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## The Kinetics of the Vapor Phase Exchange of Radioactive Bromine between Trichlorobromomethane and Bromine

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The rate of exchange of radioactive bromine between trichlorobromomethane and bromine in the vapor phase in the temperature range 420–455°K has been determined. The rate is equal to  $k[\text{Br}_2]^{\frac{1}{2}}[\text{CCl}_3\text{Br}]$ , where  $\log_{10}k(\text{moles/liter})^{-\frac{1}{2}}(\text{sec.})^{-1} = (-33,100(\pm 400))/(4.574T) + 12.75(\pm 0.20)$ . The energy of activation for the elementary reaction between bromine atoms and trichlorobromomethane molecules is 10.3 kcal., and the frequency factor is  $7.9 \times 10^{10}$ . It is proposed that the reaction proceeds via the sequence:  $\text{Br}^* + \text{BrCCl}_3 \rightarrow \text{BrBr}^* + -\text{CCl}_3$ , and  $\text{Cl}_3\text{C}- + \text{Br}_2^* \rightarrow \text{Cl}_3\text{CBr}^* + \text{Br}^*$ , rather than by a Walden inversion mechanism. The observation that chloroform is formed when hydrogen

bromide, bromine, and trichlorobromomethane are heated is cited as evidence for the presence of  $-\text{CCl}_3$  radicals and for the reaction  $\text{Cl}_3\text{C}- + \text{HBr} \rightarrow \text{Cl}_3\text{CH} + \text{Br}$ . The  $-\text{CCl}_3$  radical is then more stable than the  $-\text{CH}_3$  radical by 10 kcal. or more.

The vapor pressures of liquid trichlorobromomethane are given by the equation:  $\log_{10}p(\text{mm}) = (-8240/4.574T) + 7.64$ . The exchange reaction  $\text{Br}_2(\text{g}) + \text{AgBr}^* \rightarrow \text{Br}_2^*(\text{g}) + \text{AgBr}$  readily goes to completion and is the basis for a convenient semi-micro method for the preparation of radioactive elementary bromine.

### INTRODUCTION

THE investigation of the kinetics and mechanism of the exchange of radioactivity between atoms and molecules may be expected to contribute to an understanding of free radical reactions in general in much the same ways that the study of exchange reactions between ions and molecules in solution has contributed to the theory of ionic displacement reactions in organic chemistry.<sup>1</sup>

Wilson and Dickinson<sup>2</sup> observed a photochemically induced exchange between bromine and trichlorobromomethane in carbon tetrachloride solution at 76°C, suggesting that the exchange reaction is between bromine atoms and trichlorobromomethane molecules. In order to avoid the complications in the interpretation of photo-chemical reactions because of non-uniform intensity of light along the light path and because of uncertainties as to the rate of recombination of bromine atoms, we have chosen to investigate the thermal vapor phase exchange between bromine and trichlorobromomethane.<sup>3</sup>

Hodges and Miceli<sup>4</sup> have very briefly reported that the exchange between bromine and carbon tetrabromide in the gas or liquid phase proceeds by a bromine atom mechanism, and that the activation energy for the elementary reaction is 0–3 kcal.

### EXPERIMENTAL

#### (a) Preparation of Materials

The trichlorobromomethane was prepared by the reaction of carbon tetrachloride and aluminum bromide.<sup>5</sup> A sample boiling at 104.2°C at 745 mm was obtained by fractional distillation in an all-glass apparatus.

The vapor tensions of the substance were measured using a mercury manometer in a glass vacuum apparatus. These values,  $p(0^\circ) = 11 \pm 1$  mm,  $p(22^\circ) = 35 \pm 1$  mm,  $p(24^\circ) = 38 \pm 1$  mm, in conjunction with the boiling point at atmospheric pressure, imply the vapor pressure equation,  $\log_{10}p(\text{mm}) = (-8240)/(4.574T) + 7.64$ , and a Trouton constant of 21.8. The measured density of 1.99 g/ml at 25°C agrees with the literature values.

Hydrogen bromide was prepared by the reaction of hydrogen and bromine over a heated

\* Contribution No. 1232 from the Gates and Crellin Laboratories of Chemistry.

<sup>1</sup> L. P. Hammett, *Physical Organic Chemistry*, (McGraw-Hill Book Company, Inc., New York, 1940), p. 164.

<sup>2</sup> J. N. Wilson and R. G. Dickinson, *J. Am. Chem. Soc.* **61**, 3519 (1939).

<sup>3</sup> Just at the conclusion of our experimental work we learned that Professor J. Willard and Mr. A. Miller of the University of Wisconsin were independently engaged in a study of the same problem. *J. Chem. Phys.* **17**, 168 (1949).

<sup>4</sup> J. H. Hodges and A. S. Miceli, *J. Chem. Phys.* **9**, 725 (1941).

<sup>5</sup> H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.* **56**, 1456 (1934).

platinum filament, and purified by repeated bulb to bulb distillation in vacuum.

The radioactive isotope used was the 34.5-hr. Br<sup>82</sup>. It was prepared by irradiation of 12 liters of ethylene dibromide with neutrons from a 250-mc radon-beryllium source, extracted with 400 ml of water containing 20 mg of sodium bromide, and precipitated as silver bromide, which was washed and dried. Radioactive molecular bromine was obtained by the reaction:  $\text{AgBr}^* + \text{Br}_2 \rightarrow \text{AgBr} + \text{Br}_2^*$ . A quantity of 100–200 microliters of reagent grade bromine was distilled in vacuum into a Y-shaped vessel of ca. 50-ml volume containing the silver bromide. The tube was sealed off and heated to 160°C for several hours with occasional shaking. The radioactive bromine was then condensed in one arm of the tube. Under these conditions, there was 100 percent exchange of activity. Kolthoff and O'Brien<sup>6</sup> report 60 percent exchange between bromine vapor and freshly precipitated silver bromide at room temperature. This method of isolation on the semi-micro scale of radioactive bromine was selected and developed because of its convenience and because it was believed to be a method that was unlikely to introduce impurities, particularly the oxygen bearing impurities that are often troublesome in free radical chemistry.

#### (b) Procedure for the Exchange Reactions

Aliquots of Br<sub>2</sub><sup>\*</sup> (15–75 microliters) and trichlorobromomethane (100–300 microliters) were mixed in a test tube that could be attached to a vacuum apparatus by a ground joint. The mixture was distilled in vacuum through P<sub>2</sub>O<sub>5</sub> and condensed in liquid air with constant pumping, and then distilled into an evacuated reaction vessel of known volume. The reaction vessels had been treated with hot sulfuric acid-dichromate solution, rinsed with hot water, treated with boiling nitric acid, rinsed four times with boiling, distilled water, and outgassed by flaming in vacuum. The volumes (ca. 80 ml) of the reaction vessels were determined by observing the weights of water required to fill them to the seal-off constriction.

<sup>6</sup> I. M. Kolthoff and A. S. O'Brien, J. Chem. Phys. 7, 401 (1939).

The exchange reactions took place in the dark in an oil bath, the temperature being constant to  $\pm 0.07^\circ\text{C}$ . Temperatures were measured with a Chromel-Alumel thermocouple and a Leeds and Northrup portable precision potentiometer with a precision of  $\pm 0.05^\circ\text{C}$ . The thermocouple was calibrated against standard thermometers to an accuracy of 0.5°C.

In order to avoid possible photo-chemical exchange, reaction mixtures were stored in liquid air when not being handled. An experiment showed that there was no exchange in unheated reaction mixtures.

#### (c) Radio-Assay Procedure

After reaction, the bromine was extracted from the trichlorobromomethane with sodium nitrite solution. Mercurous bromide was precipitated from aliquots of the solution which contained an amount of bromide equivalent to 15 microliters of bromine. Reproducible counting samples were obtained by suction filtration of the precipitate through disks of S. and S. No. 576 filter paper mounted on a sintered glass plate. The area on which the smooth mercurous bromide mats were formed was defined with a glass tube pressed against the filter paper. In cases where analyses were run on two aliquots of the same solution, the results agreed within the statistical counting error, usually about 1 percent. The activity of the bromine before exchange was determined in the same way from solutions obtained by reducing measured volumes of the liquid radioactive bromine with sodium nitrite. That the transfer of bromine into the reaction vessels by distillation was quantitative was shown by radioactive assay of a reaction mixture which had not been heated.

#### (d) Chemical Analyses of Reaction Mixtures

For the semi-quantitative chemical analyses of the reaction products reported in the discussion, the components of reaction mixtures were separated and identified using a small glass column and the general type of vacuum techniques described by Stock<sup>7</sup> and Burg.<sup>8</sup>

<sup>7</sup> A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, Ithaca, 1933).

<sup>8</sup> A. B. Burg, J. Am. Chem. Soc. 56, 499 (1934).

TABLE I. Exchange reaction between Br<sub>2</sub> and CCl<sub>3</sub>Br.

Expt.		2 [Br <sub>2</sub> ] (moles/liter) × 10 <sup>3</sup>	[CCl <sub>3</sub> Br] × 10 <sup>3</sup>	<i>t</i> sec. × 10 <sup>-3</sup>	<i>T</i> °K	<i>x</i> <i>c</i>	<i>k</i> (expt.) (moles/liter) <sup>-1</sup> sec. <sup>-1</sup> × 10 <sup>3</sup>	<i>k</i> (calc.) × 10 <sup>3</sup>
1	a	6.77	33.45	194.3	419.10	0.282	2.98 ± .04	2.97
	b	6.38	31.60			0.286	3.00 ± .04	
	c	11.90	35.35			0.383	2.92 ± .08	
	d	11.57	34.30			0.382	2.99 ± .08	
2	a	7.71	35.65	36.0	432.00	0.427	9.18 ± .14	9.63
	b	6.55	11.30			0.730	10.05 ± .29	
3	a	7.30	36.05	36.1	433.80	0.346	11.30 ± .2	11.43
	b	12.42	36.85			0.457	11.09 ± .2	
	c	11.84	35.20			0.466	11.05 ± .3	
4	a	33.50	33.00	8.95	442.85	0.770	27.1 ± 1.3	25.1
	b	6.62	32.65			0.548	26.0 ± .6	
	c	6.59	32.50			0.534	27.2 ± .6	
	d	15.17	26.15			0.720	27.7 ± .8	
5	a	7.00	24.10	8.74	444.25	0.594	32.8 ± 1.0	28.2
	b	7.61	13.12			0.754	33.8 ± 1.5	
6	a	7.38	36.55	17.05	445.07	0.287	31.6 ± .4	30.3
	b	6.94	34.25			0.294	31.7 ± .4	
7	a	13.00	38.50	4.14	455.52	0.576	63.5 ± 1.4	71.4
	b	12.50	25.80			0.685	65.2 ± 1.9	
	c	10.15	34.95			0.535	70.1 ± 1.2	
8	a	6.58	32.50	7.08	455.75	0.312	72.8 ± 1.3	72.6
	b	6.82	32.70			0.310	73.3 ± 1.7	
	c	10.37	30.75			0.436	69.5 ± 1.3	
	d	12.42	36.80			0.408	71.1 ± 1.3	

## RESULTS AND DISCUSSION

## (a) Analysis of the Kinetic Data

An integrated form of the expression for the decrease of the activity of radioactive bromine due to exchange with trichlorobromomethane that is originally inactive is

$$\ln \left[ \left( \frac{a}{b} + 1 \right) \frac{c}{c - \frac{a}{b}} \right] = -R(a, b) \frac{a+b}{ab} t.$$

In this relation

- a* = concentration of elementary bromine, in units of atoms per unit volume,  
*b* = concentration of trichlorobromomethane,  
*c* = initial activity of bromine,  
*x* = activity of bromine after reaction for time *t*, and  
*R*(*a*, *b*) is the rate of exchange.

This result is a consequence of the general analysis due to McKay<sup>9</sup> of the rate of exchange between two components in chemical equilibrium.

We have tested the hypothesis that the exchange is a reaction between bromine atoms in thermal equilibrium with bromine gas and trichlorobromomethane molecules, i.e., *R*(*a*, *b*) = *k* × (*a*/2)<sup>1/2</sup>. Table I exhibits the analysis of the experiments on this basis. It is evident, particularly from experiments 2, 4, 5, that the rate constant derived in this way is essentially constant for fivefold and threefold variations in the

concentrations of bromine and trichlorobromomethane, respectively.

An experiment in a vessel packed with glass beads, in which the surface area was *ca.* 12 times that in an unpacked vessel, established that the rate of reaction was not dependent on surface area; the rate constants of Table I refer to a homogeneous, gas phase reaction.

It was also established that there were no significant side reactions taking place. The following observations bear on this point:

(1) The weight of the mercurous bromide precipitate from a reaction mixture was the same within 2 percent as that from the unreacted bromine, and in agreement with the expected value. Thus, there was no consumption or formation of bromine during the reaction.

(2) A mixture of bromine and trichlorobromomethane at concentrations of 5.1 × 10<sup>-3</sup> and 17.5 × 10<sup>-3</sup> moles/liter, respectively, in a two-liter bulb was heated to 456°K for a time such that more than 75 percent of the trichlorobromomethane would have undergone exchange. After extraction of the bromine, the organic layer was dried and fractionally distilled in vacuum. The substance was pure trichlorobromomethane with the vapor pressures reported above; there was less than ½ percent CCl<sub>4</sub> or other more volatile products and less than 1 percent of less volatile products (CCl<sub>2</sub>Br<sub>2</sub>, C<sub>2</sub>Cl<sub>6</sub>). Distillation of a known mixture showed that less than ½ percent of carbon tetrachloride could be detected by this means.

The variation of *k* with temperature is described by the equation

$$\log_{10} k = (-33,120(\pm 400))/(4.574T) + 12.75(\pm 0.20).$$

The values of the parameters were obtained by a least squares analysis of the data of Table I. For this treatment it was assumed that the temperatures were known with certainty. The standard deviations in *k* given in the table were obtained from the assumption that the error was due to statistical error of counting by using an analysis of errors in an exchange reaction that will be published separately.<sup>10</sup> The comparison

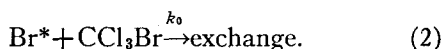
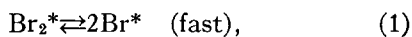
<sup>9</sup> H. A. C. McKay, *Nature* **142**, 997 (1938).

<sup>10</sup> N. Davidson and J. H. Sullivan, to be published.

of calculated and observed rate constants indicates that other sources of error were significant.

### (b) The Mechanism of the Reaction

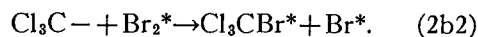
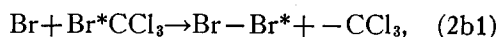
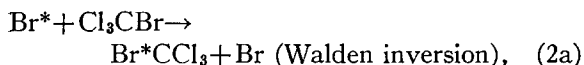
The dependence of the rate of exchange on concentrations implies that the exchange proceeds via the sequence:



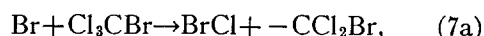
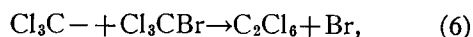
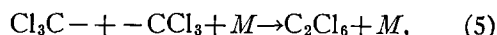
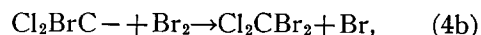
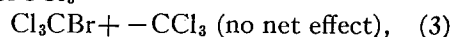
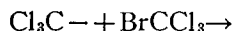
The bromine atoms liberated in reaction (2) are assumed to come rapidly into radioactive equilibrium with the rest of the elementary bromine. For  $k_0$ , the rate constant of the elementary reaction (2), we have  $k_0 = kK_c^{-1/2}$ , where  $K_c = [\text{Br}]^2/[\text{Br}_2]$  is the equilibrium constant (in concentration units) for the dissociation of bromine.

For reaction (1),  $\Delta H_{291^\circ\text{K}} = 46,110$  cal.,<sup>11</sup> taking  $\Delta C_p = 0.6$ ,<sup>12</sup>  $\Delta E_{435^\circ\text{K}} = 45,620$ . In addition,  $\Delta S_{298^\circ\text{K}} = 25.00$  e.u.,<sup>13</sup>  $\Delta S_{435^\circ\text{K}} = 26.00$  e.u. For the equilibrium constant of reaction (1) in a small temperature range around  $435^\circ\text{K}$ ,  $K_p = \exp(26.00/R) \times \exp(-(45,620 + RT)/(RT))$  and  $K_c = K_p/RT = (1/R \times 435^\circ) \exp((26.00 - R)/(R)) \exp(-45,620/RT) = (10^{3.69} \times 10^{-(45,620)/(4.574T)})$ . Since  $k_0 = kK_c^{-1/2}$ ,  $k_0 = 7.9 \times 10^{10} (\pm 0.20) \times 10^{-(10,310 (\pm 400))/(4.574T)}$  moles/liter  $\times$  sec. The activation energy of reaction (2) is 10,310 cal. The frequency factor corresponds to a mean collision diameter of 3.3Å. This frequency factor is but slightly larger than the value of  $ca. 3 \cdot 10^{10}$ , which holds for several similar reactions of bromine atoms as tabulated by Kistiakowsky and Van Artsdalen.<sup>14</sup>

The possible specific elementary exchange reactions are



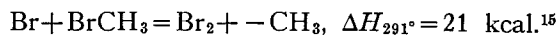
Other possible reactions of interest here are



The observation that there were no significant side reactions implies that reactions (4)–(7) are not of importance for the present research.

The heat of the Walden inversion reaction (2a) is zero, so that it is not impossible for it to have an activation energy of 10 kcal. However, there seem to be no certain examples of the Walden inversion type of reaction in the free radical reactions of organic compounds. There is no evident way of proving or disproving this mechanism except by the examination of all the other possible mechanisms.

The value of the C—H bond strength of methane of 102 kcal. determined by Kistiakowsky and Van Artsdalen (see reference 14, p. 478) implies that for the  $-\text{CH}_3$  radical,  $\Delta H(f)_{291^\circ\text{K}} = 32$  kcal.<sup>15</sup> For the reaction of methyl bromide analogous to (2b):



If the reaction scheme (2b) is responsible for the exchange, the C—Br bond in trichlorobromomethane must be at least 11 kcal. weaker than the C—Br bond of methyl bromide. Nevertheless, the experiment described below strongly supports the hypothesis that the exchange proceeds via this mechanism.

Braunworth and Schumacher<sup>16</sup> have studied the photo-chemical bromination of chloroform. The following reactions were of importance in

<sup>11</sup> F. R. Bichowsky and F. D. Rossini, *The Thermodynamics of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

<sup>12</sup> G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 80.

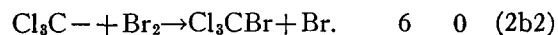
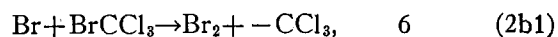
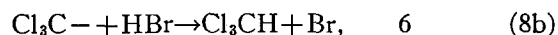
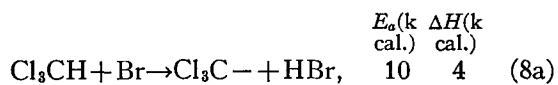
<sup>13</sup> K. K. Kelley, *The Entropies of Inorganic Substances* (1940), Bulletin 434 of the United States Department of the Interior, Bureau of Mines.

<sup>14</sup> G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 475 (1944), Table V. (The values of  $A$  in Table V should be multiplied by  $(575)^{1/2}/1000$  to make them comparable to the frequency factor quoted here.)

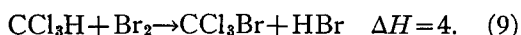
<sup>15</sup> Using the values for the heats of formation of  $\text{CH}_4$ ,  $\text{H}$ ,  $\text{Br}$ ,  $\text{Br}_2$ , and  $\text{CH}_3\text{Br}$  given in reference 11.

<sup>16</sup> V. V. Braunworth and H. J. Schumacher, *Kolloid Zeits.* **89**, 184 (1939).

their discussion of the results:



Reactions (8a) and (2b2) are the direct sequence for the bromination. Reaction (8b) accounts for the inhibition of the reaction by hydrogen bromide, and reaction (2b1) for the inhibition of the reaction by trichlorobromomethane. The temperature coefficient of the rate of reaction gives the activation energy for reaction (8a). The values for (2b) were obtained from a study of the bromine sensitized photochemical oxidation of trichlorobromomethane.<sup>17</sup> The inhibiting effect of hydrogen bromide corresponded to a rate constant for reaction (8b) of *ca.*  $\frac{1}{10}$  that of (2b2); this ratio was independent of temperature, so that the activation energies of the two reactions must be the same. The values of  $\Delta H$  were obtained as differences of activation energies, they imply that



This conclusion that the bromination of chloroform is endothermic is somewhat surprising. Since the entropy of the reaction is probably quite small, it implies that the equilibrium in the reaction should lie largely to the left. Actually the reaction has been used for the synthesis of trichlorobromomethane in a sealed tube.<sup>18</sup>

The conclusions of Schumacher and Braun-

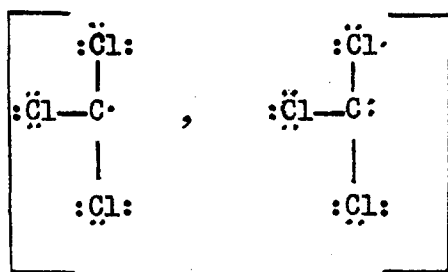


FIG. 1.

<sup>17</sup> W. Franke and H. J. Schumacher, *Zeits. f. physik. Chemie* **B42**, 297 (1939).

<sup>18</sup> E. Paterno, *Jahresb. Forts. Chemie* **24**, 259 (1871).

worth may not therefore be entirely correct. They contain, however, the interesting suggestion that reaction (8b) takes place at a rate comparable to that of (2b2) and that the formation of chloroform in the presence of hydrogen bromide be used to detect  $\cdot\text{CCl}_3$  radicals.

In an experiment in a two-liter flask the initial concentrations (in moles/liter) were:  $[\text{Br}_2] = 1.85 \times 10^{-3}$ ,  $[\text{HBr}] = 3.80 \times 10^{-2}$ ,  $[\text{CCl}_3\text{Br}] = 3.37 \times 10^{-2}$ . The mixture was heated to 460°K for a time of about a half-time for the exchange reaction of the trichlorobromomethane with bromine. After extraction of the hydrogen bromide and bromine, the organic layer was examined in a Beckmann infra-red spectrophotometer and by vacuum distillation.

The infra-red study revealed the absorption bonds of chloroform; the optical density of the  $3.3\mu\text{-CH}$  fundamental corresponded to a mole ratio of chloroform to trichlorobromomethane of 0.10. In the vacuum distillation, the only fractions isolated were chloroform and trichlorobromomethane in a mole ratio of 0.19. The chloroform was identified by its vapor tension; its vapor density corresponded to a molecular weight of 118.4 (th. 119.4).

The observation that the rate of formation of chloroform is comparable to the rate of the exchange reaction strongly suggests that the exchange proceeds via the reaction sequence (2b) involving the  $\cdot\text{CCl}_3$  radical. We are now engaged in a precise study of the kinetics of the formation of chloroform definitely to settle this point.

It is noteworthy that as part of the recent developments in free radical chain reactions in organic chemistry,  $\cdot\text{CCl}_3$  radicals, generated either from chloroform or from trichlorobromomethane, have been used as chain carriers.<sup>19,20</sup> The results of the present research suggest that the carbon bromine bond in trichlorobromomethane is weaker than the carbon bromine bond in methyl bromide. Braunworth and Schumacher's values for the activation energy and heat of reaction (8a) are much smaller than Kistiakowsky and Van Artsdalen's<sup>14</sup> values for

<sup>19</sup> M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.* **69**, 1100 (1947).

<sup>20</sup> M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.* **69**, 1105 (1947).

the corresponding reaction of methane, *viz.*,



There is, therefore, evidence that the carbon hydrogen bond in chloroform is weaker than the carbon hydrogen bond in methane. If it is in general true that the C—X bond in  $\text{CCl}_3\text{X}$  is weaker than the C—X bond in  $\text{CH}_3\text{X}$ , we may say that the  $-\text{CCl}_3$  radical is relatively more stable than the  $-\text{CH}_3$  radical. It may be that this is because of either: (a) steric repulsion of the chlorine atoms in  $\text{Cl}_3\text{CX}$  compounds, which is partly relieved in the  $\text{Cl}_3\text{C}-$  radical because the chlorine atoms are further apart; (b) reso-

nance stabilization involving the structures shown in Fig. 1.

This latter type of stabilization will be more important the more readily an electron can be removed from the ligands attached to the carbon. Judging from the present research, the extent of the stabilization of the  $-\text{CCl}_3$  radical is greater than 10 kcal.

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