THE GAS PHASE REACTIONS OF PERFLUORO-*n*-PROPYL RADICALS WITH METHANE AND ETHANE[1]

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ABSTRACT

The rate constants and activation energies for the reactions of C_3F_7 radicals with methane and ethane have been measured by photolyzing mixtures of $C_3F_7COC_3F_7$ and hydrocarbon with 3130 Å light. Photolysis of mixtures of the ketone, methane, and deuterium has been used to check previous measurements on the reaction of C_3F_7 and deuterium.

INTRODUCTION

The availability of completely fluorinated alkyl radicals obtained via a very simple mechanism from the photolysis of the corresponding ketones (1, 2) makes it worth while to study their reactions with simple hydrocarbons or other substrates, with the object of throwing further light on the effect of the structure of the reactants on the rate constants. The mechanism of production of n-C_3F_7 radicals from perfluoro di-*n*-propyl ketone has been investigated (2) and their reactions with hydrogen and deuterium have been subsequently studied (3).

While the mechanism of the photolysis is extremely simple in this case, especially compared with the non-fluorinated compound, there is one analytical feature of this system which complicates the situation. Owing to the very similar volatilities of the perfluoro di-*n*-propyl ketone and of the perfluoro-*n*-hexane, it is impossible to separate the latter from the bulk of the unreacted material by the usual low-temperature distillation technique.

This difficulty can be overcome, however, by taking advantage of the simplicity of the mechanism and estimating the hexane by a stoichiometric balance. This was done previously in the reaction of n-C_3F_7 with hydrogen and deuterium, although in this case some uncertainty affected the results because of ignorance of the fate of the hydrogen atoms produced in the system (3).

In this paper we present the analogous results obtained for the reactions of C_3F_7 radicals withm ethane and ethane, which are not affected by such a complication. This circumstance also permits an independent determination of the hydrogen reaction rate by performing experiments in the presence of both methane and deuterium.

EXPERIMENTAL

Apparatus

The apparatus was essentially the same as that used in the experiments on the hydrogen reaction. The light source was a B.T.H. high-pressure mercury lamp (ME/D, 250 watts) operated on stabilized 220 v d-c. The 3130 Å radiation was isolated by a standard set of filters. The quartz reaction cell was 10 cm long and had a capacity of 175 cc; it was fully illuminated by the parallel beam of light. The cell was maintained at the desired temperature by an aluminum block furnace and the temperature was constant to ±1° C.

The filling system was of a conventional type as was the analytical line which consisted of two Ward–LeRoy stills, one solid nitrogen trap, a small mercury diffusion pump, a

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gas burette, and a Toepler pump for sample collection. A small CuO furnace, operating at 250° C, could also be inserted in the line when necessary. All stopcocks were avoided by use of appropriate mercury cutoffs.

Materials

The ketone was supplied by Dr. L. C. Leitch of these laboratories and its purity checked by careful distillation in a Podbielniak column (b.p. 75° C) and by mass spectrometry. Deuterium was obtained from a Stuart Oxygen Company cylinder and was passed through hot palladium before storage in a 5-liter bulb connected to the line. Mass spectroscopic analysis gave a D content of 95.4% and all results have been corrected accordingly. Methane and ethane were research grade Philips products and were carefully checked for impurities in the mass spectrometer.

Procedure

After the ketone had been introduced into the cell, its pressure was measured with a constant-volume manometer. The ketone was then frozen out at liquid nitrogen temperature andm ethane or ethane was introduced at the desired pressure. The two reactants were then mixed by expanding them a few times by means of a Toepler pump. The total gas pressure was always measured as a further check. When deuterium was also present, the relative amount of the two gases was measured by reading their pressures in two separate sections of the apparatus whose volume ratio had been previously measured.

The photolysis was allowed to proceed up to 4 to 6% decomposition of the ketone. The analyses were carried out by the usual technique of low-temperature fractionation and mass spectrometry.

In the methane experiments the products of the photolysis were CO, C_3F_7H, $C_4F_7H_3$, C_2H_6, and C_6F_{14}. The first fraction was collected at $-210°$ C and it contained all the CO together with large quantities of methane. The CO was then separated by oxidation in the CuO furnace and measured in the gas burette. Blank experiments showed that no methane was oxidized during the short time of the operation. After pumping off all the remaining methane and possible traces of ethane, a second fraction was collected at $-105°$ C containing all the C_3F_7H and the $C_4F_7H_3$. The C_3F_7H content was estimated by the peak at mass 51 of its mass spectrum. The $C_4F_7H_3$ was estimated by difference and the main peaks of the mass spectrum of this compound are shown in Table I.

In the ethane experiments the products were CO, C_3F_7H, $C_5F_7H_5$, n-C_4H_{10}, and C_6F_{14}. CO was collected at $-210°$ C and a few checks by oxidation in the CuO furnace showed that it did not contain ethane. Ethane was removed at $-155°$ C. The fraction at

TABLE I

MASS SPECTRUM OF n-$C_3F_7CH_3$ (MAIN OR CHARACTERISTIC PEAKS)

Mass n	Relative height	Probable ion
169	5.6	$C_3F_7^+$
119	3.1	$C_2F_5^+$
115	1.4	$C_2F_4CH_3^+$
96	6.1	$C_2F_3CH_3^+$
77	6.0	$C_2F_2CH_3^+$
69	5.1	CF_3^+
65	100.0	$CF_2CH_3^+$
64	3.4	$CF_2CH_2^+$
45	12.9	$CFCH_2^+$

−105° C contained all the C_3F_7H, part of the $C_5F_7H_5$, and all the *n*-butane. A further fraction at −90° C contained only $C_5F_7H_5$. The mass spectrum of this compound is shown in Table II. The peak used for the analysis was the large 79 peak which does not occur with C_3F_7H, *n*-butane, or the ketone.

TABLE II

MASS SPECTRUM OF $C_3F_7C_2H_5$ (MAIN OR CHARACTERISTIC PEAKS)

Mass *n*	Relative height	Probable ion
169	27.9	$C_3F_7^+$
159	6.4	$C_3F_5C_2H_4^+$
119	20.1	$C_2F_5^+$
109	12.2	$C_2F_3C_2H_4^+$
95	8.4	$C_2F_3CH_2^+$
89	3.2	$C_2F_5C_2H_5^+$
79	100	$CF_2C_2H_5^+$
77	12.9	$CF_2C_2H_3^+$
69	75.1	CF_3^+
59	32.1	$CFC_2H_4^+$

The experiments with methane and deuterium were carried out in a manner completely analogous to that used by Miller and Steacie (3) with mixtures of hydrogen and deuterium. The peaks at mass 51 and 52 were used to measure the ratio of C_3F_7H to C_3F_7D and blank runs were performed before each experiment to check the ratio in the absence of hydrogen.

RESULTS

The results for the three sets of experiments are summarized in Tables III, IV, and V. A few runs were performed at quite different light intensities and showed that the results were independent of such changes.

TABLE III

THE REACTION OF *n*-C_3F_7 RADICAL WITH METHANE

	Reactants		Products			
Temp., ° K	Ketone pressure, mm	CH_4 pressure, mm	CO moles $\times 10^6$	C_3F_7H moles $\times 10^6$	Time, sec	$k_3/k_2^{\frac{1}{2}}$ $cc^{\frac{1}{2}}$ $molecule^{-\frac{1}{2}}$ $sec^{-\frac{1}{2}}$ $\times 10^{13}$
439	24.0	43.4	5.20	0.606	3840	2.77
424	23.9	45.7	6.31	0.486	3780	1.83
382	21.7	42.0	5.52	0.124	3780	0.482
368	27.3	67.2	6.78	0.159	3420	0.356
343	20.2	49.3	6.48	0.052_3	4140	0.136
386	21.9	62.3	6.76	0.207	3840	0.497
400	26.7	66.1	8.04	0.340	4080	0.708
402	25.2	114.8	5.70	0.425	3780	0.643
355	26.8	96.5	8.56	0.121	3960	0.150
368	23.0	96.0	7.94	0.181	3960	0.244

The mechanism postulated for the reaction with methane is the following:

$$C_3F_7COC_3F_7 \rightarrow 2\,C_3F_7 + CO, \tag*{[1]}$$

$$2\,C_3F_7 \rightarrow C_6F_{14}, \tag*{[2]}$$

$$C_3F_7 + CH_4 \rightarrow C_3F_7H + CH_3, \tag*{[3]}$$

$$CH_3 + CH_3 \rightarrow C_2H_6, \qquad [4]$$

$$CH_3 + C_3F_7 \rightarrow C_4H_3F_7. \qquad [5]$$

TABLE IV

THE REACTION OF n-C_3F_7 RADICAL WITH ETHANE

	Reactants		Products						
Temp., ° K	Ketone pressure, mm	C_2H_6 pressure, mm	CO moles $\times 10^6$	C_3F_7H moles $\times 10^6$	$C_5F_7H_5$ moles $\times 10^6$	C_4H_{10} moles $\times 10^6$	Time, sec	$k_{3'}/k_2^{\frac{1}{2}}$ $cc^{\frac{1}{2}}$ molecules$^{-\frac{1}{2}}$ sec$^{-\frac{1}{2}}$ $\times 10^{13}$	$k_{5'a}/k_{5'b}$
379	22.1	20.6	7.24	1.99	(>0.730)	Negligible	3600	10.5	
423	22.1	8.9	8.16	2.76	1.49	0.031	3840	43.7	0.40
360	22.6	21.1	9.40	1.54	0.84	0.011	4200	6.17	0.40
402	26.4	22.1	12.2	5.38	2.99	0.06	4740	20.0	0.39
372	20.8	20.3	9.17	2.03	1.11	0.02	4140	8.52	0.41
400	17.3	19.6	6.98	2.95	1.58	0.047	3780	19.5	0.39
425.5	20.5	16.2	8.54	4.66	2.39	0.16	4200	37.2	0.40
433	19.4	20.1	4.96	4.06	2.31	0.24	4020	44.7	0.37
469	18.4	14.5	4.04	4.46	2.08	0.32	3720	135	0.40
455	18.9	16.5	5.30	4.12	1.87	0.30	4020	81.3	0.42

TABLE V

THE REACTION OF n-C_3F_7 RADICAL WITH DEUTERIUM–METHANE MIXTURES*

Temp., ° K	CH_4 pressure/D_2 pressure	51/52 ratio corrected	$k_3/k_{3''}$
370	1.52	3.38	2.22
421	1.56	1.95	1.25
396	1.92	2.87	1.50
358	1.49	3.71	2.49
397	1.38	2.00	1.45
382	1.22	2.26	1.85
455	1.36	1.23	0.905

*Total pressures were of the order of 50–60 mm Hg–$k_3/k_{3''}$ calculated from $R_{C_3F_7H}[D_2]/R_{C_3F_7D}[CH_4]$.

Fluorine abstraction reactions are ruled out by the absence of C_3F_8 in the products and no other reaction of importance in determining the amount of products seems to be possible. The rate of production of C_6F_{14} is thus very simply given by:

$$[1] \qquad R_{C_6F_{14}} = R_{CO} - \tfrac{1}{2}(R_{C_3F_7H} + R_{C_4H_3F_7}).$$

The last column of Table III shows the values of

$$k_3/k_2^{\frac{1}{2}} = R_{C_3F_7H}/R_{C_6F_{14}}^{\frac{1}{2}}\,[CH_4]$$

calculated in this way,* and Fig. 1 shows the Arrhenius plot obtained. Least squares fitting of this plot give:
$k_3/k_2^{\frac{1}{2}} = 1.25 \times 10^{-8} e^{-9.5\times 10^3/RT}$ molecule$^{-\frac{1}{2}}$ cc$^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$. The value for $E_3 - \frac{1}{2}E_2$ is thus 9.5 ±0.5 kcal/mole.

The mechanism for the ethane reaction is somewhat more complicated owing to the possibility of disproportionation in radical–radical reactions:

$$C_3F_7 + C_2H_6 \rightarrow C_3F_7H + C_2H_5, \qquad [3']$$

**Under the conditions of the experiments the quantities of $C_4H_3F_7$ were so small that no accurate analysis was possible. Their exclusion from [1] cannot affect the value of $k_3/k_2^{\frac{1}{2}}$ by more than one per cent. They have therefore been omitted from the table.*

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6, \quad [4'a]$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}, \quad [4'b]$$

$$C_2H_5 + C_3F_7 \rightarrow C_3F_7H + C_2H_4, \quad [5'a]$$

$$C_2H_5 + C_3F_7 \rightarrow C_5F_7H_5. \quad [5'b]$$

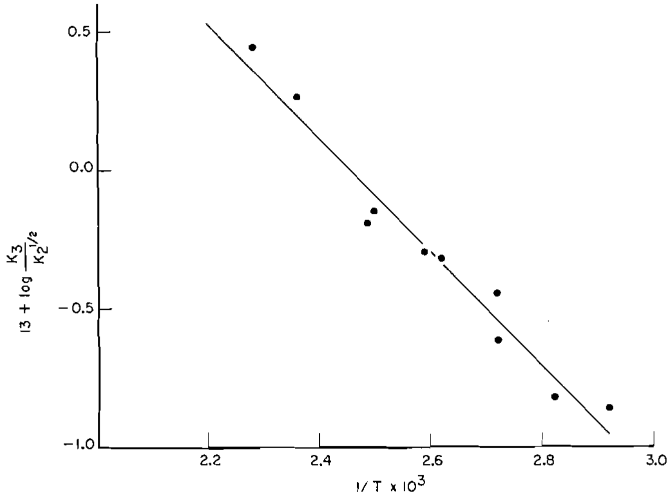

FIG. 1.

The stoichiometric balance can be carried out in this case by analyzing the products for CO, C_3F_7H, C_4H_{10}, and $C_5F_7H_5$ and assuming the ratio $k_{4'a}/k_{4'b}$ to be known. The best experimental value for the latter is 0.12, practically independent of temperature and pressure (4). The C_3F_7 radical balance will give the rate of formation of C_6F_{14} as in the former case:

$$R_{C_6F_{14}} = R_{CO} - \tfrac{1}{2}[R_{C_3F_7H} + R_{C_5F_7H_5}].$$

The balance for C_2H_5 radicals will give both the rate of formation of C_3F_7H from reaction [3′] and the ratio $k_{5'a}/k_{5'b}$:

$$(R_{C_3F_7H})_{3'} = \tfrac{1}{2}[R_{C_3F_7H} + R_{C_5F_7H_5} + 2.24\ R_{C_4H_{10}}]$$

$$k_{5'a}/k_{5'b} = [R_{C_3F_7H} - (R_{C_3F_7H})_{3'}]/R_{C_5H_5F_7}.$$

The justification of this procedure is indicated by the constancy of the value obtained for the latter expression over a range of temperatures as shown in Table IV. The table also gives the values of $k_{3'}/k_2^{\frac{1}{2}}$ obtained from

$$k_{3'}/k_2^{\frac{1}{2}} = (R_{C_3F_7H})_{3'}/R_{C_6F_{14}}^{\ \frac{1}{2}}\ [C_2H_6].$$

The Arrhenius plot of Fig. 2 gives for $E_{3'} - \frac{1}{2}E_2$ a value of 9.2 ± 0.5 kcal/mole and the expression for the rate is

$$k_{3'}/k_2^{\frac{1}{2}} = 2.24 \times 10^{-7}\ e^{-9.2 \times 10^3/RT}\ \text{mole}^{-\frac{1}{2}}\ \text{cc}^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}}.$$

The experiments in which methane and deuterium were put together into the reaction cell were devised to get a relative value of k_3 with respect to the rate constant of the reaction:

$$C_3F_7 + D_2 \rightarrow C_3F_7D + D. \quad [3'']$$

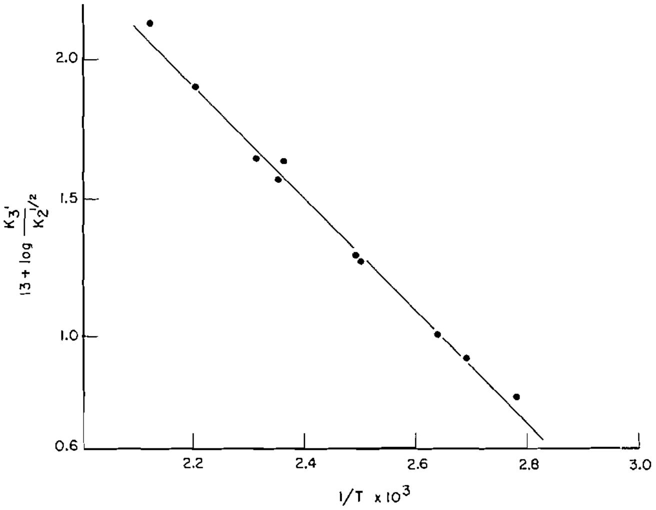

FIG. 2.

This method has already been used for the CF_3 radical by Pritchard and co-workers (5) and is simply based on the mass spectrographic estimation of the ratio RD/RH in the products. Some uncertainty arises from the fact that the fate of the D atoms produced in the abstraction is not known. In this case the possibilities are:

$$D + D + M \rightarrow D_2, \qquad [I]$$

$$D + CH_3 + M \rightarrow CH_3D, \qquad [II]$$

$$D + C_3F_7 \rightarrow C_3F_7D, \qquad [III]$$

$$D + CH_4 \rightarrow CH_3 + HD. \qquad [IV]$$

Table V gives the results of the runs performed at a total pressure of 60 to 70 mm of mercury. The Arrhenius plot is shown in Fig. 3 and the value for $E_3 - E_{3''}$ is found to be -3.4 ± 0.3 kcal/mole, the full expression for the ratio being:

$$k_3/k_{3''} = 1.99 \times 10^{-2}\, e^{3.42 \times 10^3/RT}.$$

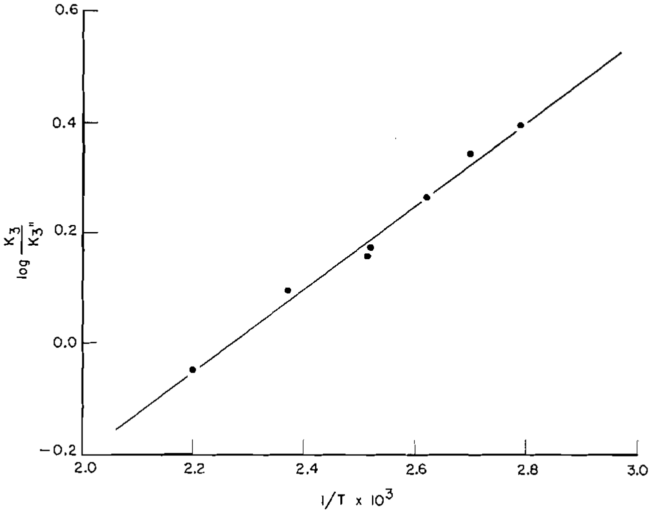

FIG. 3.

DISCUSSION

An absolute result for reaction [3″] is obtained from our data quite independently of the one obtained by Miller and Steacie (3). The value of $E_{3''} - \frac{1}{2}E_2$ obtained in the present work is 12.9±0.8 kcal/mole, which checks with the former value of 13.8±0.5, within experimental error. A comparison of the frequency factors is probably of little significance, given the somewhat large error in the activation energies. On the other hand, a comparison of the rate values in the temperature range of the experiments may be useful. At 400° K the value of Miller and Steacie (calculated assuming only reaction III to occur) is 0.24×10^{-13} molecule$^{-\frac{1}{2}}$ cc$^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$ and in the present case a reasonable agreement with that value is obtained also neglecting reaction III: 0.27×10^{-13} molecule$^{-\frac{1}{2}}$ cc$^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$. Although the uncertainty in these values is only within a factor of 2, which may be of little or no significance for these experiments, the almost complete agreement between our rate value and the former one seems to show that the same mechanism is operative in both cases. Possible occurrence of reaction IV in our case might also give a reason for the discrepancy of almost one kilocalorie per mole in our activation energy.

It is of interest to compare data for the methane, ethane, and hydrogen reactions with C_3F_7 and other radicals such as CH_3 and CF_3 for which sufficiently reliable data are available. In Table VI the activation energies, frequency factors, and the rate constants at 400° K are listed for these reactions.

TABLE VI

SUMMARY OF DATA ON REACTIONS: $R'H + R \rightarrow RH + R'$*

R =	CH_3			CF_3			C_3F_7		
R′H	$E-\frac{1}{2}E_R$	$A/A_R^{\frac{1}{2}} \times 10^8$	$k/k_R^{\frac{1}{2}} \times 10^{13}$	$E-\frac{1}{2}E_R$	$A/A_R^{\frac{1}{2}} \times 10^8$	$k/k_R^{\frac{1}{2}} \times 10^{13}$	$E-\frac{1}{2}E_R$	$A/A_R^{\frac{1}{2}} \times 10^8$	$k/k_R^{\frac{1}{2}} \times 10^{13}$
H_2	10.0[a]	28.1[a]	3.0	8.8[a]	10.8[a]		12.3[c]	56.3[c]	
(D_2)	11.8[a]	16.7[a]		9.7[a]	7.5[a]		13.8[c]	77.6[c]	
CH_4	13.0[b]	3.3	0.029[b]	10.3[b]	12.5	3.5[b]	9.5[d]	1.25[d]	0.81
C_2H_6	10.4[b]	3.6	0.83[b]	7.5[b]	12.1	104[b]	9.2[d]	22.4[d]	20.4

*The subscript R refers to the recombination reaction $R + R \rightarrow R_2$. Units for k's and A's are molecules^{-1} cc sec^{-1}. E's in kcal/mole.

[a] From ref. 5.

[b] From Steacie, E. W. R. J. Chem. Soc. 3991 (1956).

[c] From ref. 3.

[d] Obtained in the present work.

It is very difficult to find some trend in the activation energies or in the frequency factors. The only general feature is that activation energies for the D_2 reactions are always 1.5 to 2.0 kcal/mole greater than those for H_2 and this seems to be due to the zero energy effect (3).

A striking feature can be noted in the behavior of the rate constants, however. It is apparent that great changes in reactivity (over 100-fold variation) are shown by the different radicals reacting with the hydrocarbons, while the hydrogen reaction is more or less insensitive to changes in the attacking radical.

It seems that there are two quite different types of reaction. It is interesting in this respect to point out that in the case of $R + H_2$ there is an almost linear relationship between log A and E for the three different radicals. Such a "compensation" behavior has been found already in other cases, and there has been a recent attempt to justify it on theoretical grounds (6), especially for the case of diatomic molecules. Such a relationship does not hold for $R + R'H$ where, on the other hand, a different regularity is apparent. The relative reactivity of each radical toward methane and ethane is approximately constant, as shown by the ratio of the rate values of Table VI. This behavior is analogous to the findings of Smid and Szwarc for radical abstractions and additions in solution (7). It will be of interest to see if the mentioned regularities still hold in reactions with other similar radicals.

The value of the disproportionation-to-recombination ratio for the reaction between C_3F_7 and C_2H_5 is the first one reported for a reaction between a completely fluorinated radical and a completely hydrogenated one. Since C_3F_7 is seemingly more reactive toward hydrocarbons than CH_3 the ratio was expected to be greater than the one reported for $CH_3 + C_2H_5$, which is of the order of 0.03 (8); this expectation is amply justified by the value found, 0.40.

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