

cause of this, group rotation is less probable. Since the Stuart-Briegleb models indicate that steric hindrance to rotation of the acetyl groups should be low, it appears probable that the energy of resonance of the acetyl groups with the benzene ring is the main source of the hindering potential barriers. The large relaxation time  $\tau_1$ , presumably due to the over-all molecular rotation, is consistent with the size of the molecule, which is roughly the same as that of *p*-phenylphenol. The small relaxation time  $\tau_2$  for the acetyl group rotation is indistinguishable from those previously determined for this group.

**Energies of Activation.**—The free energies  $\Delta F^*$ , heats  $\Delta H^*$  and entropies  $\Delta S^*$  of activation for dielectric relaxation, calculated from values for  $\tau_1$  in the usual manner,<sup>20</sup> are given in Table IV. The second decimal place has no absolute significance but is retained for  $\Delta F^*$  as possibly showing trends with temperature.

It is to be noted that the values of  $\Delta H^*$  and  $\Delta S^*$  for *p*-phenylphenol and *p*-phenylacetophenone are very close to those for 2-naphthol and 2-acetonaphthone, respectively, and that the values of  $\Delta S^*$  for *p*-phenylacetophenone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl, where the acetyl groups are in similar environments, are practically indistinguishable from each other. For similar molecules, the values of  $\Delta H^*$  increase with increase of the molecular size. Thus

(20) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4102 (1948).

the values of  $\Delta H^*$  are 1.8 for 2-acetonaphthone, 2.0, for *p*-phenylacetophenone, 2.5 for 4-acetyl-*o*-terphenyl, 0.7 for 2-naphthol and 1.0 for *p*-phenylphenol. The values of  $\Delta H^*$  for the acetyl and hydroxy group rotations may be related to the resonance energy contribution by the groups to their respective molecules.<sup>13</sup> The  $\Delta H^*$  value, 1.5 kcal./mole, in Table IV for the acetyl group rotation is the energy barrier which the group encounters as it rotates. It is indistinguishable from the value previously determined for the acetyl group rotation in the 2-acetonaphthone and 4-acetyl-*o*-terphenyl molecules<sup>13</sup> and the value for the resonance energy contribution of 1 kcal. to the acetophenone molecule<sup>21</sup> by the acetyl group determined calorimetrically. The  $\Delta H^*$  value for the OH group rotation is calculated from the small relaxation times  $\tau_2$  for 2,6-dimethylphenol. It has been possible to obtain the small temperature dependence of the OH group relaxation time for this molecule because of the predominance of the intramolecular group relaxation mechanism. The zero value of  $\Delta H^*$  does not necessarily mean that the OH group makes no resonance energy contribution to the aromatic system. It only suggests that its resonance energy contribution is of the order of, or smaller than, the average kinetic energy,  $kT$ . This finding is again in accord with the resonance study made on phenol by calorimetry.<sup>21</sup>

(21) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 99.

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## Radical Recombination Reactions. III. Methyl and Heptafluoro-*n*-propyl Radicals

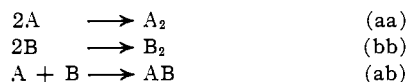
BY G. O. PRITCHARD, Y. P. HSIA AND G. H. MILLER

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The temperature dependence for the cross-combination ratio of the rate constants for  $\text{CH}_3$  and  $\text{C}_3\text{F}_7$  radicals is  $k_{ab}/(k_{aa}k_{bb})^{1/2} = 0.743 \pm 0.046 \exp(1440 \pm 50/RT)$  over the range 300 to 579°K. This is mainly due to the polar nature of perfluoroalkyl radicals, which results in a small potential barrier to their recombination.

### Introduction

Kerr and Trotman-Dickenson<sup>1</sup> have found that the ratio of the rate constants  $k_{ab}/(k_{aa}k_{bb})^{1/2}$  for the cross-combination radical reactions is close to 2.0 in many



gas-phase systems. This is the expected value, calculated from simple collision theory, for reactions with no activation energy, and it is suggested that the results are a strong indication that all the combinations occur on every collision. Calvert<sup>2</sup> has pointed out that although the data are convincing for non-polar radicals, for the case of combinations between highly polar radicals the rate of association may be appreciably slower. A small temperature dependence for the cross-combination ratio for  $\text{CH}_3$  and  $\text{CF}_3$  radicals has been observed,<sup>3</sup> which was ascribed to the polar nature of the  $\text{CF}_3$  radical, leading to an activation energy for  $\text{CF}_3$  radical recombination of approximately 2 kcal./mole. This interpretation gains support from the recent studies by Szwarc and his co-workers<sup>4</sup> on the photolysis of hexafluoroazomethane in iso-octane at

65°, which indicate a value of 1.5 kcal./mole for  $\text{CF}_3$  radical recombination. Kerr and Trotman-Dickenson<sup>1</sup> question the validity of the temperature dependence, but note that the high value of the ratio (3.2, and independent of the temperature) calculated by them from the results of Giacometti and Steacie<sup>5</sup> for  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{F}_7$  radicals is not unexpected for a case involving such a polar radical. (The inaccuracies in this determination will be discussed further.)

Subsequently in the system where  $A = \text{CF}_3$  and  $B = \text{C}_3\text{F}_7$  we obtained<sup>6</sup> a ratio of  $1.77 \pm 0.10$ , which was independent of temperature. This shows that  $E_{ab} = \frac{1}{2}(E_{aa} + E_{bb})$ , but the values are not necessarily zero, and that  $p_{ab} = (p_{aa}p_{bb})^{1/2}$ , but again not necessarily that the steric factors are all unity. For the recombination of  $\text{C}_3\text{F}_7$  radicals the value may be much less than unity.<sup>7</sup>

More recently, the possibility of a potential barrier to  $\text{CCl}_3$  radical recombination has been suggested by Johnston and Goldfinger<sup>8</sup> owing to the unfavorable orienting effect of permanent dipoles.

The present investigation is concerned with the cross-combination ratio for  $\text{CH}_3$  and  $\text{C}_3\text{F}_7$  radicals. These were produced by the co-photolysis of  $\text{CH}_3\text{COCH}_3$  and  $\text{C}_3\text{F}_7\text{CHO}$  in the region of 3130 Å. The photo-decomposition of acetone is well established, and that

(1) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," G. Porter, Editor, Vol. 1, Pergamon Press, New York, N. Y., 1961, pp. 109-110.

(2) J. G. Calvert, *Ann. Rev. Phys. Chem.*, **11**, 41 (1960).

(3) G. O. Pritchard and J. R. Dacey, *Can. J. Chem.*, **38**, 182 (1960).

(4) L. Herk, M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961); A. P. Stefani, L. Herk and M. Szwarc, *ibid.*, **83**, 4732 (1961).

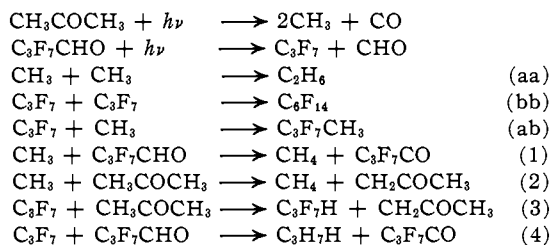
(5) G. Giacometti and E. W. R. Steacie, *Can. J. Chem.*, **36**, 1493 (1958).

(6) G. O. Pritchard, G. H. Miller and J. R. Dacey, *ibid.*, **39**, 1968 (1961).

(7) G. O. Pritchard, G. H. Miller and J. K. Foote, *ibid.*, **40**, 1830 (1962).

(8) H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37**, 700 (1962).

of heptafluorobutanal has been recently studied.<sup>7</sup> The reactions of interest are



It is assumed that the products  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{C}_3\text{F}_7\text{CH}_3$ ,  $\text{CH}_4$  and  $\text{C}_3\text{F}_7\text{H}$  are not formed in any reactions other than those given above.

### Experimental

The purification of materials and the apparatus have been described previously.<sup>3,7</sup> Transmitted light was reflected back into the cell by a polished aluminum reflector to promote radical-radical reactions.

$\text{CH}_4$ ,  $\text{CO}$  and traces of  $\text{H}_2$  (from formyl radical decomposition) were collected at  $-210^\circ$  and measured. The  $\text{CH}_4$  was estimated after oxidation of the  $\text{CO}$  and  $\text{H}_2$  in a  $\text{CuO}$  furnace at  $260^\circ$ , and its purity checked mass spectroscopically.  $\text{C}_2\text{H}_6$  was collected at  $-175^\circ$  and measured, and its purity was also checked periodically. The remainder of the reaction mixture was condensed onto a column of dry, out-gassed, 30–40 mesh firebrick, previously impregnated with an equal weight of concd.  $\text{H}_2\text{SO}_4$ . The column was allowed to warm to room temperature and left overnight. This procedure completely removed the undecomposed starting materials (or reduced them to trace quantities), which would have interfered with the subsequent analysis. Other carbonyl-containing substances formed in the photolysis are presumably also removed.

A fraction was then collected at  $-125^\circ$ . This was found to contain most of the  $\text{C}_3\text{F}_7\text{H}$  and approximately half of the  $\text{C}_3\text{F}_7\text{CH}_3$ . The  $\text{C}_3\text{F}_7\text{H}$  was estimated from the 51 ( $\text{CF}_2\text{H}^+$ ) ion-peak in the mass spectrum of the mixture, and the  $\text{C}_3\text{F}_7\text{CH}_3$  was obtained by difference, as a pure standard was not available.<sup>9</sup> The principal peaks in the mass spectrum of  $\text{C}_3\text{F}_7\text{CH}_3$  are given in Table I, as the previously published spectrum<sup>8</sup> is in error. These authors treated  $\text{C}_3\text{F}_7$  radicals with methane and collected  $\text{C}_3\text{F}_7\text{CH}_3 + \text{C}_3\text{F}_7\text{H}$  at  $-105^\circ$ . At this temperature some  $\text{C}_6\text{F}_{14}$  is also carried over; we have established this by distillation of mixtures of  $\text{C}_3\text{F}_7\text{H}$  and  $\text{C}_6\text{F}_{14}$  at  $-105^\circ$ , leading to an enrichment of the C- and F-containing ion-peaks in the mass spectrum of  $\text{C}_3\text{F}_7\text{H}$ .<sup>12</sup>

TABLE I  
MAIN PEAKS IN THE MASS SPECTRUM OF  $\text{C}_3\text{F}_7\text{CH}_3$

<i>m/e</i>	Ion	Rel. abundance	<i>m/e</i>	Ion	Rel. abundance
45	$\text{C}_2\text{F}_7\text{H}_2^+$	163	96	$\text{C}_3\text{F}_3\text{H}_3^+$	42
64	$\text{C}_2\text{F}_2\text{H}_2^+$	59	115	$\text{C}_3\text{F}_4\text{H}_3^+$	10
65	$\text{C}_2\text{F}_2\text{H}_3^+$	1000 <sup>a</sup>	119	$\text{C}_2\text{F}_5^+$	14
69	$\text{CF}_3^+$	79	150	$\text{C}_3\text{F}_6^+$	5
77	$\text{C}_3\text{F}_2\text{H}_3^+$	50	169	$\text{C}_3\text{F}_7^+$	7

<sup>a</sup> No isotope correction.

A final fraction (always smaller than the  $-125^\circ$  fraction) was collected at  $-80^\circ$  and measured. This contained  $\text{C}_6\text{F}_{14}$ , and the remainder of the  $\text{C}_3\text{F}_7\text{CH}_3$  and  $\text{C}_3\text{F}_7\text{H}$ .<sup>13</sup> The  $\text{C}_6\text{F}_{14}$  was estimated from the 169 ( $\text{C}_3\text{F}_7^+$ ) ion-peak, and the  $\text{C}_3\text{F}_7\text{H}$  from the 51 ( $\text{CF}_2\text{H}^+$ ) ion-peak.  $\text{C}_3\text{F}_7\text{H}$  and  $\text{C}_3\text{F}_7\text{CH}_3$  give small ion-peaks at mass 169, which was the reason for the separation of most of

(9) It is assumed that the cracking pattern of  $\text{C}_3\text{F}_7\text{CH}_3$  does not contribute significantly to the 51 ion-peak. Similar assumptions were made<sup>5</sup> in the analyses of  $\text{C}_3\text{F}_7\text{CH}_3 + \text{C}_3\text{F}_7\text{H}$  and  $\text{C}_3\text{F}_7\text{C}_2\text{H}_5 + \text{C}_3\text{F}_7\text{H}$  mixtures, and in  $\text{C}_2\text{F}_5\text{CH}_3 + \text{C}_2\text{F}_5\text{H}$  mixtures.<sup>10</sup> The 51 ion-peak in the mass spectrum of  $\text{CF}_3\text{CH}_3$  is very small.<sup>11</sup>

(10) S. J. W. Price and K. O. Kutschke, *Can. J. Chem.*, **38**, 2128 (1960).

(11) J. R. Majer, "Advances in Fluorine Chemistry," ed. by M. Stacey, J. C. Tatlow and A. G. Sharpe, Vol. 2, Butterworths, Washington, D. C., 1961, p. 60; W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3450 (1962).

(12) Due to this error, these results<sup>5</sup> are suspect, as  $\text{C}_6\text{F}_{14}$  was further determined by radical balance. This is especially so for the experiments involving  $\text{C}_3\text{F}_7$  radicals with ethane, where sizable amounts of  $\text{C}_3\text{F}_7\text{C}_2\text{H}_5$  were obtained and the radical balance procedures were complex.

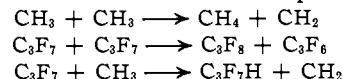
(13) In a previous method of separation<sup>7</sup>  $\text{C}_3\text{F}_7\text{H}$  was not found in this fraction, due to its volatility at  $-125^\circ$ . In separate experiments we found that some  $\text{C}_3\text{F}_7\text{H}$  was retained on the firebrick at  $-125^\circ$ . Experiments were also conducted to ensure the complete removal of the  $\text{C}_6\text{F}_{14}$  at  $-80^\circ$ .

the excess  $\text{C}_3\text{F}_7\text{H}$  at  $-125^\circ$ , when  $\text{C}_6\text{F}_{14}$  is involatile. Specimen sensitivities on the mass spectrometer for the 169 ion-peak were 18.35 units peak-height per micron for  $\text{C}_6\text{F}_{14}$  and 0.22 unit peak-height per micron for  $\text{C}_3\text{F}_7\text{H}$ . Based on the 65 ( $\text{C}_2\text{F}_2\text{H}_3^+$ ) ion-peak in the  $\text{C}_3\text{F}_7\text{H} + \text{C}_3\text{F}_7\text{CH}_3$  mixtures, a sensitivity value of 0.8 unit peak-height per micron for  $\text{C}_3\text{F}_7\text{CH}_3$  was obtained. These values did not change appreciably during the course of the work. The sample at  $-80^\circ$  was usually composed of about 25%  $\text{C}_6\text{F}_{14}$ , and <40% each of  $\text{C}_3\text{F}_7\text{H}$  and  $\text{C}_3\text{F}_7\text{CH}_3$ . With these mixtures, the correction to the  $\text{C}_6\text{F}_{14}$  (based on the 169 ion-peak) amounted to less than 10%.<sup>14</sup>

The  $\text{C}_3\text{F}_7\text{CH}_3$  in the  $-80^\circ$  fraction was found by difference, or from the estimated 65 ( $\text{C}_2\text{F}_2\text{H}_3^+$ ) ion-peak sensitivity; no disparity was found between the two methods.

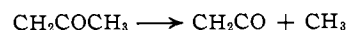
### Results

The relevant data are collected in Table II. Analysis for  $\text{CH}_4$  was not performed in all experiments. No evidence of products from the possible disproportionation reactions was found in this or previous work.<sup>3,6</sup>



and they are considered to be unimportant. Propane, which could arise from the insertion reaction between methylene and ethane, was not observed.

The tendency toward greater ethane yields at the higher temperatures may be roughly correlated with the increasing aldehyde decomposition, calculated from the expression  $(\text{C}_3\text{F}_7\text{H} + \text{C}_3\text{F}_7\text{CH}_3 + 2\text{C}_6\text{F}_{14})/(\text{C}_3\text{F}_7\text{CHO})_0$ . The initial concentrations of aldehyde and acetone were such that about 75% of the active incident radiation was absorbed; >50% of the absorption was due to the aldehyde (extinction coefficients, based on  $\log I_0/I = \epsilon cl$ , are 22.8 l. mole<sup>-1</sup> cm.<sup>-1</sup> for  $\text{C}_3\text{F}_7\text{CHO}$  (3190 Å.)<sup>7</sup> and  $\sim 2.5$  l. mole<sup>-1</sup> cm.<sup>-1</sup> for acetone in the 3130 Å. region<sup>15</sup>). The reduction in the intensity gradient and the increased reflection of transmitted light raises the over-all intensity at higher aldehyde decompositions, leading to increasing  $\text{CH}_3$  radical concentrations, and thus ethane yields.<sup>16</sup> Also, the consumption of  $\text{CH}_3$  by  $\text{C}_3\text{F}_7$  radicals is constantly reduced with the fall-off in the  $\text{C}_3\text{F}_7$  radical concentration. Finally, the production of the acetyl radical in reactions 2 and 3 increases with the temperature, and above  $250^\circ$  the reaction



may play an added role in producing  $\text{CH}_3$  radicals.<sup>17</sup>

As long as  $\text{CH}_3\text{COCH}_3$  and  $\text{C}_3\text{F}_7\text{CHO}$  have not been completely consumed, we may write  $R_{ab}/(R_{aa}R_{bb})^{1/2} = k_{ab}/(k_{aa}k_{bb})^{1/2}$  where  $A = \text{CH}_3$  and  $B = \text{C}_3\text{F}_7$ , and  $R$  denotes rate of formation. An Arrhenius plot of the data is given in Fig. 1 and compared with the corresponding line obtained in the  $\text{CF}_3 + \text{CH}_3$  radical system.<sup>3</sup> A least squares treatment gives  $k_{ab}/(k_{aa}k_{bb})^{1/2} = 0.743 \pm 0.046 \exp(1,440 \pm 50/RT)$ . If  $E_{ab} = E_{aa} = 0$ , we have  $E_{bb} = 2.9 \pm 0.1$  kcal./mole for  $\text{C}_3\text{F}_7$  radical recombination; this is probably a limiting value. As there are no third body restrictions in the system, all three activation energies are small and positive<sup>3</sup>; obviously all three cannot be identical, nor can they all be zero. If we assign the major cause of the temperature dependence to the  $\text{C}_3\text{F}_7$  radical recombination reaction, the polar effect is established.

One experiment was conducted at room temperature with 41.5 cm. of argon added, but no change in the

(14) A synthetic mixture containing 20.0%  $\text{C}_6\text{F}_{14}$  and 80.0%  $\text{C}_3\text{F}_7\text{H}$  analyzed on the mass spectrometer gave 19.9%  $\text{C}_6\text{F}_{14}$  and 80.0%  $\text{C}_3\text{F}_7\text{H}$  (20.5%  $\text{C}_6\text{F}_{14}$ , uncor.).

(15) J. Caldwell and D. E. Hoare, *J. Am. Chem. Soc.*, **84**, 3987 (1962).

(16) Based on blank experiments, the acetone photodecomposition was never more than about 10%. Photolysis of  $2.32 \times 10^{-6}$  mole/cc. for 1200 sec. at  $494^\circ\text{K}$ . yielded  $\text{CO} = 2.49 \times 10^{-7}$ ,  $\text{CH}_4 = 4.43 \times 10^{-7}$  and  $\text{C}_2\text{H}_6 = 1.56 \times 10^{-7}$  mole/cc.

(17) R. C. Ferris and W. S. Haynes, *J. Am. Chem. Soc.*, **72**, 893 (1950)

TABLE II

Time, sec.	Temp., °K.	Reactants, mole/cc. × 10 <sup>7a</sup>		Products, mole/cc. × 10 <sup>8a</sup>						decompn. %	$k_{ab}/(k_{aa}k_{bb})^{1/2}$	$k_2/k_{bb}^{1/2}$ , mole <sup>-1/2</sup> cc. <sup>1/2</sup> sec. <sup>-1/2</sup>	$k_1/k_{aa}^{1/2}$ , mole <sup>-1/2</sup> cc. <sup>1/2</sup> sec. <sup>-1/2</sup>
		[(CH <sub>3</sub> ) <sub>2</sub> CO] <sub>0</sub>	[C <sub>3</sub> F <sub>7</sub> CHO] <sub>0</sub>	CH <sub>4</sub>	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> F <sub>7</sub> H	C <sub>3</sub> F <sub>7</sub> CH <sub>2</sub>	C <sub>3</sub> F <sub>14</sub>				
920	300	55.9	15.4	17.5		0.396	2.49	5.11	1.74	7.40	6.22	0.499	....
1411	301	62.8	11.1	27.2		.267	2.20	3.53	0.698	6.50	8.16	.521	....
1260 <sup>b</sup>	302	57.4	11.6			.302	2.30	4.49	1.18	7.89	7.53	.540	....
1020	320	51.1	11.8	3.20	25.5	.449	2.96	4.95	1.01	8.41	7.35	.840	13.2
960	327	49.6	14.3	2.61	25.6	.700	1.87	3.37	0.294	4.25	7.43	1.02	7.15
660	328	56.8	13.8	22.9		.301	3.43	3.79	0.786	6.40	7.80	1.70	....
600	339	42.6	13.2	45.2		.264	3.40	3.54	1.35	7.30	5.93	1.32	....
1020	368	52.1	13.9	6.77	45.9	3.00	12.3	12.6	2.07	19.9	5.05	3.24	9.32
900	381	39.1	11.6	8.40	41.2	1.33	12.4	8.49	1.75	19.6	5.58	5.66	22.8
760	409	38.4	9.90	69.0		0.914	35.4	12.4	8.20	52.8	4.25	9.42	....
819	418	39.5	11.0			3.11	20.1	12.2	1.38	30.6	5.77	11.6	....
886	422	42.7	10.1	109		1.67	34.7	7.00	1.65	44.3	4.26	18.3	....
660	455	39.3	14.1	33.8	44.6	2.40	59.1	10.2	3.09	53.1	3.73	27.4	81.6
600	500	36.0	13.1	44.0	40.8	3.03	55.6	11.2	4.14	56.1	3.16	24.6	98.0
510	510	40.6	9.25	38.2	41.1	3.28	54.3	7.97	2.30	65.2	2.91	34.5	121
360	524	38.4	12.9	62.6	16.4	4.86	76.5	10.2	2.58	71.9	2.89	56.9	153
160	575	36.3	9.99	70.4	33.4	3.80	58.9	9.94	3.97	76.8	2.56	55.2	380
240	578	36.1	12.5	70.1	34.0	2.80	110	4.97	1.50	93.9	2.43	151	324
120	579	38.9	13.8	53.0	45.9	1.90	72.5	4.40	1.59	58.4	2.53	121	300

<sup>a</sup> Reaction cell volume 161 ml. <sup>b</sup> Run with 41.5 cm. of argon.

ratio was observed. This discounts the possibility that the temperature dependence is caused by "hot" radical effects, which diminish with temperature due to

least squares treatment leads to the expression  $k_1/k_{aa}^{1/2} = (3.4 \pm 0.9) \times 10^4 \exp(-5,550 \pm 200/RT)$  mole<sup>-1/2</sup> cc.<sup>1/2</sup> sec.<sup>-1/2</sup>.

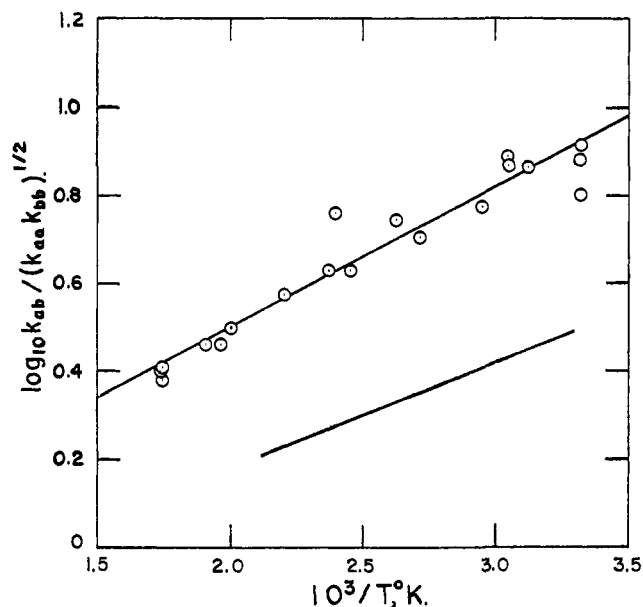


Fig. 1.—Arrhenius plot of  $k_{ab}/(k_{aa}k_{bb})^{1/2}$  for CH<sub>3</sub> + C<sub>3</sub>H<sub>7</sub> system; lower line is for CH<sub>3</sub> + CF<sub>3</sub> system (ref. 3).

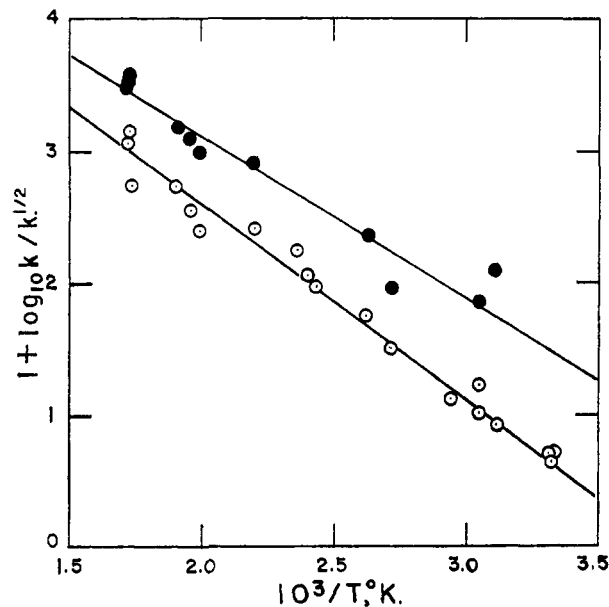
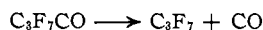


Fig. 2.—Arrhenius plots for  $k_1/k_{aa}^{1/2}$  (solid circles) and  $k_2/k_{bb}^{1/2}$  (open circles).

the increasing formation of thermally equilibrated C<sub>3</sub>F<sub>7</sub> radicals, *via* abstraction reactions 1 and 4, followed by



From the data it is also possible to establish the rates of reactions 1 and 3, relative to the respective recombination reactions. For reaction 1 we have

$$k_1/k_{aa}^{1/2} = R_{CH_4}/R_{C_2H_6}^{1/2}[Ald]_{Av.} - k_2[Ac]_0/k_{aa}^{1/2}[Ald]_{Av.}$$

where  $[Ald]_{Av.}$  is the mean aldehyde concentration during the run, and  $[Ac]_0$  is the initial acetone concentration. This method of treatment has been discussed previously.<sup>7</sup> The ratio  $k_2/k_{aa}^{1/2}$  may be evaluated from the data of Trotman-Dickenson and Steacie.<sup>18</sup> An Arrhenius plot of the data is given in Fig. 2. A

(18) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950).

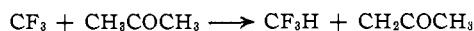
Also included in Fig. 2 are the data obtained from the expression

$$k_2/k_{bb}^{1/2} = R_{C_3F_7H}/R_{C_3F_{14}}^{1/2}[Ac]_0 - k_4[Ald]_{Av.}/k_{bb}^{1/2}[Ac]_0$$

The ratio  $k_4/k_{bb}^{1/2}$  has been determined.<sup>7</sup> A least squares treatment yields  $k_2/k_{bb}^{1/2} = (6.7 \pm 2.6) \times 10^4 \exp(-7,200 \pm 400/RT)$  mole<sup>-1/2</sup> cc.<sup>1/2</sup> sec.<sup>-1/2</sup>. No great accuracy is claimed for these two results, due to the general lack of steady radical concentrations resulting from the high light absorption, especially at the lower temperatures, and the high aldehyde decomposition at the higher temperatures. However, the values of the Arrhenius parameters are those expected for these reactions.  $E_1$  compares favorably with other known activation energies for free radical abstraction of an aldehydic hydrogen,<sup>7,19</sup> and  $E_2$  cor-

(19) Reference 1, pp. 116-117.

relates well with the small amount of available data which indicates a non-variance in the activation energy for H-abstraction from a substrate by a perfluoroalkyl radical.<sup>6,7</sup> The activation energy for the reaction



is  $6.9 \pm 0.1$  kcal./mole,<sup>3</sup> assuming  $E = 0$  for  $\text{CF}_3$  radical recombination.

### Discussion

Other values of cross-combination ratios involving simple alkyl and perfluoroalkyl radicals are unreliable, primarily because the measurement of the ratio was not the object of the experiments. From the work of Giacometti and Steacie<sup>5</sup> on the reaction between  $\text{C}_3\text{F}_7$  and  $\text{C}_2\text{H}_6$ , ratios for  $\text{C}_3\text{F}_7$  and  $\text{C}_2\text{H}_5$  radicals varying from 1.99 to 4.31 may be obtained (previously quoted<sup>1</sup> as 3.2), scattered over the temperature range 360 to 469°K. The quantities of *n*-butane obtained in these experiments were extremely small compared to the other products, amounts varying from  $1.8 \times 10^{-9}$  to  $6 \times 10^{-11}$  mole/cc., which renders the cross-combination values very inaccurate, and, as previously noted, the analysis further suffered from lack of precision in the separation of  $\text{C}_3\text{F}_7\text{C}_2\text{H}_5$  and  $\text{C}_6\text{F}_{14}$ .<sup>12</sup>

In a similar system involving the reaction of  $\text{C}_2\text{F}_5$  radicals with  $\text{CH}_4$ , Price and Kutschke<sup>10</sup> find that in the majority of their experiments a cross-combination ratio for  $\text{C}_2\text{F}_5$  and  $\text{CH}_3$  radicals of approximately  $2 \pm 1$  is obtained. The range of values is from 0.6 up to 6.77, over the temperature range 423 to 545°K.; again the quantities of ethane obtained,  $2.0 \times 10^{-9}$

to  $2.5 \times 10^{-10}$  mole/cc., are very much less than the other products involved in the cross-combination ratio.

An interpretation of the pre-exponential ratio  $A_{ab}/(A_{aa}A_{bb})^{1/2}$  obtained in this work is not obvious, and no theoretical relationship is expected if the steric factor for the sum of mutual disproportionation plus combination for some radical species is much less than unity.<sup>20</sup> The ratio of the collision numbers  $Z_{ab}/(Z_{aa}Z_{bb})^{1/2} = 2.97$ , using values for the collision diameters of  $\sigma_{\text{CH}_3} = 3.5 \text{ \AA.}$ ,  $\sigma_{\text{CF}_3} = 4.0 \text{ \AA.}$  and  $\sigma_{\text{C}_2\text{F}_5} = 6.5 \text{ \AA.}$  This gives the ratio of the steric factors,  $P_{ab}/(P_{aa}P_{bb})^{1/2} = 0.743/2.97 = 0.25$ . There is no *a priori* reason to expect a steric factor of unity for the reaction between two  $\text{C}_3\text{F}_7$  radicals, especially since disproportionation does not occur.

A previous attempt<sup>21</sup> to use the pre-exponential ratio obtained in the  $\text{CF}_3 + \text{CH}_3$  system as a test of transition state theory is incorrect, as an erroneous value was used for the entropy of  $\text{C}_2\text{F}_6$  at 298.16°K. and 1 atm. Better values<sup>22</sup> are 79.18 and 79.06 cal. deg.<sup>-1</sup> mole<sup>-1</sup>; use of these values does not lead to any correspondence between the experimental and theoretical *A*-factor ratios.

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## Some Observations Related to the Photoreduction of Chlorophyll<sup>1</sup>

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The efficiency of quenching of the triplet state of chlorophyll *a* by ascorbic acid in pyridine increases with the water content of the solvent. The bimolecular quenching constant is approximately  $10^4 M^{-1} \text{ sec.}^{-1}$  for dry pyridine, but increases to about  $1.5 \times 10^5 M^{-1} \text{ sec.}^{-1}$  for pyridine containing 25% water. The quenching of the triplet is accompanied by the formation of a labile intermediate, whose absorption spectrum has a maximum near 480 m $\mu$ . Under our experimental conditions, the decay of this intermediate was first order, with a half-life of about 10 msec. The product of this decay appears to be, in part, Krasnovsky's pink pigment.

### Introduction

Recent studies demonstrate that the photoreduction of chlorophyll occurs by way of the triplet state,<sup>3-6</sup> that the efficiency of the reaction depends upon the water content of the solvent when ascorbic acid is the reductant,<sup>4-7</sup> and that the formation of the pink, fully-reduced chlorophyll is preceded by one or more intermediates.<sup>4-6,8</sup> The present work consists of an experimental re-examination of some of these findings.

**Materials.**—Reagent grade pyridine was used. It was dried by distilling over  $\text{CaH}_2$  and then degassing in the presence of

$\text{CaH}_2$ . Ascorbic acid was either Mallinckrodt, USP or Eastman, White Label, used as supplied. In a few experiments, it was crystallized from water and dried by evacuation. The dehydroascorbic acid, a Nutritional Biochemicals Corp. product, was used without further purification. The methods of preparation and purification of chlorophyll *a* have been described elsewhere.<sup>9</sup>

**Preparation of Solutions.**—All solutions were deoxygenated by four or more cycles of freezing, pumping, thawing, freezing, etc. The pumping reduced the pressure to a "black vacuum" ( $\leq 10^{-6}$  mm.), while the solution was at a liquid nitrogen temperature. In preparing solutions containing ascorbic acid, a weighed sample of the crystalline acid and a known volume of pyridine were evacuated in separate vessels which were attached to the same vacuum manifold. After the solvent had been deoxygenated, it was distilled into the vessel containing the solid, and the resulting solution was again subjected to successive freezing, pumping and thawing. Preliminary experiments had demonstrated that even exhaustive pumping did not effectively remove the  $\text{O}_2$  dissolved in the crystalline solid. In all experiments, the concentration of chlorophyll *a* was  $5 \times 10^{-6} M$ .

**Apparatus.**—The flash-photolytic apparatus has been described elsewhere.<sup>10</sup> The scanning light was rendered approximately monochromatic by means of second-order interference filters.

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