# **Radiolysis of Chloroform Vapor.** Effects of Phase on the Arrhenius

## Parameters of the Hydrogen-Atom Abstraction Reaction of

## **Dichloromethyl Radicals with Chloroform**

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The products of the radiolytic decomposition of air-free CHCl<sub>s</sub> vapor are the same as those formed in the radiolysis of liquid CHCl<sub>s</sub>, except that CCl<sub>4</sub> is not formed in the irradiated vapor under conditions of these experiments. The effects of irradiation temperature on the rates of formation of major organic products are also the same as in the liquid phase. An interpretation of data based upon assumption of the homogeneous liquid phase radiolysis mechanism provides values of  $A/A_{\circ}^{1/2}$  and  $E - E_{\circ}/2$  for the reaction,  $CHCl_{2} + CHCl_{3} \rightarrow CH_{2}Cl_{2} + CCl_{3} \cdot$ , equal to 8.1 (±0.4)  $\times 10^{-10}$  (cc molecule<sup>-1</sup> sec<sup>-1</sup>)<sup>1/2</sup> and 6.4 ± 0.5 kcal mol<sup>-1</sup>, respectively. The cross-combination ratio for CHCl<sub>2</sub> and CCl<sub>3</sub> radicals is equal to 2.1 ± 0.1 at 79-100°. Estimates of absolute values of the Arrhenius parameters indicate that the activation energy of the abstraction reaction is the same in both phases, but that the frequency factor is an order of magnitude smaller in the liquid phase.

### Introduction

Although there is a considerable body of literature concerning reactions of fluoromethyl and fluorochloromethyl radicals,<sup>2</sup> information on the gaseous phase reaction kinetics of partially chlorinated methyl radicals is very limited and is currently confined to that presented in a report on the photochlorination of several partially chlorinated methanes.<sup>3</sup> This situation is understandable, because the direct photolysis of partially chlorinated analogs of convenient sources of methyl and fluoromethyl radicals does not produce partially chlorinated methyl radicals.<sup>4-7</sup> Similarly, empirical knowledge of the effects of phase on the Arrhenius parameters of elementary steps which have been shown to require thermal activation in the gaseous phase is almost nonexistent, although such effects have been a subject of interest for a half century.<sup>8-12</sup> This, too, is understandable, because although the apparently most promising techniques for study of such effects are those of the very active area of photochemistry, it has been difficult to identify photolytic systems in which the same primary processes and secondary reaction steps predominate in both liquid and gaseous phases. It appears that the photolysis of chloroform would satisfy this requirement, but there are, unfortunately, no reports on the photolysis of liquid chloroform, and only two cursory investigations of the direct photolysis of chloroform vapor have been reported, and these at a single temperature.<sup>13,14</sup> Results of earlier investigations<sup>15,16</sup> of the radiolytic decomposition of liquid chloroform suggested to the present authors that an examination of the radiolysis of chloroform vapor might provide estimates of the Arrhenius parameters of elementary reactions of CHCl<sub>2</sub> radicals in the gaseous phase and

thereby make possible a determination of the effects of phase on these parameters.

It has been shown that CHCl<sub>2</sub> and CCl<sub>8</sub> radicals are immediate precursors of all organic products of the radiolysis of liquid chloroform and that the observed dependence of their rates of formation upon temperature and dose rate is caused by competition between H-atom abstraction from chloroform by CHCl<sub>2</sub> radicals and radical combination steps.<sup>15,16</sup> Numerical solutions of the steady-state equations for the free radicals have led to estimates of the frequency factor and activation energy of the abstraction step in the liquid

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phase.<sup>16</sup> This article reports effects of temperature on the rates of formation of organic products in chloroform vapor exposed to 50-pkV X-rays. The results provide values of the radical cross-combination ratio and estimates of the Arrhenius parameters of the abstraction reaction in the gaseous phase and make possible a comparison of liquid and gaseous phase values of these parameters.

#### **Experimental Section**

Mallinckrodt AR grade chloroform was purified by means described previously.<sup>16</sup> Ohio Chemical and Surgical U.S.P. grade nitrous oxide was prepared for use as a dosimeter gas by successive trap-to-trap distillation at  $-196^{\circ}$  until mass spectrometric analysis indicated that oxygen had been reduced below the limit of detectability (ca. 0.1%). Pure, air-free samples of chloroform vapor were irradiated with X-rays from a Machlett OEG-60 X-ray tube operated at 35 mA and 50 kV. The irradiation vessel was a 500-ml spherical Pyrex flask; the X-rays were admitted through a thin dome shaped section blown in the wall of the flask. The temperature of the vessel and its contents was held constant within  $\pm 0.5^{\circ}$  during irradiations. Each vapor sample was irradiated for 1.00 hr. Yields of organic reaction products were determined quantitatively by gas chromatography, and the presence or absence of inorganic products was established as described previously.<sup>16</sup> Quantitative data reported below are averaged values of three or more replicate experiments.

The absorbed dose has been estimated from measured yields of  $N_2$  from the X-ray induced decomposition of  $N_2O$  in the irradiation vessel at 25°. The yield of  $N_2$  was observed to be directly proportional to the pressure of N<sub>2</sub>O between 47.6 and 1270 Torr.  $G(N_2)$  is equal to 10.0 molecules/100 eV under these conditions.<sup>17</sup> It has been assumed that the respective rates of energy dissipation per unit mass in CHCl<sub>3</sub> and N<sub>2</sub>O vapors bear the same proportionality to their respective photoelectric mass absorption coefficients. Atomic mass absorption coefficients have been evaluated by interpolating those of Berger<sup>18</sup> to the mean energy of the distribution (30 keV), and molecular coefficients have been equated with the mass fraction weighted sums of atomic coefficients. The absorbed dose has thereby been estimated to have been approximately  $5 \times 10^{17}$ eV/cc of chloroform vapor in each experiment. This datum is not directly relevant to the interpretation of results, but simply indicates that the 100-eV yields of products were equal within a factor of approximately two to those from the radiolysis of liquid chloroform<sup>15,16</sup> and that the vapor phase mechanism was of nonchain character.

#### Results

Products observed were those which are formed in the radiolysis of liquid chloroform above room temperature excepting  $CCl_4$  which was absent from the irradiated vapor samples. Time average rates of product formation at 79, 90, and 100° are presented in Table I. All data were obtained by irradiating chloro-

<b>Fable I:</b> Rates of Product Formation <sup>a</sup> in the Radiolysis of CHCl <sub>3</sub> Vapor			
		Temp, °C	
	79	90	100
$\rm CH_2 Cl_2$	$8.1\pm0.6$	$9.7\pm0.8$	$11.7 \pm 1.1$
$C_2H_2Cl_4$	$3.5 \pm 0.2$	$3.9\pm0.2$	$2.7\pm0.3$
C <sub>2</sub> HCl <sub>5</sub>	$16\pm1$	$17 \pm 1$	$16 \pm 1$
$C_2Cl_6$	$15 \pm 1$	$16 \pm 1$	$20\pm 1$

<sup>a</sup> Rates are expressed in units of molecules  $cc^{-1} \sec^{-1} \times 10^{-11}$ . Experimental uncertainties are average deviations from the means of three or more replicate experiments.

 $1.3 \pm 0.4$ 

 $1.3 \pm 0.3$ 

form vapor at a concentration equal to  $1.50 \times 10^{19}$ molecules cc<sup>-1</sup> for 1.00 hr. The fraction of chloroform converted to products in each experiment was less than 0.002. Measurements made in this laboratory by R. C. Bair have shown that the yield of each organic product was directly proportional to irradiation time at 0.50 and 1.00 hr, at this vapor concentration at temperatures up to 100°. It was observed that spontaneous thermal decomposition of pure, air-free chloroform vapor did not take place under conditions of experiments whose results are reported here. The presence of air was observed to greatly increase the variety of products and the rate of decomposition.

#### Discussion

 $C_2Cl_4$ 

The form of the effects of temperature is the same as that observed in the radiolysis of liquid chloroform at low dose rates.<sup>15,16</sup> These effects in the liquid phase have been shown to be quantitatively consistent with a homogeneous mechanism comprising the following steps.<sup>16</sup> There is no evidence for radical dispropor-

$$\operatorname{CHCl}_{3} \longrightarrow \operatorname{CHCl}_{2} \cdot , \operatorname{Cl} \cdot$$
 (1)

$$\operatorname{CHCl}_2 \cdot + \operatorname{CHCl}_3 \longrightarrow \operatorname{CH}_2 \operatorname{Cl}_2 + \operatorname{CCl}_3 \cdot$$
 (2)

$$Cl_{\cdot} + CHCl_{s} \longrightarrow HCl_{+} + CCl_{s}$$
 (3)

$$2CHCl_2 \cdot \longrightarrow C_2H_2Cl_4 \tag{4}$$

$$\operatorname{CCl}_3 \cdot + \operatorname{CHCl}_2 \cdot \longrightarrow \operatorname{C}_2 \operatorname{HCl}_5$$
 (5)

$$2\mathrm{CCl}_3 \cdot \longrightarrow \mathrm{C}_2\mathrm{Cl}_6$$
 (6)

tionation steps in either phase. Reaction 3 consumes all Cl atoms at  $0^{\circ}$  and above in the liquid phase. It is certain that it also does so in the vapor phase under conditions of these experiments as may be readily demonstrated with relative rate constant values from

 $1.1 \pm 0.4$ 

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earlier work<sup>3,19-22</sup> from which  $k_3$ , e.g., has been estimated to be of the order  $10^{-11}e^{-(3.3 \times 10^8)/RT}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>.

Detailed investigations of effects of temperature, dose rate, and the presence of free halogens in the radiolysis of liquid chloroform<sup>15,16</sup> have suggested that dichlorocarbene is the precursor of  $C_2Cl_4$  in the liquid phase *via* reactions 7 and 8, below

$$\operatorname{CCl}_2 + \operatorname{CHCl}_3 \longrightarrow \operatorname{C}_2 \operatorname{HCl}_5^*$$
 (7)

$$C_2HCl_5*$$
 $M$ 
 $C_2HCl_5$ 
 $C_2H$ 

as appears to be the case, as well, in the pyrolysis of chloroform vapor.<sup>23</sup> It has been observed that the rate of  $C_2Cl_4$  formation exhibits a pronounced positive temperature coefficient in the liquid phase<sup>15,16</sup> but is essentially independent of temperature in chloroform vapor. This difference might reasonably have been anticipated because reactions 9 and 10 must be much less effective in the vapor phase, in the absence of solvent cage effects and at a several hundredfold lesser chloroform concentration.

Measured rates of formation of CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>HCl<sub>5</sub>,  $C_2H_2Cl_4$ , and  $C_2Cl_6$  may be used variously to evaluate the cross-combination ratio for CHCl<sub>2</sub> and CCl<sub>3</sub> radicals and to estimate the activation energy of reaction 2 and the frequency factor of reaction 2 relative to that of reaction 4. Assuming time-independent rates of product formation the cross-combination ratio,  $k_5/(k_4k_6)^{1/2}$ , equals the ratio of the rate of pentachloroethane formation to the square root of the product of the rates of formation of tetrachloroethane and hexachloroethane and has been found to be equal to  $2.1 \pm 0.1$  and to be independent of temperature at 79-100°. This value is consistent with measured values for halogenated methyl radical pairs<sup>2</sup> and for small alkyl radical pairs in the gaseous phase.<sup>24,25</sup> Values of  $k_2(\text{CHCl}_3)/k_4^{1/2}$  are given by the ratio of the rates of formation of methylene chloride to the square root of the rates of formation of tetrachloroethane at 79, 90, and 100°. These values indicate that  $E_2 - E_4/2$  equals  $6.4 \pm 0.5$  kcal/mol. It follows that  $A_2/A_4^{1/2}$  is equal to  $8.1 \ (\pm 0.4) \ \times \ 10^{-10}$ (cc molecule<sup>-1</sup> sec<sup>-1</sup>)<sup>1/2</sup> and that  $k_2/k_4^{1/2} = 8.1 \ \times \ 10^{-10}$  $e^{-(6.4 \times 10^3)/RT}$  (cc molecule<sup>-1</sup> sec<sup>-1</sup>)<sup>1/2</sup> at 79–100°.

An estimate of the absolute value of  $k_2$  must depend either upon the single published estimate of  $k_4$  (4.2 ×  $10^{-12}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>)<sup>3</sup> or upon consideration of the probable value of  $k_4$  relative to  $k_6$  and the several quite different published estimates of  $k_6$ .<sup>3,22,26</sup> The best source of a reliable value of  $k_4$  relative to  $k_6$  appears to be data from the study of the direct photolysis of chloroform vapor reported by Semeluk and Unger.<sup>14</sup> These were measured under conditions which precluded occurrence of reaction 2 and which effected quantitative removal of Cl atoms by reaction 3 in the absence of primary photolytic rupture of the CH bond of CHCl<sub>3</sub>, thus causing formation of CHCl<sub>2</sub> and CCl<sub>3</sub> radicals at equal rates. Under these conditions the ratio of measured rates of tetrachloroethane and hexachloroethane was equal to  $k_4/k_6$ . These data indicate that  $k_4/k_6$  is equal to 1.3, in close agreement with hard-sphere collision theory estimates.<sup>27</sup> Assuming the value of  $k_6$ reported in ref 22 to be most nearly accurate and that  $k_4$  like  $k_6$  is independent of temperature,<sup>22,26</sup>  $k_2$  is represented most reliably by the expression,  $k_2 = 3 \times 10^{-15}e^{-(6.4 \times 10^4)/RT}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>. The probable uncertainty in  $A_2$  is a factor of two, up or down, based upon data of ref 26 or 3, respectively.

There are no other published estimates of the Arrhenius parameters of reaction 2 in the gaseous phase, and there are few estimated values for reactions of other halogenated methyl radicals with chloroform. Available information indicates that the frequency factor and activation energy of the reaction

$$CF_3 \cdot + CHCl_3 \longrightarrow CHF_3 + CCl_3 \cdot$$
(11)

are approximately equal to  $A_2$  and  $E_2$ , respectively.<sup>28,29</sup>  $A_{11}$  appears to lie between (0.6 and 5)  $\times 10^{-14}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>, and  $E_{11}$  lies near 6.3 to 6.6 kcal/mol.

It has been estimated<sup>16</sup> that in liquid chloroform,  $k_2 = 2 \times 10^{-16} e^{-(6.7 \times 10^8)/RT}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>, an absolute value which is subject to the same kinds of uncertainties as the gaseous phase value, but which can reasonably be expected to be better than an order of magnitude estimate. Pending future independent determinations, it may be tentatively concluded that  $E_2$  is independent of phase, but that  $A_2$  is an order of magnitude smaller in the liquid phase. For diffusion-limited reactions, such as radical combination steps, rate constants are, of course, markedly smaller in the liquid phase. For reactions which have significant activation energies in the gaseous phase, however, there is simply not sufficient experimental information to establish an empiri-

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cal rule. Excepting the present instance and, possibly, the cases of dimerization and reverse dissociation of cyclopentadiene, for which the respective liquid and gaseous phase A and E values seem to be roughly equal,<sup>12</sup> there are no available data concerning effects of phase

on the Arrhenius parameters of an elementary reaction which requires thermal activation in the gaseous phase.

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## **Reactions of Electrons and Free Radicals in Glassy Ethanol**<sup>1</sup>

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Experiments designed to increase understanding of the mechanisms of trapping and reaction of electrons and free radicals in  $\gamma$ -irradiated glassy ethanol at 77°K are reported. They show that the concentration of electrons grows with increasing  $\gamma$  dose to a maximum at  $6 \times 10^{20}$  eV g<sup>-1</sup> and then decreases, accompanied by a decrease in G(free radicals). Free radicals are produced during thermal decay of trapped electrons, as well as by photobleaching. There is a blue shift in the optical absorption spectrum ( $\lambda_{max}$  535 nm) of trapped electrons during thermal decay and also during photobleaching with 650-nm radiation, but not with 540 nm. Prolonged annealing of C<sub>2</sub>H<sub>5</sub>OH glass at 90°K prior to  $\gamma$  irradiation alters the available trapping sites in such a manner that the trapped electron spectrum is shifted to the red, the yield is reduced, and the decay rate is increased. CH<sub>3</sub>CHOH radicals produced in the radiolysis decay by second-order kinetics. Parallel growth and decay of the esr free-radical signal and absorption at 200 nm are consistent with the conclusion that the latter is in part attributable to free radicals.

#### Introduction

The concentration of trapped electrons produced in hydrocarbon glasses by  $\gamma$  irradiation increases to a maximum and then decreases to zero with increasing  $\gamma$ dose.<sup>2</sup> This phenomenon is attributed to competing reactions involving free radicals and trapped and mobile positive charge and electrons.<sup>2b</sup> It does not occur in solid alcohols<sup>3</sup> at the doses thus far reported.<sup>4</sup> This may be because the polarity of the matrices increases the trapping probability for electrons and positive charge in such a way as to allow a higher concentration to be achieved than in hydrocarbons before neutralization processes and reaction of electrons with radicals compete effectively. In the work of the present paper we have tested higher  $\gamma$  doses with ethanol and isobutyl alcohol glasses. Secondly, we have sought clarifying evidence as to whether the thermal decay of trapped electrons in ethanol glass generates free radicals as does photobleaching<sup>5,6</sup>—a question on which differing opinions have been advanced.<sup>4a,5b,6</sup> We have also obtained information on the correlation between the uv absorption of  $\gamma$ -irradiated ethanol glass and the CH<sub>3</sub>CHOH esr signal, the kinetics of CH<sub>3</sub>CHOH decay, and the effect of annealing at 90°K on the trapping capability of ethanol glass at 77°K.

#### **Experimental Section**

Absolute ethanol was further purified by refluxing with 2,4-dinitrophenylhydrazine to remove aldehydes and ketones and by distillation, following which it showed less than 0.25% impurity by gas chromatography. It was allowed to react with sodium and distilled before introduction to the vacuum line where it was degassed and stored over sodium prior to distillation into the reaction cell. Isobutyl alcohol was purified by preparative gas chromatography to >99.6% purity,

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