RADICAL RECOMBINATION REACTIONS PART II. TRIFLUOROMETHYL AND HEPTAFLUORO-*n*-PROPYL RADICALS^{1,2}

G. O. PRITCHARD,³ G. H. MILLER,³ AND J. R. DACEY⁴

ABSTRACT

Mixtures of hexafluoroacetone and perfluoro-di-*n*-propyl ketone were photolyzed, and the ratio of the rates of formation of the three fluorocarbons, $R_{C_4F_{10}}/R_{C_2F_6}^{1/2}R_{C_6F_{14}}^{1/2}$, was found to equal 1.77 ± 0.10 over a 107° temperature range.

INTRODUCTION

In this paper we are concerned with the photolytic cogeneration of CF_3 and C_3F_7 radicals in a gas-phase system, and the temperature dependence, if any, of the three recombination reactions:

$$CF_3 \cdot + CF_3 \cdot \xrightarrow{k_{1-1}} C_2F_6,$$
 [1-1]

$$CF_{3} \cdot + C_{3}F_{7} \cdot \xrightarrow{R_{1-2}} C_{4}F_{10}, \qquad [1-2]$$

$$C_3F_7 \cdot + C_3F_7 \cdot \xrightarrow{k_{2-2}} C_6F_{14}, \qquad [2-2]$$

with respect to each other.

In a steady-state condition we have

$$k_{1-2}/k_{1-1}^{1/2}k_{2-2}^{1/2} = R_{C_4F_{10}}/R_{C_2F_6}^{1/2}R_{C_6F_{14}}^{1/2},$$
 [I]

provided these reactions are the only sources of the three fluorocarbons.

At the pressures used there are no third-body restrictions affecting the recombinations, and the small temperature dependence associated with the collision number will cancel out in expression [I]. Thus any temperature variation of this ratio must be due to differing activation energies for one or all of the processes.

EXPERIMENTAL

The apparatus has essentially been described previously (1). The 3130-Å radiation was collimated by a single quartz lens and a stop, passed through a blue glass (Corning 9863), and into a 157-ml, cylindrical, 10-cm-long quartz reaction cell, fully illuminating it. The cell was surrounded by an outer steam jacket. Refluxing liquids used to attain temperatures other than 100° were xylene, 140°; o-dichlorobenzene, 180°; and tetralin, 207°.

The radical sources were the two ketones, $(CF_3)_2CO$ and $(C_3F_7)_2CO$, purified as described previously (2, 3). No detectable impurities were found in the mass spectra. Photolysis of the ketones individually in the temperature range of our experiments yields CO and the corresponding fluorocarbon in a 1:1 ratio via a free-radical mechanism (2, 3).

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| Contribution from the Chemistry Department, University of California, at Santa Barbara, Goleta, California, and the Chemistry Department, Royal Military College, Kingston, Ontario.

²For Part I of this series see reference 1. ³University of California. ⁴Royal Military College.

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A Toepler pump was attached to the reaction cell to ensure complete mixing of the ketones before irradiation. After photolysis, the CO was separated at -195° and measured in a gas burette. The remainder of the reaction mixture was condensed into a tube containing thoroughly outgassed distilled water. After the contents had warmed up, the tube was shaken vigorously and reattached to the vacuum system. Blank experiments showed that this procedure removed all of the $(CF_3)_2CO$ and most of the $(C_3F_7)_2CO$ as hydrates. C_2F_6 was then separated on Ward – Le Roy stills at -160° , and C_4F_{10} at -120° . The purity of all the products was checked mass spectrometrically. A fraction collected at -80° was slightly larger than that required by radical balance and contained C_6F_{14} and some unreacted $(C_3F_7)_2CO$. Perfluorohexane was identified unambiguously from the relative peak heights at masses 119 $(C_2F_5^+)$, 131 $(C_3F_5^+)$, and 169 $(C_3F_7^+)$ in the mass spectrum (4).

The ultraviolet spectrum of the heavier ketone was taken on a Cary Model 14 recording spectrophotometer. There is strong absorbance between 2500 and 3600 Å, with structure between 3000 and 3500 Å. The absorbance maximum is at 3130 Å; molar extinction coefficient 32.0 l. mole⁻¹ cm⁻¹. This is about four times as large as that for $(CF_3)_2CO$ at 3130 Å (2). Mixtures of the ketones gave additive spectra.

RESULTS

The data are collected in Table I. Due to the clear-cut nature of the photolysis mechanisms, C_6F_{14} has been calculated from $CO - (C_2F_6 + C_4F_{10})$. Consideration of runs 4 to 10 indicates the constancy of the ratio $k_{1-2}/k_{1-1}^{1/2}k_{2-2}^{1/2}$ over 107°, so that further experimentation did not appear worth while.

No experiments below 100° were envisaged due to the temperature and pressure dependence of the quantum yields, especially for $(CF_3)_2CO$, in this range. However, even at 100° in the early experiments (run 3 is given as an example), a suppression of CF_3 · products was found. Ratios deduced from them were not considered reliable due to the small amounts of C_2F_6 obtained. Runs 1 and 2 give data for the ketones when they were photolyzed separately. The percentage decompositions are in accord with the high-pressure quantum yields, 0.6 for $(CF_3)_2CO$ and 1.0 for $(C_3F_7)_2CO$ at 100°, and the enhanced absorbance of the heavier over the lighter ketone at 3130 Å. Examination of runs 3, 4, and 5 shows suppression of the $(CF_3)_2CO$ photodecomposition with increasing $(C_3F_7)_2CO$ concentration. This can only be due to the very efficient deactivation of the excited species $(CF_3)_2CO^*$ by the heavier ketone. As expected, this effect lessens with rising temperature.⁵ Decrease in the initial $(C_3F_7)_2CO$ concentrations enabled us to approximate to the ideal fluorocarbon product ratio of 1:2:1.

Percentage decompositions were calculated from the ratios $(C_2F_6 + \frac{1}{2}C_4F_{10})/(CF_3)_2CO$ and $[CO - (C_2F_6 + \frac{1}{2}C_4F_{10})]/(C_3F_7)_2CO$. On a time basis the latter are not entirely self-consistent as the voltage to the lamp was not stabilized. For the short period of a particular experiment constant light intensity can be assumed. In any case small sporadic intensity fluctuations are of no consequence. Expression [I] is not subject to stationary-state limitations, and will remain constant until either ketone is completely consumed. We conclude that expression [I] = 1.77 ± 0.10 .

⁵The other possibility of losing CF₃. products,

 $CF_3 \cdot + (C_3F_7)_2CO \rightarrow [CF_3(C_3F_7)_2CO \cdot] \rightarrow C_3F_7 \cdot + CF_3COC_3F_7,$

would lead to excess C_3F_7 products, which was not observed, and contrary to the experimental findings, the effect would increase with temperature as such reactions require an activation energy of about 6-7 kcal/mole (see reference 10).

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TABLE I

Run	Temp. (°C)	Time (sec)	Reactants (mole $cc^{-1} \times 10^6$)		Products (mole $\times 10^6$)			k_{1-2}	% decomposition		
			(CF ₃) ₂ CO	$(C_{3}F_{7})_{2}CO$	CO	C_2F_6	C_4F_{10}	C6F14	$k_{1-1}^{1/2} k_{2-2}^{1/2}$	(CF ₃) ₂ CO	$(C_3F_7)_2CC$
1	100	600	2.24	_	20.1	20.0	_			5.72	
2	100	300		1.38	46.7						21.6
3	100	150	4.30	1.89	32.9	0.64	4.90	27.4	1.17	0.47	10.0
4	100	150	4.81	0.687	19.7	6.10	9.16	4.44	1.76	1.41	8.36
5	100	150	4.38	0.860	26.3	1.95	9.26	15.1	1.71	0.96	14.6
6	100	600	2.06	0.430	58.6	5.85	24.1	28.7	1.86	5.54	60.3
7	140	300	3.65	0.543	38.1	6.57	17.5	14.0	1.82	2.67	26.7
8	180	150	2.15	1.29	25.9	1.24	8.05	16.6	1.78	1.56	10.2
9	180	300	4.81	0.637	50.1	13.3	23.2	13.6	1.73	3.30	25.2
10	207	300	3.61	0.668	46.6	11.7	21.6	13.2	1.74	3.97	23.0

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DISCUSSION

(a) Pre-exponential Ratios

Assuming identical activation energies and steric factors for radical recombination reactions we have $k_{1-2}/k_{1-1}^{1/2}k_{2-2}^{1/2} = Z_{1-2}/Z_{1-1}^{1/2}Z_{2-2}^{1/2}$. By simple collision theory this reduces to approximately 2 in radical-radical systems. (The picture is somewhat more complicated if disproportionation reactions occur.) Using $\sigma CF_3 \cdot = 4.0$ Å and $\sigma C_3F_7 \cdot = 6.5$ Å, we obtain 2.2.

Kerr and Trotman-Dickenson (5) have shown that the experimental values for the combination of unlike radicals, in many cases, lie close to 2, and are independent of temperature, indicating that combination occurs on every collision. Calvert (6) has pointed out while this may be so for simple alkyl radicals, it is not true where one of the radicals is highly polar as a potential barrier to recombination exists. In the $CH_3 + CF_3$ system (1) we noted a decreas from 3.0 to 1.8 over 140°, which was attributed to the polarity of the CF_3 radical, leading to a value of $E_{1-1} = 2$ kcal/mole. It has been pointed out (6, 7) that radicals formed in photolytic systems may not be thermally equilibrated, as evidenced in some cases by increasing disproportionation/recombination ratios with rising temperatures and falling pressure. If the disproportionation,

$$CF_3 \cdot + CH_3 \cdot \rightarrow CF_3H + CH_2 \cdot$$
,

occurred to a large extent, increasing with temperature, it could account for the observed decrease in $k_{1\cdot2}/k_{1\cdot1}^{1/2}k_{2\cdot2}^{1/2}$. There was no positive evidence for it (1); also, the reaction has not been suggested in other $CH_3 \cdot + CF_3 \cdot$ systems (8, 9). The polar effect appears to be real.

Data from other similar systems are scant, as the determination of expression [I] was not the objective of the experiments. For $C_2H_5 + C_3F_7$, it is 3.0, and admittedly scattered (5), and 2 ± 1 for $CH_3 + C_2F_5$ (10), both ratios being temperature independent. Other gas-phase values at room temperature are 2.2 for $CF_2Cl + CF_2ClCF_2$. (11) and 1.9 for $CF_2Cl + CFCl_2$. (12).

Polar effects are being further studied by the cophotolysis of $(CH_3)_2CO$ and $(C_3F_7)_2CO$; the results will be presented in a later publication.

(b) Activation Energies

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In the present system we have $E_{1\cdot 2} - \frac{1}{2}E_{1\cdot 1} - \frac{1}{2}E_{2\cdot 2} = 0$. The only reasonable assumption is that all three activation energies are equal. We may infer that there is a barrier to recombination of about 2 kcal/mole for all simple perfluoroalkyl radicals.

If we consider the system

$$X \cdot + R - H \rightarrow X - H + R \cdot$$
$$X \cdot + X \cdot \rightarrow X_{0}$$

where $X \cdot \text{ is } CF_3 \cdot, C_2F_5 \cdot, \text{ or } C_3F_7 \cdot, \text{ the activation energy of the first reaction will be determined mainly by the R—H and X—H bond strengths, and the repulsive forces between X \cdot and R—H, and X—H and R. (13). As the activation energy for the second reaction remains constant, we may assume that the repulsive forces in the first do not vary significantly with X \cdot. If <math>D(X$ —H) is constant, the activation energy should not vary with X \cdot .

Price and Kutschke (10) have summarized the available data for $CF_3 \cdot$, $C_2F_5 \cdot$, and $C_3F_7 \cdot$ radicals. For CH_4 we have the following $E - \frac{1}{2}E$ values (±0.5 kcal): 10.3, 10.6, and 9.5 kcal, and for H_2 : 8.8, 11.9, and 12.3 kcal. For $CF_3 \cdot$ and $C_3F_7 \cdot$ radicals only, we

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have for D_2 : 9.7 and 13.8 kcal, and for C_2H_6 : 7.5 and 9.2 kcal. However, the last figure may be high by 1–2 kcal (14). Some correlation does exist, although $CF_3 + H_2$ and CF_3 . $+ D_2$ are exceptions.

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