Abstraction of Halogen Atoms by Methyl Radicals

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Previous work on the abstraction of chlorine atoms by methyl radicals has been extended to include the abstraction of bromine and iodine atoms, mainly from halogenated methanes. The results obtained for CF_3Br and CF_3I suggest that in general, $D(CF_3\text{–}X)$ is about 4 kcal/mole greater than $D(CH_3\text{–}X)$. Several new recombinations of methyl with halogenated methyl radicals in which elimination of HX occurs have been observed.

It was previously shown by Tomkinson, Galvin, and Pritchard[2] that reactions of the type

$$CH_3 + CCl_4 \longrightarrow CH_3Cl + CCl_3 \qquad (1)$$

could be conveniently studied using di-*t*-butyl peroxide as a thermal source of methyl radicals. The measured rate constants were related to that of the recombination reaction

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (2)$$

In the present work, rate constants for reactions of the type

$$CH_3 + RX \longrightarrow CH_3X + R \qquad (3)$$

were measured relative to the rate constants for reaction 1 by decomposing peroxide in the presence of mixtures of RX and CCl_4 and analyzing for the relative rates of formation of CH_3X and CH_3Cl, and so on.

Experimental Section

The experimental procedure was identical with that used previously[2] with the exception that analyses were performed using a vapor phase chromatograph instead of a mass spectrometer. Column packings, temperatures, and flow conditions were chosen to suit each particular determination (see ref 3 for full details).

Results

Since almost all the rate constants determined in this work are related to the previously measured rate constants for reaction 1, we felt it advisable to check the Arrhenius parameters for this reaction using chromatographic instead of mass spectrometric analysis. A least-squares Arrhenius plot on the results of 15 experiments carried out between 90 and 145° gave $E_1 - {}^1/_2E_2 = 12.4 \pm 0.8$ kcal/mole and $\log (A_1/A_2^{1/2})$ $(\text{ml}^{1/2}\ \text{mole}^{-1/2}\ \text{sec}^{-1/2}) = 6.5$. The activation energy obtained is not significantly different from that obtained previously, *viz*, 13.4 ± 0.8 kcal/mole (the error limits quoted in Table I of ref 2 were incorrect and should all have been about ± 0.8 kcal/mole). There is, however, a discrepancy of about a factor of 2.5 in the observed values of $k_1/k_2^{1/2}$ at any temperature; this may have arisen in the mass spectrometer calibration, since all the vpc calibrations were repeated and carefully rechecked, but unfortunately we could not confirm this because the mass spectrometer used was no longer operational. (The previous rate constants for C_2Cl_6 and CCl_3COCCl_3 were also too low by the same factor.) The mass spectrometer results were scaled by adding 0.415 to the $\log (k_1/k_2^{1/2})$ values, giving a homogeneous set of 28 points corresponding to $E_1 - {}^1/_2E_2 = 12.9 \pm 0.7$ kcal/mole and $\log (A_1/A_2^{1/2}) (\text{ml}^{1/2}\text{mole}^{-1/2}\text{sec}^{-1/2}) = 6.7$. In the new experiments, variations of about a factor of 5 in both the peroxide and the carbon tetrachloride concentrations were made without any effect on the observed rate constants. We also note in passing that ethylene is a by-product (*ca.* 0.5–1% yield) of the thermal decomposition of di-*t*-butyl peroxide, and in experiments where both the temperature and the halide concentration were high, the amount of ethylene formed was comparable to the ethane.

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[2] D. M. Tomkinson, J. P. Galvin, and H. O. Pritchard, *J. Phys. Chem.*, **68**, 541 (1964).

[3] Full details of all mixtures studied and analysis systems used are given by D. M. Tomkinson, Ph.D. Thesis, University of Manchester, 1965.

Initially, a survey of reactivities relative to CCl_4 at 130° was carried out by comparing various bromides with CCl_4. Then the reactivities of iodides and other chlorides were established by comparing these molecules with bromides.[3] A summary of the relative reactivities is shown in Table I, and it is clear that the trends are similar to those found in the liquid phase.[4] The third column of this table shows the reactivities of several hydrogen-containing iodides, but similar figures could not be obtained for chlorides and bromides because hydrogen abstraction was usually the dominant process.

Table I: Relative Rates[a] for the Reaction, $CH_3 + RX \rightarrow CH_3X + R$, at 130° in the Gas Phase

Chlorides		Bromides		Iodides	
$CFCl_3$	~0.1	CF_3Br	2	C_6H_5I	1.5
$CFCl_2CF_2Cl$	~0.1	CF_2Br_2	13	n-C_3H_7I	140
C_2Cl_4	~0.1	CF_2ClBr^b	17	sec-C_3H_7I	270
$C_6H_5CCl_3$	0.5	CCl_3Br^b	1000	CF_3I	2150
C_2Cl_6	0.7	$CCl_2Br_2^b$	2300	CH_2I_2	2800
CCl_4	1	CBr_4	4300		
CCl_3COCCl_3	5				
CCl_3CN^c	7				

[a] Per molecule, *not* per halogen atom. [b] Reaction of CH_3 radicals with these molecules individually does not produce detectable quantities of CH_3Cl. [c] Reaction of CH_3 radicals with CCl_3CN alone does not produce detectable quantities of CH_3CN.

Temperature coefficients were studied for a number of competing pairs of halides, and Arrhenius parameters, determined relative to that for CCl_4, are listed in Table II. Also shown in Table II is our reassessment of the previous results on hexachloroethane and hexachloroacetone, and a new determination for benzotrichloride. The most striking feature about the chlorides is the very close similarity between the activation energies for chlorine abstraction and the activation energies for hydrogen abstraction from the corresponding hydrocarbon. The pattern presented by the bromides is also reasonable, except perhaps the low figures for CF_2Br_2 (where complications could possibly arise owing to the stability of the CF_2 radical). The reactivity of CF_3I is reasonable in comparison with CF_3Br.

Dissociation Energies. Recently, Alcock and Whittle[5] have measured the activation energies of the two reactions

$$CF_3 + CH_3Br \longrightarrow CF_3Br + CH_3 \qquad E = 8.3 \pm 0.3 \text{ kcal/mole}$$

$$CF_3 + CH_3I \longrightarrow CF_3I + CH_3 \qquad E = 3.3 \pm 0.2 \text{ kcal/mole}$$

and our measurements show that the activation energies for the reverse reactions are

$$CH_3 + CF_3Br \longrightarrow CH_3Br + CF_3 \qquad E \simeq 12.5 \pm 1.0 \text{ kcal/mole}$$

$$CH_3 + CF_3I \longrightarrow CH_3I + CF_3 \qquad E \simeq 7.5 \pm 1.0 \text{ kcal/mole}$$

We conclude therefore that

$$[D(CF_3\text{–}Br) - D(CH_3\text{–}Br)] \simeq [D(CF_3\text{–}I) - D(CH_3\text{–}I)] \simeq 4 \text{ kcal/mole}$$

This result is consistent with the higher value for $D(CF_3\text{–}H)$ derived from chlorination and bromination studies on fluoroform[6] and supported by preliminary results from these laboratories on the iodination of fluoroform.[7] On the other hand, there is published evidence that $D(CF_3\text{–}X) \simeq D(CH_3\text{–}X)$ for X = iodine,[8] X = bromine,[9] and X = hydrogen,[10,11] some of which is not too easy to refute.

Elimination Following Radical Combination. Two products which are formed as a result of the thermal decomposition of di-*t*-butyl peroxide in the presence of carbon tetrachloride are large amounts of isobutylene oxide and some 1,1-dichloroethylene; at the same time, there was always more CH_4 than would have been formed by the decomposition of peroxide alone. The formation of these two molecules and the extra methane is consistent with the following set of reactions.

$$CH_3 + CCl_3 \longrightarrow CH_3CCl_3^* \qquad (4)$$

$$CH_3CCl_3^* + M \longrightarrow CH_3CCl_3^{\ddagger} \qquad (5)$$

$$CH_3CCl_3^{\ddagger} + M \longrightarrow CH_3CCl_3 \qquad (6)$$

$$CH_3CCl_3^{\ddagger} \longrightarrow CH_2CCl_2 + HCl \qquad (7)$$

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Table II: Arrhenius Parameters for the Gas Phase Reaction, $CH_3 + RX \rightarrow CH_3X + R$, over the Temperature Range 90–145°

Molecule	Reaction no.	Log A (ml mole^{-1} sec^{-1})[a]	E, kcal/mole
CCl_4	1	$^1/_2 \log A_2 + 6.7 \simeq 13.4$	$^1/_2E_2 + 12.9 \pm 0.7 \simeq 12.9 \pm 0.7$
CCl_3CN	3g	$\log A_{3d} - 0.3 \simeq 12.9$	$E_{3d} + 3.3 \pm 0.5 \simeq 10.4 \pm 1.0$
C_2Cl_6	1a	$^1/_2 \log A_2 + 5.1 \simeq 11.8$	$^1/_2E_2 + 10.1 \pm 0.9 \simeq 10.1 \pm 0.9$
CCl_3COCCl_3	1b	$^1/_2 \log A_2 + 5.9 \simeq 12.6$	$^1/_2E_2 + 9.7 \pm 0.8 \simeq 9.7 \pm 0.8$
$C_6H_5CCl_3$	1c	$^1/_2 \log A_2 + 3.6 \simeq 10.3$	$^1/_2E_2 + 7.6 \pm 0.8 \simeq 7.6 \pm 0.8$
CF_3Br	3a	$\log A_1 - 0.1 \simeq 13.3$	$E_1 - 0.4 \pm 0.5 \simeq 12.5 \pm 1.0$
CBr_4	3b	$\log A_{3f} + 0.4 \simeq 14.2$	$E_{3f} + 0.4 \pm 0.4 \simeq 7.9 \pm 1.1$
CCl_2Br_2	3c	$\log A_{3f} + 0 \simeq 13.8$	$E_{3f} + 0.1 \pm 0.4 \simeq 7.6 \pm 1.1$
CCl_3Br	3d	$\log A_1 - 0.2 \simeq 13.2$	$E_1 - 5.8 \pm 0.5 \simeq 7.1 \pm 0.9$
CF_2Br_2	3e	$\log A_1 - 2.4 \simeq 11.0$	$E_1 - 6.5 \pm 0.5 \simeq 6.4 \pm 1.0$
CF_3I	3f	$\log A_{3d} + 0.6 \simeq 13.8$	$E_{3d} + 0.4 \pm 0.4 \simeq 7.5 \pm 1.0$

[a] Per molecule, *not* per halogen atom.

The possible existence of such a reaction sequence was first investigated by Galvin and Pritchard[2,12]; however, the first authentic example was discovered by Pritchard, Venugopalan, and Graham,[13] and numerous other examples have been found since (see, *e.g.*, ref 5 and, 14–17).

However, all the HCl formed in reaction 7 will not remain in the system, as it will be readily attacked by methyl radicals, *i.e.*

$$CH_3 + HCl \longrightarrow CH_4 + Cl \qquad (8)$$

The principal fate of the chlorine atoms is that they abstract from the peroxide substrate, which is itself very resistant to methyl radical attack,[18] forming more HCl, more CH_4, etc. From the work of Hogg and Kebarle,[19] we know that under such conditions one of the major products of free-radical attack on di-*t*-butyl peroxide is isobutylene oxide—whereas in the thermal decomposition of the peroxide on its own, where the methyl radical concentration is maximal, only traces of isobutylene oxide are formed.

In addition to reaction 7, possible evidence was found for similar reactions as follows.

$$C_6H_5CCl_2CH_3^{\ddagger} \longrightarrow CCl_2CH_2 + C_6H_6$$

(formation of CCl_2CH_2)

$$CCl_2CNCH_3^{\ddagger} \longrightarrow CCl_2CH_2 + HCN$$

(formation of CCl_2CH_2)

$$CCl_2CNCH_3^{\ddagger} \longrightarrow CClCNCH_2 + HCl?$$

(formation of isobutylene oxide and methane)

$$CFCl_2CH_3^{\ddagger} \not\longrightarrow CCl_2CH_2 + HF$$

(absence of CCl_2CH_2)

$$CFCl_2CH_3^{\ddagger} \longrightarrow CFClCH_2 + HCl?$$

(formation of isobutylene oxide and methane)

$$CF_2ClCH_3^{\ddagger} \longrightarrow CF_2CH_2 + HCl?$$

(formation of isobutylene oxide and methane)

The system is too complicated for any quantitative information concerning these reactions to be obtainable.

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