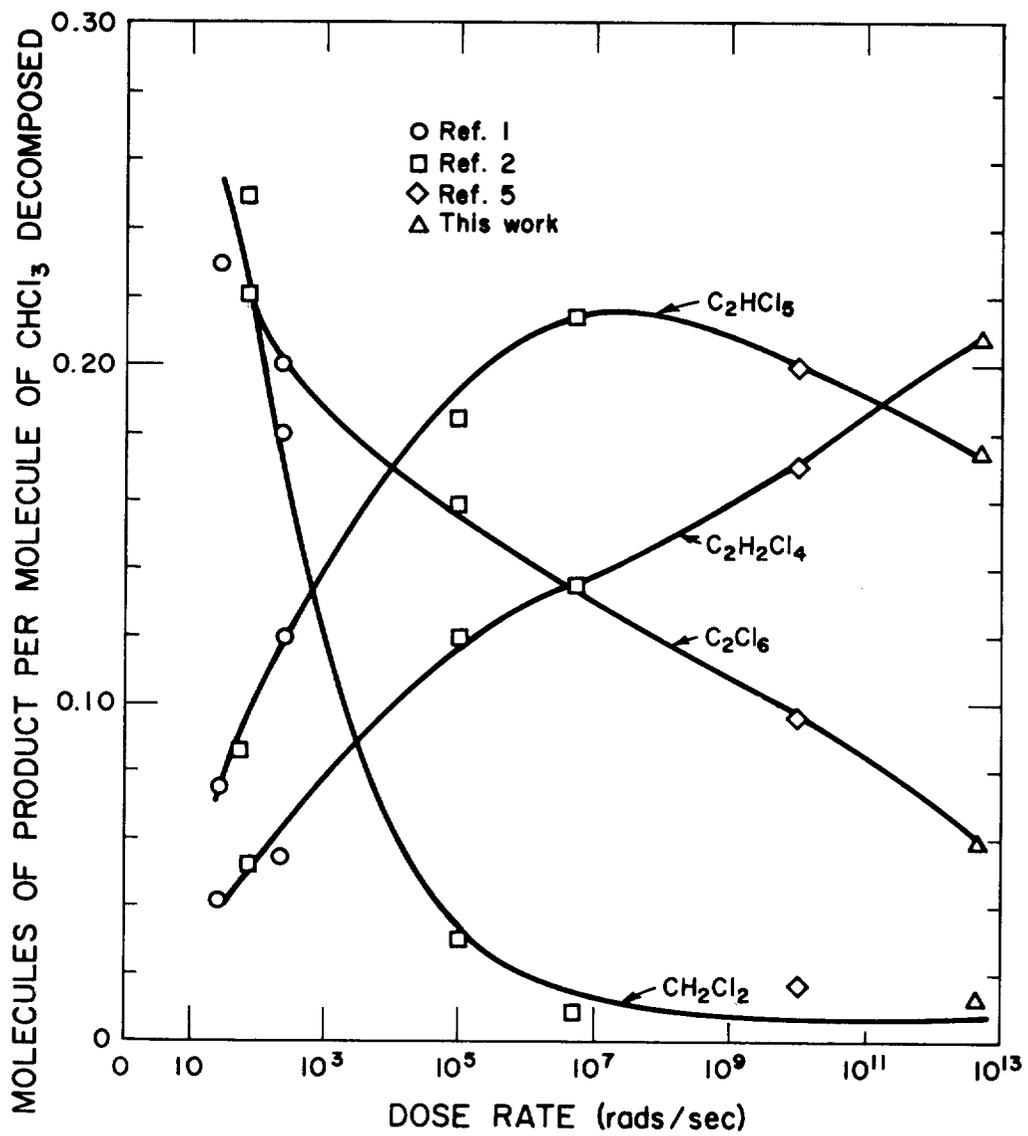


FIG. 1 DOSE RATE DEPENDENCE OF THE NUMBER OF PRODUCT MOLECULES FORMED PER MOLECULE OF CHCl₃ DECOMPOSED IN THE RADIOLYSIS OF PURE CHLOROFORM.