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KINETICS OF THE ABSTRACTION OF H FROM CH_3GeCl_3, $(CH_3)_4Ge$ AND $(C_2H_5)_4Ge$ BY CF_3 AND C_2F_5 RADICALS

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Summary

The H abstraction by CF_3 and C_2F_5 radicals (produced from the photolysis of hexafluoroacetone and perfluoropropionic anhydride, respectively) from germanes has been studied in the gas phase. The Arrhenius parameters for CF_3 reactions, based on log k (cm^3 mol^{-1} s^{-1}) = 13.36 and $E = 0$ for the recombination reactions of CF_3 radicals, are:

Germane	log A (cm^3 mol^{-1} s^{-1})	E (kJ mol^{-1})
CH_3GeCl_3	12.08 ± 0.04	33.2 ± 0.3
$(CH_3)_4Ge$	11.55 ± 0.09	28.2 ± 0.6
$(C_2H_5)_4Ge$	11.95 ± 0.02	21.7 ± 0.2

while those for C_2F_5 reactions, based on log k (cm^3 mol^{-1} s^{-1}) = 13.40 and $E = 0$ for the recombination reactions of C_2F_5 radicals, are:

Germane	log A (cm^3 mol^{-1} s^{-1})	E (kJ mol^{-1})
CH_3GeCl_3	11.25 ± 0.07	29.4 ± 0.5
$(CH_3)_4Ge$	11.16 ± 0.06	25.5 ± 0.5
$(C_2H_5)_4Ge$	11.68 ± 0.03	21.2 ± 0.2

The relative reactivities of CF_3 and C_2F_5 are discussed, and interpreted in terms of their different electrophilicities.

Introduction

The kinetics of hydrogen atom abstractions by free radicals have been widely studied [1—5], but few studies have been made on molecules containing germanium [6—11]. Accordingly, we have studied the reactions of trifluoromethyl

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and pentafluoroethyl radicals with the structurally related compounds methyltrichlorogermane, tetramethylgermane and tetraethylgermane. The work was undertaken to extend knowledge of the Arrhenius parameters of such reactions and to enable comparisons to be made between the reactivities of CF_3 and C_2F_5 radicals.

Experimental

Materials

Methyltrichlorogermane, tetramethylgermane and tetraethylgermane were obtained from Alpha Inorganics Ventron, and were purified by low temperature distillation in a stream of dry nitrogen (20 kN m^{-2}) with rejection of large head and tail fractions. The collected fractions were stored below a greaseless tap and thoroughly degassed before use. Hexafluoroacetone (Matheson Gas Products) and perfluoropropionic anhydride (Fluorochem) were bulb to bulb distilled, degassed, and stored in a blackened vessel. Hexafluoroethane (Fluorochem), trifluoromethane (Matheson Gas Products), perfluorobutane (Fluorochem) and pentafluoroethane (Fluorochem) were thoroughly degassed and used for calibration of the gas chromatograph.

The purities of all materials were checked by gas chromatography. No impurities were observed.

Apparatus and procedure

The experimental procedure and apparatus were described previously [9,12]. The light source was a 125 W medium pressure mercury arc, and the output was filtered (using a Corning 053 filler, which transmits only 260 nm and longer wavelength mercury lines) only when hexafluoroacetone systems were photolysed. In all cases there was no decomposition of the germanium-containing compound when photolysed alone. No dark reaction occurred when a mixture of germane substrate with hexafluoroacetone or perfluoropropionic anhydride was heated over the temperature range involved in the kinetic studies.

The possible products of the abstractions reactions, CF_3H and C_2F_6 as well as C_2F_5H and n-C_4F_{10}, were analysed by gas chromatography on a 3.5 m column of 100—120 mesh activated alumina and a 1.5 m column of 60—80 mesh Poropak Q, respectively, maintained at 295 K. The calibration graphs of peak areas against micromole of gas were accurately linear in each case.

Carbon monoxide was separated from the reactant-product mixture by low temperature distillation at about 73 K, and measured in a Toepler-gas burette.

Results

Photolysis of hexafluoroacetone in the presence of germanes

The photolysis of hexafluoroacetone was used as a source of trifluoromethyl radical. Equation 1 adequately describes the process occurring [13]. Examination of the volatile products of reaction showed the presence of CO, C_2F_6 and

$$CF_3COCF_3 \xrightarrow{h\nu} 2\,CF_3 + CO \tag{1}$$

CF_3H when CF_3COCF_3 was photolysed in the presence of germane R'H: CH_3GeCl_3, $(CH_3)_4Ge$, and $(C_2H_5)_4Ge$. In our previous study [9] on the photolysis of CF_3COCF_3 in the presence of $HMCl_3$ (where M = C, Si, Ge) the same products were found to arise from the radical reactions.

The most probable source of CF_3H is the hydrogen abstraction reaction 2,

$$CF_3 + R'H \rightleftharpoons CF_3H + R' \tag{2}$$

while the C_2F_6 formation can be ascribed to reaction 3.

$$CF_3 + CF_3 \rightleftharpoons C_2F_6 \tag{3}$$

Making the assumption that CF_3H formation from CF_3 + R', a radical/radical disproportionation reaction, is negligible, we obtain from eq. 2 and 3 eq. 4,

$$\frac{R_{CF_3H}}{R_{C_2F_6}{}^{1/2}} = \frac{k_2}{k_3{}^{1/2}}\,[R'H] \tag{4}$$

where R_x denotes the rate of formation of product x in mol cm^{-3} s^{-1}, and R'H refers to the initial concentration of germane in mol cm^{-3}.

A test of eq. 4 was performed at different pressures of CH_3GeCl_3 at 478 K, $(CH_3)_4Ge$ at 392 K, and $(C_2H_5)_4Ge$ at 396 K. The experimental results are presented in Fig. 1, where $R_{CF_3H}/R_{C_2F_6}{}^{1/2}$ ratio is plotted against initial concentration of germane compounds.

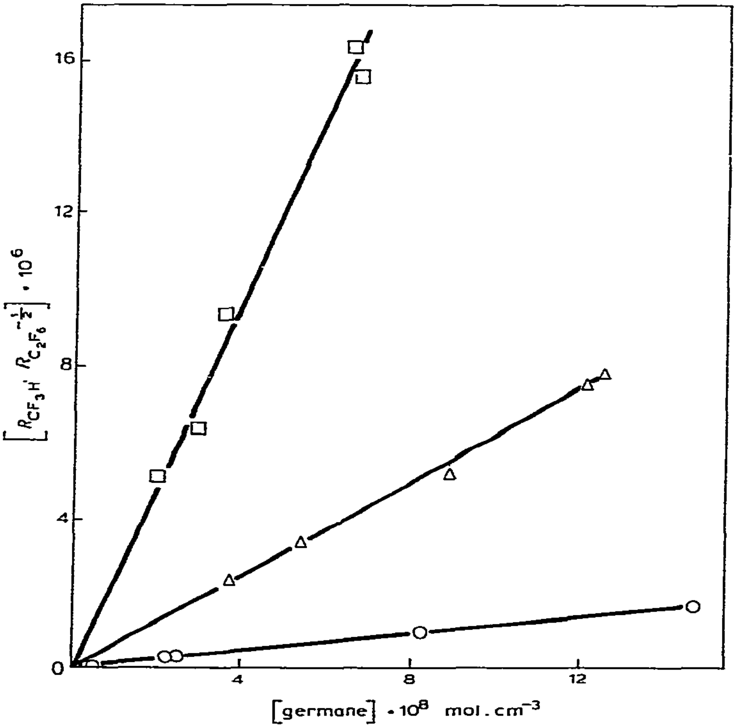

Fig. 1. Variation of $R_{CF_3H}/R_{C_2F_6}{}^{1/2}$ with initial concentration of germane. △ CH_3GeCl_3 at 478 K, ○ $(CH_3)_4Ge$ at 392 K, □ $(C_2H_5)_4Ge$ at 396 K.

TABLE 1

PHOTOLYSIS OF HEXAFLUOROACETONE IN THE PRESENCE OF GERMANES

Compound	Run	Temperature range ΔT (K)	Pressure range of R'H (kN m^{-2})	Pressure range of CF_3COCF_3 (kN m^{-2})	Reaction time range (s · 10^3)
CH_3GeCl_3	30	349—561	0.2—0.8	1.5—6.6	0.42—2.16
$(CH_3)_4Ge$	19	323—473	0.1—1.2	1.7—6.6	0.30—3.60
$(C_2H_5)_4Ge$	37	323—563	0.1—0.3	1.5—3.7	0.48—1.98

Straight lines passing through the origin were obtained, thus justifying the use of eq. 4. Variation of CF_3COCF_3 pressure had no effect on the $k_2/k_3^{1/2}$ ratio.

The results of the photolysis of hexafluoroacetone in the presence of germane are summarized in Table 1. The Arrhenius plots of log $k_2/k_3^{1/2}$ against $1/T$ are shown in Fig. 2. The Arrhenius parameters for the abstraction of hydrogen from CH_3GeCl_3, $(CH_3)_4Ge$ and $(C_2H_5)_4Ge$ by the trifluoromethyl radical were evaluated using the least-squares method. The results, summarized in Table 2, are based on log k_3 (cm^3 mol^{-1} s^{-1}) = 13.36 and $E_3 = 0$ for recombination of trifluoromethyl radicals [5].

Our Arrhenius parameters for the reaction of CF_3 with $(CH_3)_4Ge$ are in good agreement with those obtained by Bell and Platt [7].

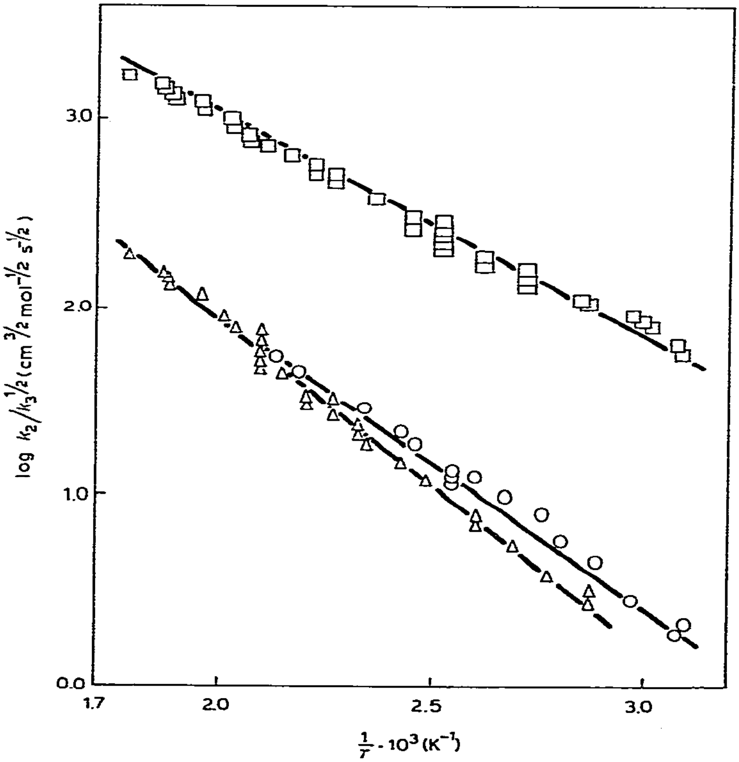

Fig. 2. Arrhenius plot for the H abstraction by CF_3 from △ CH_3GeCl_3, ○ $(CH_3)_4Ge$, □ $(C_2H_5)_4Ge$.

TABLE 2

ARRHENIUS PARAMETERS FOR ABSTRACTION OF HYDROGEN BY TRIFLUOROMETHYL RADICALS FROM GERMANES

Compound	Temperature range ΔT (K)	E (kJ mol^{-1})	log A (mol^{-1} cm^3 s^{-1})	log $k_{400\ K}$ (mol^{-1} cm^3 s^{-1})	log $k_{400\ K}$ per H-atom (mol^{-1} cm^3 s^{-1})
CH_3GeCl_3	349—561	33.2 ± 0.3	12.08 ± 0.04	7.75	7.27
$(CH_3)_4Ge$	323—473	28.2 ± 0.6	11.55 ± 0.09	7.84	6.76
$(C_2H_5)_4Ge$	323—563	21.7 ± 0.2	11.95 ± 0.02	9.12	7.82

Photolysis of perfluoropropionic anhydride in the presence of germanes

Chamberlain and Whittle [14,15] have shown that the photolysis of perfluoropropionic anhydride is a useful source of C_2F_5 radicals, its photodecomposition being described by the overall reaction 5.

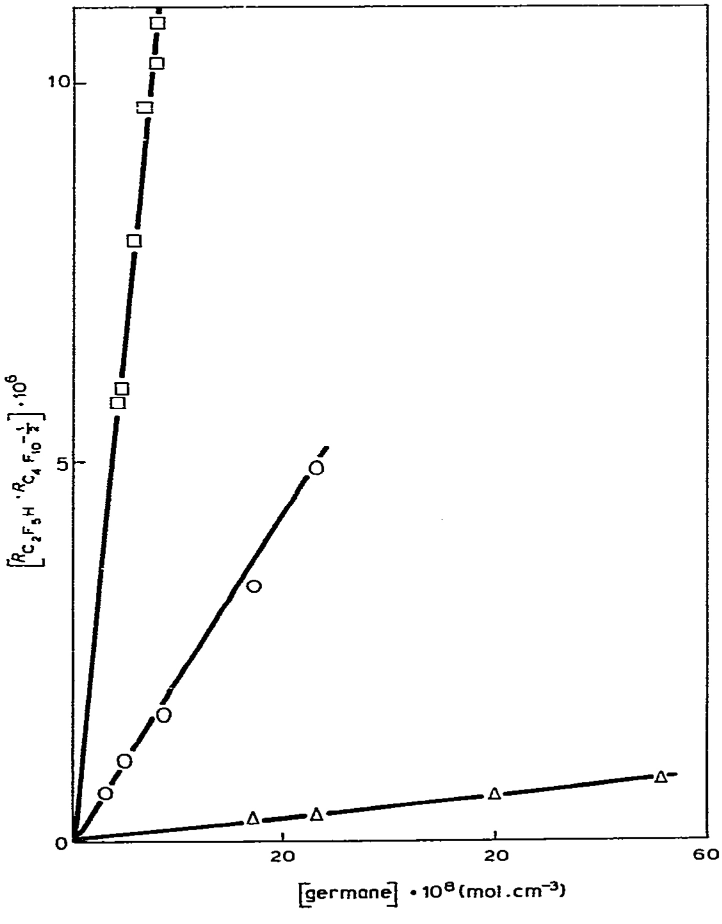

Fig. 3. Variation of $R_{C_2F_5H}/R_{C_4F_{10}}^{1/2}$ with initial concentration of germane. △ CH_3GeCl_3 at 354 K, ○ $(CH_3)_4Ge$ at 424 K, □ $(C_2H_5)_4Ge$ at 385 K.

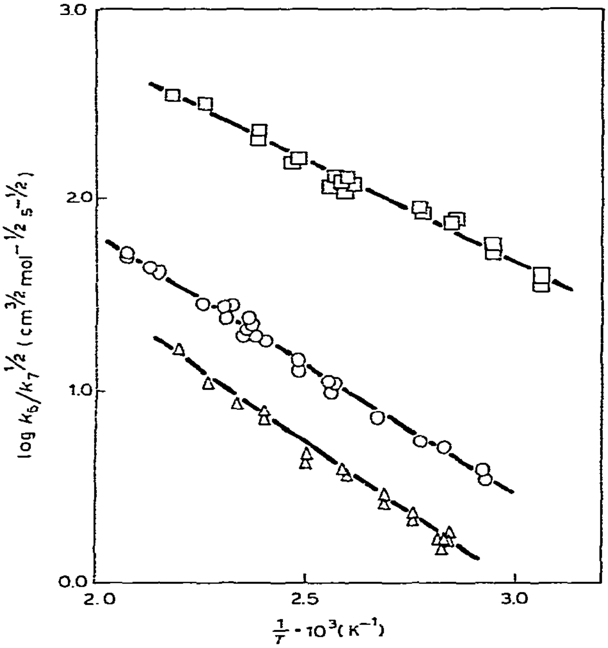

Fig. 4. Arrhenius plot for H abstraction by C_2F_5 from △ CH_3GeCl_3, ○ $(CH_3)_4Ge$, □ $(C_2H_5)_4Ge$.

$$(C_2F_5CO)_2O \xrightarrow{h\nu} CO + CO_2 + 2\,C_2F_5 \qquad (5)$$

If germane (R'H) is present, some expected reactions are eq. 6 and 7, and eq. 8 follows, where R_x is the rate of formation of product x in mol cm^{-3} s^{-1}, and

$$C_2F_5 + R'H \rightarrow C_2F_5H + R' \qquad (6)$$

$$C_2F_5 + C_2F_5 \rightarrow \text{n-}C_4F_{10} \qquad (7)$$

$$\frac{R_{C_2F_5H}}{R_{C_4F_{10}}^{1/2}} = \frac{k_6}{k_7^{1/2}}\,[R'H] \qquad (8)$$

R'H denotes the initial concentration of germane in mol cm^{-3}.

A test of eq. 8 was performed at various pressures of CH_3GeCl_3 at 354 K, $(CH_3)_4Ge$ at 424 K, and $(C_2H_5)_4Ge$ at 385 K, and the results are shown in

TABLE 3

PHOTOLYSIS OF PERFLUOROPROPIONIC ANHYDRIDE IN THE PRESENCE OF GERMANES

Compound	Run	Temperature range ΔT (K)	Pressure range of R'H (kN m^{-2})	Pressure range $(C_2F_5CO)_2O$ (kN m^{-2})	Reaction time range (s · 10^3)
CH_3GeCl_3	18	351—455	0.5—1.2	0.6—2.2	0.90—3.60
$(CH_3)_4Ge$	25	342—481	0.1—1.0	0.5—2.0	0.60—1.50
$(C_2H_5)_4Ge$	21	328—457	0.1—0.3	0.5—1.5	0.42—0.90

TABLE 4

ARRHENIUS PARAMETERS FOR ABSTRACTION OF HYDROGEN BY PERFLUOROETHYL RADICALS FROM GERMANES

Compound	Temperature range ΔT (K)	E (kJ mol^{-1})	log A (mol^{-1} cm^3 s^{-1})	log $k_{400\,\mathrm{K}}$ (mol^{-1} cm^3 s^{-1})	log $k_{400\,\mathrm{K}}$ per H-atom (mol^{-1} cm^3 s^{-1})
CH_3GeCl_3	351—455	29.4 ± 0.5	11.25 ± 0.07	7.41	6.93
$(CH_3)_4Ge$	342—481	25.5 ± 0.5	11.16 ± 0.06	7.83	6.75
$(C_2H_5)_4Ge$	328—457	21.2 ± 0.2	11.68 ± 0.03	8.91	7.61

Fig. 3. Variation of $(C_2F_5CO)_2O$ pressure over the range employed had no effect on $k_6/k_7^{1/2}$ ratio. A series of photolytic experiments were carried out for each of the germanes over a wide temperature range in order to determine the $k_6/k_7^{1/2}$ ratio. The results are summarized in Table 3. From a least-squares analysis of the data and assuming a value of log k_7 (cm^3 mol^{-1} s^{-1}) = 13.40 and $E_7 = 0$ for the recombination of perfluoroethyl radicals [5], Arrhenius parameters were derived for the H-abstraction from CH_3GeCl_3, $(CH_3)_4Ge$ and $(C_2H_5)_4Ge$ by C_2F_5 radicals. These are given in Table 4.

Discussion

The data in Table 2 and Table 4 show that the log A factor for the reactions of C_2F_5 radicals obtained in this study (~11.4) are a little lower than those obtained for a similar studies involving CF_3 radicals (~11.9). This may be due to the larger size of C_2F_5 radicals [16].

At 400 K, CF_3 and C_2F_5 radical attack on CH_3GeCl_3 is faster than on $(CH_3)_4Ge$ by a factor of 3.2 and 1.5 (relative reactivities per H atom) owing to a lowering in activation energy by 5.0 kJ mol^{-1} and 3.9 kJ mol^{-1}, respectively. At 400 K, CF_3 and C_2F_5 radical attack on $(C_2H_5)_4Ge$ is faster than on $(CH_3)_4$-Ge by a factor of 19 and 12, respectively. This is mainly due to a lowering in activation energy of 6.5 kJ mol^{-1} and 4.3 kJ mol^{-1} for CF_3 and C_2F_5 radicals, respectively. The differences in reactivity reflect differences in bond dissociation energies of the primary and secondary hydrogen atoms of the alkyl substituents. The Table 5 shows the differences in the Arrhenius parameters for the H abstraction from germane by CF_3 and C_2F_5 radicals.

Table 5 indicates that $E_{CF_3} > E_{C_2F_5}$ for the reaction with germanes. The dif-

TABLE 5

RELATIVE REACTIVITIES OF CF_3 AND C_2F_5 RADICALS $R + R'H \rightleftharpoons RH + R'$ (where $R = CF_3, C_2F_5$)

R'H	$E_{CF_3} - E_{C_2F_5}$ (kJ mol^{-1})	$A_{CF_3}/A_{C_2F_5}$	$k_{CF_3}/k_{C_2F_5}$
CH_3GeCl_3	3.8	6.76	2.19
$(CH_3)_4Ge$	2.7	2.19	1.02
$(C_2H_5)_4Ge$	0.5	1.86	1.62

ferences in the activation energy are similar to those for the H abstraction from methylfluorosilanes by CF_3 and C_2F_5 radicals [16,17]. Since the bond dissociation energies for CF_3—H and C_2F_5—H are 441 kJ mol^{-1} [18—20] and 424 kJ mol^{-1} [18], respectively, thus, the enthalpy differences between reactions of CF_3 and C_2F_5 radicals with any one germane or silane substrate is 17 kJ mol^{-1}. This enthalpy difference would imply that $E_{C_2F_5} > E_{CF_3}$, even if only a fraction of the enthalpy difference of 17 kJ mol^{-1} is reflected in the activation energy difference ($E_{C_2F_5} - E_{CF_3}$). However, since CF_3 and C_2F_5 radicals are polar and strongly electronegative [21], presumably their different electrophilicities account for the high relative reactivity of C_2F_5 radicals towards C—H bonds in the organogermanium compounds. Bell et al. [16,17] have shown the importance of polar effects in similar reactions with organosilanes. However, more kinetic data are required for the detailed analysis of these effects in organogermanium systems.

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