# The Radiation-Induced Oxidation of Trichloroethylene<sup>1</sup>

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The radiation-induced oxidation of trichloroethylene was investigated. It was found that a chain reaction is operable, producing extremely high radiation yields. The three major products are dichloroacetyl chloride, phosgene, and trichloroethylene oxide. The effects of dose rate, temperature, and inhibitor on the overall reaction were examined. The reaction was found to continue after the irradiation was stopped. A mechanism is postulated to account for these effects.

## Introduction

The radiation-induced oxidation of unsaturated organic compounds has not received much attention. In particular, the study of chlorinated hydrocarbons would be of interest because of the extremely high yields and the postirradiation effect that has been experienced in this investigation. No previous investigations had been made on trichloroethylene (TCE). There are two previous reports on the radiation-induced oxidation of tetrachloroethylene, which would be expected to be very similar to that of trichloroethylene. One of these reports<sup>2a</sup> does not mention a postirradiation effect, while the other<sup>2b</sup> explains the effect as a delayed reaction of the products with water. The present work does not indicate this to be true for trichloroethylene. The postirradiation effect is real and has to be included in the mechanism.

#### **Experimental Section**

Materials. The trichloroethylene used was unstabilized Baker reagent grade. Chromatographic analysis showed that batches of this reagent usualy contain 0.1-0.2% impurities. Most of these impurities can be removed by allowing the solvent to remain in contact with Linde molecular sieve. However, some batches contained less than 0.01% impurities and were used to obtain the quantitative results presented here. The less pure TCE was used for qualitative work. The purity of the material appeared to be very critical, as discussed later. Oxygen was used as received, and its purity was greater than 99.6%.

Irradiation. Irradiations were carried out in a Gammacell-220, a commercial source containing about 3200 Ci of cobalt-60. All irradiations were carried out at the source temperature of 28–30°, unless otherwise stated. Energy absorption was measured with a Fricke dosimeter and corrections for material differences were made on the basis of electron fraction. The usual unshielded dose rate was  $2.70 \times 10^{17} \text{ eV}/(\text{ml min})$  (2.53  $\times 10^5 \text{ rads/hr})$  and could be attenuated more than tenfold by the use of lead shields.

Since the radiation yields were very sensitive to irradiation conditions, a uniform procedure was adopted and followed throughout. The liquid was always irradiated in a particular Pyrex flask under an oxygen pressure of 500 Torr. Other conditions, which would vary the amount of oxygen available to the TCE during irradiations, would change the total yields. As long as there is more than ample oxygen for the complete oxidation, one would obtain yields similar to those reported here.

Method of Analysis. Analysis was difficult because of the reactivity of the radiolysis products. However, satisfactory results were obtained using a variety of analytical methods. One commonly used measure of the product yield was the total water-extractible acid. This was determined by shaking the irradiated solvent with  $H_2O$  and titrating the mixture with a base. Chloride ion was also analyzed in some solutions.

Attempts to analyze the radiolysis products directly by gas chromatography were unsuccessful. Product peaks were observed occasionally, but they were not reproducible, probably due to the reactivity on the columns. Nevertheless, this method was used to analyze dichloroacetyl chloride indirectly. Quantitative yields were obtained by adding methyl alcohol to produce the methyl ester before injection into a silicone oil (DC-200) column.

Although mass spectrometry and nuclear magnetic resonance spectroscopy were used to obtain some information, infrared spectrometry proved to be the most valuable method of analysis. A typical spectrum from the Perkin-Elmer 137 instrument is shown in Figure 1. Quantitative measurements were made on the basis of peak heights. A standard curve was made up for the quantitative determination of dichloroacetyl chloride by ir spectrometry. A single solution of phosgene in tri-

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 <sup>(2) (</sup>a) V. A. Poluektov, I. V. Dobrov, and S. A. Lyapina, *High Energy Chem.*, 2, (6) 461 (1968); (b) J. W. Sutherland and J. W. T. Spinks, *Can. J. Chem.*, 37, 79 (1959).



Figure 1. Infrared spectrum of trichloroethylene irradiated in the presence of oxygen.

chloroethylene was also prepared to verify the above procedure for the quantitative determination of phosgene.

## **Results and Discussion**

Product Identification. The three major radiolysis products are dichloroacetyl chloride (DCAC), phosgene, and trichloroethylene oxide (TCE oxide). There was no HCl or  $Cl_2$  formed, as determined by specific spot tests and mass spectrometry.

Dichloroacetyl chloride was positively identified by forming the *p*-toluidide derivative. The unknown had the same melting point  $(156^{\circ})$  and the same infrared spectrum as the known compound. Phosgene was identified by forming the anilide derivative (diphenylurea, mp 246°). Phosgene could also be detected by its odor.

Dichloroacetyl chloride was also analyzed qualitatively and quantitatively by adding methyl alcohol to irradiated TCE to form the methyl ester and then using gas chromatography to separate and identify the ester. Mass spectrometry could also detect DCAC, but quantitative analysis was very poor.

Infrared analysis was used most successfully for the three products. A spectrum is shown in Figure 1. The 1070-cm<sup>-1</sup> peak (a C–H bending frequency) was used to analyze dichloroacetyl chloride quantitatively. The doublet (C==O stretch) at 1782 and 1812 cm<sup>-1</sup> could also be used since it followed Beer's law. However, phosgene also has a C==O peak at this frequency. This contribution from phosgene could be accounted for by making use of the constant ratio between the 1070 and 1782-1812-cm<sup>-1</sup> peaks of DCAC. The use of a standard solution of phosgene in TCE showed this procedure to be a valid analytical method for phosgene.

A strong infrared absorption at  $1354 \text{ cm}^{-1}$  also emerged when the purer batches of TCE were used. The fact that this peak was either absent or small during the earlier irradiations was attributed to an impurity. The  $1354\text{-cm}^{-1}$  peak has been assigned to trichloroethylene oxide by Derkosch, *et al.*,<sup>3</sup> who attribute this peak to a symmetrical ring pulsation and find that there is an accompanying peak at 962 cm<sup>-1</sup> due to a symmetrical ring deformation. This peak was highly evi-

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dent in those spectra where matched cells were used to eliminate the strong TCE absorptions below 1000  $\text{cm}^{-1}$ .

Nuclear magnetic resonance spectroscopy was of limited value because of the scarcity of H atoms. The simple spectra of three singlets at 6.48, 6.13, and 5.26 ppm were ascribed to TCE, DCAC, and TCE oxide, respectively. The peak at 5.26 ppm was deductively assumed to be TCE oxide. Some of the possible compounds in the mechanism were eliminated because they contained more than one hydrogen. Such compounds would have generated more than the one peak that was available for assignment.

Trichloroethylene oxide could not be determined directly because of the lack of the pure compound to use as a standard. Trichloroethylene oxide is not commercially available, and the many attempts to isolate the compound were unsuccessful. This compound was referred to (as trichloroethylene epoxide) in a report by Bertrand, et al.,<sup>4</sup> but the preparational details were not included. However, the TCE oxide yield could be determined by difference, using the total acidity produced by reacting the three products with water. Dichloroacetyl chloride and phosgene each produce 2 mol of acid (reactions 1 and 2), whereas TCE oxide can produce either 2 mol of acid (reaction 3a) or 3 mol of acid (via reaction 3b-according to the work of Frankel, et al.,<sup>5</sup> on tetrachloroethylene oxide). Using 2 mol as the basis of calculation, the total yield is made up of 56% TCE oxide, 31% DCAC, and 13% COCl<sub>2</sub>. These values were obtained from a number of runs using our purest TCE. Since the TCE oxide yields were much higher using relatively more pure TCE, there is the possibility that a larger fraction or even all of the radiation yield could consist of TCE oxide. Trichloroethylene oxide may isomerize to DCAC under certain conditions<sup>5</sup> and sometimes did so when irradiated samples were kept at elevated temperatures.

Product yields from the irradiation of trichloroethylene under vacuum were relatively small. The two major products were hydrogen chloride and chloroacetylene, each with a G value of about 0.25. This work under vacuum was not extended.

Acid Yields. Irradiation of trichloroethylene in the presence of oxygen produces very large amounts of acidic products. Figure 2 shows that the  $G(H^+)$  values are in the thousands, indicating a chain reaction. These are the total water-extractible acid yields that are produced by the following reactions

$$CHCl_2COCl + H_2O \longrightarrow CHCl_2COOH + HCl$$
 (1)

<sup>(3)</sup> J. Derkosch, E. Ernstbrunner, E. G. Hoffman, F. Osterreicher, and E. Ziegler, Monatsh. Chem., 98, 956 (1967).

<sup>(4)</sup> L. Bertrand, J. A. Franklin, P. Goldfinger, and G. Huybrechts, J. Phys. Chem., 72, 3926 (1968).

<sup>(5)</sup> G. M. Frankel, C. E. Johnson, and H. M. Pitt, J. Org. Chem., 22, 1119 (1957).

$$\operatorname{COCl}_2 + \operatorname{H}_2 O \longrightarrow 2\operatorname{HCl} + \operatorname{CO}_2$$
 (2)



Equation 3 is not balanced. The trichloroethylene oxide may partially isomerize and partially decompose to HCl,  $CO_2$ , and  $CO.^4$ 

The first two reactions were found to be rapid, whereas the third reaction occurs over a period of hours. In those samples in which both  $Cl^-$  and  $H^+$  were analyzed after a short  $H_2O$  shakeout (*i.e.*, only reactions 1 and 2 occurring) the  $H^+/Cl^-$  ratio was about 1.5:1. This ratio would be obtained from a dichloroacetyl chloride to phosgene yield ratio of 2:1, in general accord with later findings. It should be noted that the acid titration using phenolphthalein indicator did not include the  $CO_2$ . It was shown that the  $CO_2$  was removed in our procedure of shaking an acidic solution.



Figure 2. Total acid yield from trichloroethylene irradiated in the presence of oxygen.

Effect of Dose Rate. The  $G(\mathrm{H^+})$  value was 4600 at a dose rate of  $2.70 \times 10^{17} \mathrm{eV/(ml~min)}$  and 14,800 at a dose rate of  $2.33 \times 10^{16} \mathrm{eV/(ml~min)}$  (see Figure 2). Theoretical examination of the kinetics of a simple radiation-initiated chain reaction shows that the yield is inversely proportional to the square root of the dose rate. The dose rate dependence of the above values is to the -0.48 power. This very good agreement with theory shows that the radiation-induced oxidation is a normal chain reaction.

Effect of Temperature. The overall yields were sensitive to changes in temperature indicating that one of the reactions in the mechanism has a strong thermal dependence. Irradiations were made at -196 (frozen state) and at  $-70^{\circ}$  (liquid state). In both cases the total acid yields became almost negligible, about 1/100

of that at  $30^{\circ}$ . On the other hand, irradiations above room temperature showed increased yields as indicated in Table I.

Table I:	Effect of Temperature on Yields	
	Temp, °C	G(H *)
	30	4600
	47	5300
	71	6900
	87	8300

An Arrhenius plot of the above data generates an activation energy value of 2.2 kcal/mol. It is not known which reactions in the mechanism would have such an activation energy, although reactions 6, 7, or 8 are the most likely possibilities.

Effect of Inhibitor. Diisopropylamine is used as a stabilizer in trichloroethylene. Solutions of 0.05% of this compound in TCE were irradiated for various times. The acid yields were negligible at the relatively short exposure but continued to increase with increasing exposure. The diisopropylamine was found to function as a radical scavenger. Its concentration was very inadequate to neutralize the acid products. Its original effectiveness in prohibiting the chain reaction declines as it is decomposed by radiation.

Diphenylpicrylhydrazyl (DPPH) is used as a radical scavenger in radiation studies. A  $5 \times 10^{-3} M$  solution of DPPH in TCE was irradiated. There was no acid produced, adding confirmation to the presence of free radicals in the mechanism.

Postirradiation Effect and Mechanism. The radiation-induced oxidation of TCE exhibited a striking postirradiation effect. After the exposure periods, which varied from 10 min to 1 hr, the product yields continued to increase two- to fourfold over a period of days. Behavior of this type could only be attributed to the slow decomposition of a metastable intermediate. All of the analytical techniques described in the previous section were used in an attempt to identify the intermediate. Although these attempts were unsuccessful, information has been gathered about the system.

The intermediate is fairly stable in TCE at room temperature. The rate of product buildup, after irradiation, takes place over a period of days. At 85° the reaction is accelerated so that it is essentially complete in about 2 hr. The presence of oxygen is essential to this process. If the oxygen or air is evacuated from an irradiated sample, there is no further increase in products.

Experiments have shown that the concentrations of all three products continue to increase after the irradiation is stopped. None of the individual yields are enhanced at the expense of others. The mechanism will have to be consistent with this fact.

The mechanism believed most likely to be in accord with the experimental facts is the following.

$$C_2 H Cl_3 \longrightarrow Cl_{\cdot} + C_2 H Cl_2 \cdot \tag{4}$$

$$C_2HCl_3 + Cl \cdot \longrightarrow CHCl_2CCl_2 \cdot \tag{5}$$

$$\operatorname{CHCl}_2\operatorname{CCl}_2\cdot + \operatorname{O}_2 \longrightarrow \operatorname{CHCl}_2\operatorname{CCl}_2\operatorname{OO} \cdot$$
 (6)

 $2CHCl_2CCl_2OO \cdot \longrightarrow$ 

$$CHCl_2CCl_2OOCCl_2CHCl_2 + O_2 \quad (7)$$

$$CHCl_2CCl_2OO \cdot + CHCl_2CCl_2 \cdot \longrightarrow$$

$$CHCl_2CCl_2OOCCl_2CHCl_2$$
 (8)

$$CHCl_2CCl_2OOCCl_2CHCl_2 \rightleftharpoons 2CHCl_2CCl_2O \cdot (9)$$

$$CHCl_2CCl_2O \longrightarrow CHCl_2COCl + Cl$$
(10)

0

$$CHCl_2CCl_2O \longrightarrow ClHC \longrightarrow CCl_2 + Cl (11)$$

$$CHCl_2CCl_2O \longrightarrow CHCl_2 \cdot + COCl_2 \quad (12)$$

$$\operatorname{CHCl}_2 + 0.5O_2 \longrightarrow \operatorname{CO} + \operatorname{HCl} + \operatorname{Cl}$$
 (13)

Reactions 4 through 6 appear to be most reasonable and fairly well established by previous work in this general area.<sup>2,4,6</sup> References 4 and 6 report on the chlorinephotosensitized oxidation of trichloroethylene, whereas ref 2a and b are on the radiation-induced oxidation of tetrachloroethylene. The mechanism beyond reaction 6 is still questionable. Only one of the radiation reports<sup>2b</sup> even mentions a postirradiation effect, and no accounting is made for this effect in their mechanisms. Huybrechts,<sup>6</sup> on the other hand, using a gas phase chlorine-photosensitized reaction noted that some oxidation occurred after the light was switched off. This small fraction of the overall reaction was explained by reaction 9 occurring in the gas phase or on the walls. It was postulated that the bulk of the reaction took place by the combination of peroxy radicals to form alkoxy radicals. Also in this gas phase work, DCAC was the main product while TCE oxide and phosgene were only side products.

Although complete quantitative data on the kinetics of the postirradiation effect were not obtained, it was found that a larger fraction of the products were produced after short irradiation times than after long irradiation times. This implies that the concentration of the intermediate builds up to a steady state. The intermediate, which has been postulated to be the peroxide compound in reaction 9, would then decompose to yield additional products over a period of days at room temperature and much faster at elevated temperatures. These facts are in agreement with the postulated mechanism.

Identification of the peroxide would substantiate the mechanism. Although the intermediate is fairly stable, peroxides are difficult to analyze and attempts thus far have been unsuccessful.

Since this paper was submitted for publication, an abstract of a Russian report on the subject has appeared.<sup>7</sup> The authors studied the radiation chemical oxidation of TCE and analyzed the three products by gas chromatography. The TCE oxide was separated and identified. Its ir spectrum is shown, and the prominent peaks at 1350 and 970 cm<sup>-1</sup> correspond to those used in this work. A postirradiation effect was not mentioned and may have been missed because of their long irradiations and large conversions. This may account for a mechanism different from ours, but we cannot comment on this as we have been unable to obtain the original full publication.

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