Photolysis of Mixtures of Acetone and Hexafluoroacetone

Combination Reactions of Methyl and Trifluoromethyl Radicals

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The photolysis of mixtures of acetone and hexafluoroacetone has been studied in the range 23-240°C. In addition to C_2H_6 , C_2F_6 and CH_3CF_3 , the products also contained $CH_2 = CF_2$. The following reactions are therefore proposed :

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2}$$

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

$$1a$$
 CH₃CF₃ (4)

$$CH_3 + CF_3 \rightarrow CH_3 CF_3^* CH_2 = CF_2 + HF$$
(5)

Reaction (5) as not previously been observed. Defining ϕ^* by $\phi^* = k_{1a}/k_2^{\frac{1}{2}}k_3^{\frac{1}{3}}$, $\phi^* = (2\cdot0\pm0\cdot2)$ exp (170±80)/RT. These results indicate that $E_{1a} = E_2 = E_3 \sim 0$. The product of reaction (1a) is a "hot" molecule which can be stabilized to CH₃CF₃ by

The product of reaction (1*a*) is a "hot" molecule which can be stabilized to CH_3CF_3 by collisions. The ratio $R_{CH_3CF_3}/R_{CH_2=CF_2}$ is dependent on both pressure and temperature. The relative efficiencies of deactivation of $CH_3CF_3^*$ by acctone, hexafluoroacetone, nitrogen and perfluorocyclohexane were measured. The Arrhenius parameters have been measured of the various hydrogen abstraction reactions and also of the reaction, $CH_3+CF_3-CCF_3-CCF_3-CCF_3$. The

importance of the reaction, $CF_3+CH_2=CF_2\rightarrow CF_3-(CH_2-CF_2)$ —is discussed in an appendix.

The reactions

$$CH_3 + CF_3 \rightarrow CH_3 CF_3$$
 (1)

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2}$$

$$CF_3 + CF_3 \rightarrow C_2F_6$$
 (3)

have been studied by Pritchard and Dacey,¹ who photolyzed mixtures of acetone and hexafluoroacetone, HFA, to generate CH₃ and CF₃ radicals in the same system. They found the ϕ factor given by

$$\phi = R_{\rm CF_3CH_3}/R_{\rm C_2H_6}^{\pm}R_{\rm C_2F_6}^{\pm} = k_1/k_2^{\pm}k_3^{\pm}$$

to be temperature dependent, and suggested that reaction (3) had an activation energy of $2 \cdot 14 \pm 0 \cdot 20$ kcal mole⁻¹, assuming that $E_1 = E_2 = 0$. This result was unexpected since for simple radical combinations ϕ is usually independent of temperature ² and approximately equal to 2; Pritchard and Dacey's values of ϕ varied in the range 1.8-3.5.

Alcock and Whittle ³ studied the reaction

$$CF_3 + CH_3I \rightarrow CF_3I + CH_3.$$

This is so fast that a significant concentration of CH_3 radicals was present, consequently the products contained CH_3CF_3 as well as C_2F_6 (but not C_2H_6 because

 $[CF_3] > [CH_3]$). Surprisingly, $CH_2 = CF_2$ was also formed and it was proposed that the combination reaction (1) may follow two paths:

$$CH_3 + CF_3$$

$$CH_2 = CF_2 + HF$$
(4)
(5)

Reaction (5) is a new example of an unusual type of elimination reaction discovered by Pritchard and co-workers ⁴ in the photolysis of $(CH_2F)_2CO$, the products of the reactions corresponding to (4) and (5) being CH_2FCH_2F and $CH_2=CHF$.

If reactions (4) and (5) both occur, then $CH_2=CF_2$ should have been formed in the original work of Pritchard and Dacey on reactions (1), (2) and (3). It was not detected but the analyses were done by mass spectrometry which is a very insensitive way of analyzing mixtures of CH_3CF_3 and $CH_2=CF_2$, particularly if $CH_3CF_3>CH_2=CF_2$ which would be the case. Also, elimination reactions, such as (5), were not then known to occur. If $CH_2=CF_2$ were present, then a failure to detect it could invalidate the calculations of ϕ and E_3 . The latter is important since reaction (3) is frequently used as a reference in competitive work. A study by Dawidowicz and Patrick ⁵ of the photolysis of CH_3COCF_3 at 45°C yielded a value of ϕ in fair agreement with that of Pritchard and Dacey. No $CH_2=CF_2$ was found but again the analyses utilized mainly mass spectrometry. We have therefore made a further study of the photolysis of mixtures of acetone and HFA to learn more about reactions (1), (3), (4) and (5).

EXPERIMENTAL

A.R. acetone was dried over anhydrous CaSO₄ and given bulb-to-bulb distillations *in vacuo*, a middle cut being retained and stored at -80° C. Nitrogen was made by heating sodium azide in vacuum. Perfluorocyclohexane from Imperial Smelters was purified and stored as for acetone. All other materials, apparatus and procedure were as described previously.⁶ The light from the mercury lamp passed through 3 cm of an aqueous solution containing 0.5 g/l. of potassium hydrogen phthalate which absorbs all wavelengths below 3130 Å. During photolysis, about 0.5-1 % of acetone and 0.3-0.5 % of HFA were decomposed.

ANALYSIS

The reaction products were partly separated using two Ward stills. The -196° C fraction contained CO+CH₄ which was measured using a gas burette and analyzed by combustion of the CO on CuO. The next fraction was removed with the stills at -135 and -145° C and contained CF₃H, C₂H₆, C₂F₆, CH₃CF₃ and CH₂ = CF₂ which were identified as described elsewhere.³ After determining the total pressure and volume in the gas burette, the fraction was divided since a complete V.P.C. analysis required the use of two separate columns at room temperature. The first portion passed through an alumina column and the relative appearance times were C₂H₆+C₂F₆ (not resolved), 1·0; CF₂ = CH₂, 1·8; CF₃H, 5·0; CH₃CF₃, 9·3. Using a column of silica gel for the second portion, the relative appearance times were: C₂H₆, 1·0; C₂F₆, 1·4; CH₂ = CF₂, 2·0; CF₃H, 2·1; CH₃CF₃, >10. In certain runs, the Ward stills were next warmed to -125 and -135° C and a further fraction was removed and analyzed by V.P.C. The fraction was always pure HFA showing that, in the previous fraction, removal of the least volatile component, CH₃CF₃, was complete. The residual HFA in the Ward stills contained CH₃COCF₃ which was identified and determined by i.-r. as before.³

RESULTS AND DISCUSSION

When mixtures of acetone and HFA are photolyzed the products are CO, CH₄, CF₃H, C₂F₆, CH₃CF₃, CH₂=CF₂ and CH₃COCF₃. Quantitative analyses for all were obtained and some typical results are shown in tables 1 and 2. The analyses for CH₂=CF₂ are discussed in the appendix.

Table 1.—Typical results of the photolysis of mixtures of acetone and hexafluoroacetone at various temperatures *

temp., °C	photolysis time, sec	rate of formation of products, mole $cm^{-3} sec^{-1} \times 10^{13}$					
		CO	CH4	CF ₃ H	CH3COCF3		
23	3905	15.6	0.682	1.22			
62	2820	103	2.37	16.4	38		
102	1200	128	3.66	54.8	59		
200	600	557	86.1	444	387		

acetone pressure~60 mm, HFA pressure~10 mm. * analysis of C_2 products of these and other runs given in table 2.

Table 2.— C_2 products in the photolysis of mixtures of acetone and hexafluoroacetone

temp.,	rat	e of formation of produ	cts, mole cm ⁻³ sec ⁻¹ \times 10)13
°Č	C ₂ H ₆	C ₂ F ₆	CH ₃ CF ₃	$CH_2 = CF_2$
23	1.80	1.87	4.09	0.83
62	2.07	42.1	17.4	5.1
63	3.87	52.4	29.0	9.6
102	1.57	51.9	151	6.2
157	49.1	79 ·8	98.4	67
200	19.8	27.5	34-2	19
241	9.47	10.4	11.1	9.9
244	25.9		18.7	16

acetone pressure ~ 60 mm, HFA pressure ~ 10 mm.

The presence of $CH_2 = CF_2$ in the products confirms the prediction ³ that reaction (5) is an alternative to reaction (4). All the products may be explained by reactions (2), (3), (4) and (5) together with

$$CH_{3}COCH_{3} + hv \rightarrow 2CH_{3} + CO \tag{6}$$

$$CF_3COCF_3 + hv \rightarrow 2CF_3 + CO$$
 (7)

$$CH_3 + CH_3 COCH_3 \rightarrow CH_4 + CH_2 COCH_3$$
(8)

$$CF_3 + CH_3COCH_3 \rightarrow CF_3H + CH_2COCH_3$$
(9)

$$CH_3$$

$$(10a) | (10b)$$

$$CH_3 + CF_3COCF_3 \rightarrow CF_3 - C - CF_3 \rightarrow CH_3COCF_3 + CF_3.$$

$$|$$

$$O$$

$$(10)$$

The kinetics of these reactions were investigated as follows.

ABSTRACTION AND ADDITION REACTIONS

If CH₄, CF₃H, C₂H₆ and C₂F₆ are formed only by reactions (8), (9), (2) and (3) respectively, then

 $k_8/k_2^{\frac{1}{2}} = R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$ [acetone], and $k_9/k_3^{\frac{1}{2}} = R_{CF_3H}/R_{C_2F_6}^{\frac{1}{2}}$ [acetone].

1427

Mixtures of 60 mm acetone and 10 mm HFA were photolyzed in the range 23-240°C. Arrhenius plots for $k_8/k_2^{\frac{1}{2}}$ and $k_9/k_3^{\frac{1}{2}}$ are shown in fig. 1. Both plots show curvature at lower temperatures.

At higher temperatures (>140°C) the values of $k_8/k_2^{\frac{1}{2}}$ agree well with those of Trotman-Dickenson and Steacie⁷ which are shown by a solid line in fig. 1. The curvature at lower temperatures ⁸ implies an additional production of methane. Ausloos and Steacie⁹ suggest that this is formed by the reaction

$$CH_3 + CH_3CO \rightarrow CH_4 + CH_2CO,$$
 (11)

and also by a heterogeneous reaction between CH₃ radicals and acetone.

The curvature of the $k_9/k_3^{\frac{1}{3}}$ plot may be explained by the occurrence of the analogue of reaction (11), i.e.,

$$CF_3 + CH_3CO \rightarrow CF_3H + CH_2CO.$$
(12)

Heterogeneous reactions may also occur. Pritchard and Dacey ¹ drew a straight line through their Arrhenius plot of k_9/k^{\pm} but in fact their results could lie on a curve





Curve A, $k_{\rm H}/k_{\rm f}^{\frac{1}{2}} = k_9/k_{3}^{\frac{1}{2}}$, cm^{$\frac{3}{2}$} mole^{$-\frac{1}{2}$} sec^{$-\frac{1}{2}$}, X = 1.0. \bullet , ref. (1); \bigcirc , this work. Curve B $k_{\rm H}/k_{\rm f}^{\frac{1}{2}} = k_8/k_{3}^{\frac{1}{2}}$, cm^{$\frac{3}{2}$} mole^{$-\frac{1}{2}$} sec^{$-\frac{1}{2}$}, X = 2.5. Θ , this work; solid line, ref. (7).

similar to those of fig. 1. We include their data in fig. 1 to prove this. The agreement between their rate constants and ours is excellent. Neglecting the curvature, Pritchard and Dacey obtained

 $k_{\rm o}/k_{\rm a}^{1} = 1.24 \times 10^{4} \exp \left[-6900 \pm 100\right]/RT \, {\rm cm}^{\frac{3}{2}} \, {\rm mole}^{-\frac{1}{2}} \, {\rm sec}^{-\frac{1}{2}}.$

A least-squares treatment of both sets of data in fig. 1 but ignorning points in the region of curvature $(10^3/T > 2.8)$ leads to

$$k_9/k_3^{\frac{1}{2}} = [6.9 \pm 1.2] \times 10^4 \exp \left[-8270 \pm 170\right]/RT \text{ cm}^{\frac{3}{2}} \text{ mole}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

1429

When Pritchard and co-workers ⁴ photolyzed CH₂FCOCH₂F they obtained an Arrhenius plot for the analogue of $k_9/k_3^{\frac{1}{3}}$ involving CH₂F radicals. This plot also showed a curvature at lower temperatures which was explained in a similar manner to that given above.

The occurrence of the addition reaction (10a) followed by (10b) was first proposed by Pritchard and Steacie¹⁰ from work on the reactions of CH₃ radicals with HFA, without the latter being photolyzed. The mixed ketone produced by reaction (10b) was not detected by these authors but it was identified as a product of the photolysis of HFA in the presence of CH₃I by Alcock and Whittle³; in that system the ketone was almost certainly formed by reactions (10a) and (10b). The ketone was also obtained in the present work but here it could also be formed by the reactions

$$CH_3 + CF_3CO \rightarrow CH_3COCF_3$$
 (13)

$$CF_3 + CH_3 CO \rightarrow CH_3 COCF_3. \tag{14}$$

Reaction (13) seems unlikely in view of the instability of the CF₃CO radical.¹¹ We shall also neglect reaction (14) since we find that the rate of formation of CH₃COCF₃ increases with temperature whereas the CH₃CO radical becomes much less stable as the temperature rises. Furthermore our earlier discussion implies that reaction (12) is unimportant at higher temperatures so that this is probably true of reaction (14) also.

If the product of reaction (10a) is regarded as a transition state, then

$$k_{10a}/k_2^{\pm} = R_{\text{CH}_3\text{COCF}_3}/R_{C_2\text{H}_6}^{\pm}[\text{HFA}].$$

From six experiments in the range $48-240^{\circ}$ C, the analyses for CH₃COCF₃ were used for an Arrhenius plot giving

$$\log \left(k_{10a} / k_2^{\frac{1}{2}} \right) = (5 \cdot 0 \pm 0 \cdot 5) - (7000 \pm 1000) / 2 \cdot 3RT,$$

the units of $k_{10a}/k_2^{\frac{1}{2}}$ being cm^{$\frac{3}{2}} mole^{<math>-\frac{1}{2}}$ </sup> sec^{$-\frac{1}{2}$}. Taking ^{12, 13} $k_2 = 2.3 \times 10^{13}$ cm³ mole⁻¹ sec⁻¹ and $E_2 = 0$ leads to $A_{10a} = 5 \times 10^{11}$ cm³ mole⁻¹ sec⁻¹. Using collision diameters of 3.5 and 7.1 Å for CH₃ and HFA respectively, we have $P_{10a} = 10^{-3}$. Alcock and Whittle ³ obtained $E_{10a} = 6.2$ kcal mole⁻¹ and $A_{10a} = 2.6 \times 10^{11}$ cm³ mole⁻¹ sec⁻¹ using a calculation based on CH₃CF₃ and C₂F₆ analyses since the C₂H₆ was too small to measure. However, the yield of CH₃CF₃ is now known to be dependent on pressure (see below) so their results are rather less reliable than the values given above. Even the latter is of limited accuracy owing to the difficulty of analyzing for CH₃COCF₃ in the presence of a large excess of HFA. Pritchard and Steacie ¹⁰ estimated that $P_{10a} \sim 10^{-5}$ and $E_{10a} \sim 6$ kcal mole⁻¹.</sup>

COMBINATION REACTIONS

We first photolyzed mixtures of 60 mm acetone and 10 mm HFA in the range 23-240°C. The C₂ fraction of the products consisted of C₂H₆, C₂F₆, CH₃CF₃ and CH₂=CF₂; analyses for these are given in table 2.

The ϕ factor was calculated in the usual way and a plot of log ϕ against $10^3/T$ is shown in fig. 2. By least squares,

$$\phi = [0.56 \pm 0.06] \exp [830 \pm 80]/RT.$$

From this, $E_1 - \frac{1}{2}(E_2 + E_3) = -0.83 \pm 0.08$ kcal mole⁻¹. This treatment follows exactly that of Pritchard and Dacey, whose data are also shown in fig. 2. They obtained $E_1 - \frac{1}{2}(E_2 + E_3) = -1.07 \pm 0.10$ kcal mole⁻¹. Hence we confirm the apparent temperature dependence of ϕ observed by them and the two sets of data are in complete accord.

So far we have ignored the formation of $CH_2 = CF_2$ by reaction (5). Let us suppose that reactions (4) and (5) involve the same transition state, i.e.,

$$CH_3 + CF_3 \xrightarrow{(1a)} CH_3 CF_3 \xrightarrow{(1a)} CH_3 CF_3 \xrightarrow{(4)} CH_2 = CF_2 + HF \xrightarrow{(5)} CH_2 = CF_2 + HF$$

where $CH_3CF_3^*$ is an energy-rich molecule. Now for combination reactions of many simple radicals, ϕ is approximately 2 and this is readily explained in terms of simple collision theory. In applying this theory to reactions (1), (2) and (3), we must



FIG. 2.—Variation with temperature of ϕ and ϕ^* . Curve A, X = 0, $Y = \phi$; \bigcirc , this work, \bigcirc , ref. (1); curve B, X = 0.2, $Y = \phi^*$.

use not $R_{CH_3CF_3}$ but $R_{CH_3CF_3}$ which is equal to $R_{CH_3CF_3} + R_{CH_2-CF_2}$. Failure to include the second term invalidates the calculations of ϕ . Denoting the corrected ϕ by ϕ^* , we have

$$\phi^* = (R_{\rm CH_3CF_3} + R_{\rm CH_2 = CF_2})/R_{\rm C_2H_6}^{\frac{1}{2}}R_{\rm C_2F_6}^{\frac{1}{2}}$$

An Arrhenius plot for ϕ^* is shown in fig. 2 and leads to

 $\phi^* = [2.02 \pm 0.23] \exp [170 \pm 80]/RT$

so that $E_{1a} - \frac{1}{2}(E_2 + E_3) = -0.17 \pm 0.08$ kcal mole⁻¹. This result is most simply explained if all three activation energies are close to zero; it is no longer necessary to postulate an activation energy of 2 kcal mole⁻¹ for the combination of CF₃ radicals as was done by Pritchard and Dacey.

Using appropriate collision diameters, Pritchard and Dacey calculated that, on the basis of collision theory, ϕ should equal 2.3 if $E_1 = E_2 = E_3 = 0$. From our data for ϕ^* above, the pre-exponential factor is 2.0 which agrees well with the collision theory value. Alternatively, if we assume that ϕ^* is independent of temperature and take the simple average of the values in fig. 2, we obtain $\phi^* = 2.5$, again in good agreement with collision theory.

R. D. GILES AND E. WHITTLE

Racctions (1*a*), (4) and (5) collectively represent a second example of a type of reaction discovered by Pritchard and co-workers ⁴ in which radical combinatoin is followed either by stabilization or elimination of HF. These authors proposed the following sequence involving CH_2F radicals,



It was found that the ratio $R_{C_2H_4F_2}/R_{CH_2=CHF}$ is dependent on temperature and on the pressure of the ketone, $(CH_2F)_2CO$, used as a source of the radicals. Another possible example of this type of reaction occurs in the fluorination of ethane.¹⁴ There is some evidence that "hot" ethyl fluoride is formed which may then decompose,

$$C_2H_5F^* \rightarrow C_2H_4 + HF.$$

However, this reaction is much less amenable to study than the other examples. Majer and Phillips ¹⁵ have suggested that CF_2Cl radicals may undergo a disproportionation reaction as an alternative to normal combination,



It is possible that both reactions have a common transition state in which case the ratio $CF_2Cl_2/C_2F_4Cl_2$ would probably be pressure dependent; this cannot be determined from the data available.

We wish to know why HF elimination can occur when the corresponding reaction

$$CH_3 + CH_3 \rightarrow C_2H_6^* \rightarrow C_2H_4 + H_2$$
(15)

does not occur. Reaction (1*a*) followed by (4) or (5) liberates about 88 and 77 kcal mole⁻¹ respectively, whereas for reactions (2) and (15) the corresponding figures are 86 and 53 kcal mole⁻¹. Thus on thermochemical grounds the production of CH₃CF₃ or CH₂=CF₂ is almost equally plausible whereas the formation of C₂H₆ is much preferred to C₂H₄+H₂. The difference arises mainly because D(H--F) > D(H--H).

VARIATION OF $R_{CH_3CF_3}/R_{CH_2=CF_2}$ WITH PRESSURE

The product of reaction (1*a*) is an energy-rich molecule $CH_3CF_3^*$ which may be stabilized by collision with a third body M or may eliminate HF to form $CH_2 = CF_2$. On this basis,

$$R_{CH_3CF_3} = k_4[M][CH_3CF_3^*]$$
, and $R_{CH_2=CF_2} = k_5[CH_3CF_3^*]$.

If we denote the ratio of the rates of formation of the ethane and olefine by θ , then

$$\theta = R_{\rm CH_3CF_3}/R_{\rm CH_2=CF_2} = k_4[M]/k_5, \tag{16}$$

The third body M may be acetone, HFA or some added molecule, each of which may have different values of k_4 , hence eqn. (16) is better written as

$$\theta = \{k_{4a}[\text{acetone}] + k_{4b}[\text{HFA}] + k_{4c}[\text{M}]\}/k_5, \tag{17}$$

where M now denotes an added third body.

Eqn. (17) was checked in various ways. First, we photolyzed mixtures of acetone and HFA so that [M] = 0. In a series of runs with a constant HFA pressure of 10 mm at 150°C, the acetone pressure was varied in the range 7-65 mm. A plot of θ against acetone pressure is seen in fig. 3 to be a straight line in agreement with eqn. (17). In a second series the acetone pressure was constant at 60 mm at 150°C



pressure in mm of acetone, or HFA

FIG. 3.—Variation of θ with variation of acetone pressure \bullet , and HFA pressure, \bigcirc .



FIG. 4.—Variation of θ with variation of cyclo-C₆F₁₂ pressure, \bullet , and N₂ pressure, \bigcirc .

and the HFA pressure was varied in the range 5-42 mm with the results shown in fig. 3. Next, the efficiencies of N_2 and perfluorocyclohexane as third bodies were tested separately using the following conditions: 60 mm acetone; 10 mm HFA; N_2 , 90-510 mm, cyclo-C₆F₁₂, 43-168 mm, all at 150°C. The results are shown in fig. 4.

Treatment of the data in fig. 3 and 4 by least squares gives the results shown in table 3. The separate variations of acetone and of HFA lead to independent

R. D. GILES AND E. WHITTLE

estimates of k_{4a}/k_5 and k_{4b}/k_5 , given in table 3, which are in good agreement. For the variation of N₂ and of cyclo-C₆F₁₂, the intercept should give the value of θ corresponding to [M] = 0. Taking from table 3, k_{4a}/k_5 (average) = 4.4×10^5 and k_{4b}/k_5 (average) = 1.0×10^6 cm³ mole⁻¹, we obtain $\theta = 1.38$ for pressures of acetone and HFA of 60 and 10 mm respectively at 150°C. The observed intercepts for M = N₂ and M = cyclo-C₆F₁₂ agree with this within experimental error. The linear plots in fig. 3 and 4 together with the internal consistency of the results provide strong support for a mechanism involving reactions (4) and (5).

TABLE 3.—VA RIATION WITH PRESSURE OF THE RATIO $R_{CH_3CF_3}/R_{CH_2=CF_2}$

	$slope \times 10^2$	• • • • • • • •	k4a/k5	k4b/k5	k4c/k5	
variable	mm ⁻¹	intercept	cm ³ mole ⁻¹ × 10 ⁻⁵			
acetone	1.5	0.43	4.0	11		
HFA	3.4	1.10	4.8	9.0		
N_2	0.28	1.50	<u> </u>		0.74	
cyclo-C ₆ F ₁₂	5.3	1.21			14	

slopes and intercepts refer to fig. 3 and 4.

The ratio k_4/k_5 measures the efficiency of any given molecule for deactivation of CH₃CF₃^{*} by transfer of vibrational energy. From table 3, the relative values are cyclo-C₆F₁₂, 1·0; HFA, 0·71; acetone, 0·31; N₂, 0·053. Since deactivation is by collision, we can replace any given k_4 by λZ , where $\lambda \leq 1$ and Z is the collision number between CH₃CF₃^{*} and the quenching molecule. The relative values of λ , which measure the quenching efficiency on a collision-for-collision basis, are then cyclo-C₆F₁₂, 1·0, HFA, 0·75; acetone, 0·39; N₂, 0·075. These relative efficiencies are of the same order as those given by Trotman-Dickenson ¹⁶ for comparable quenching processes.

Since the efficiencies of acetone, HFA and cyclo- C_6F_{12} are similar, it is tempting to assume that every collision of one of these molecules with $CH_3CF_3^*$ leads to deactivation; this is a common assumption in energy transfer studies. It is reasonable that the three molecules should be about equally efficient since each is fairly complex and all have chemical features in common with the molecule being quenched. However, a closer analysis of the de-activation process does not sustain the idea of quenching at each collision. When reaction (1a) occurs, the CH₃CF₃^{*} will dissociate back to CH_3+CF_3 unless the molecule is stabilized by collision (neglecting reaction (5)); $D(CH_3 - CF_3) = 88 \text{ kcal mole}^{-1}$ is the energy to be removed.¹⁷ If only 1-2 kcal mole⁻¹ are removed by a collision then the molecule can no longer dissociate to $CH_3 + CF_3$ and will eventually be thermalized by successive collisions. In the range of pressures used in our work, the rates of combination of CH₃ radicals and of CF₃ radicals are both independent of pressure 18, 19and we shall assume that this is also true for the cross-combination of CH_3 and CF_3 radicals, in the sense that, $CH_3CF_3^*$, once formed, does not dissociate back to CH_3 and CF_3 . However, a molecule of $CH_3CF_3^*$ may be de-activated with respect to simple dissociation (energy < 88 kcal mole⁻¹) and yet may still have sufficient energy to undergo reaction (5); let us denote such a molecule by $CH_3CF_3^{**}$. Pritchard 4 estimates that a reaction such as (5) will have an activation energy of \sim 45 kcal mole⁻¹, hence, if $CH_3CF_3^{**}$ has an energy greater than this, reaction (5) may occur. It is essential to postulate two different kinds of activated molecules in order to explain a pressure dependence for the production of olefine at pressures where the rate of combination, reaction (1a), is independent of pressure. From this argument, it follows that although a molecule of $CH_3CF_3^*$ may be de-activated by a single collision as far as

1433

the dissociation reaction, (1*a*), is concerned, it cannot be totally de-activated by one collision with respect to reaction (5); if it were, no $CH_2 = CF_2$ would be formed. In order to suppress reaction (5) completely by one collision, $CH_3CF_3^*$ would have to lose 88-45 = 43 kcal mole⁻¹ on collision which seems unlikely. From the work of Rabinovitch and colleagues,²⁰ a transfer of ~10-20 kcal mole⁻¹ at each collision is more plausible.

It follows from the discussion above that the life-time of a CH₃CF₃^{**} molecule should be longer than that of CH₃CF₃^{*}. The latter is not known since the combination of CH₃ and CF₃ radicals at low pressure has not been studied. In table 3, we give values of k_4/k_5 and if we assume that $k_4 = \lambda Z$ where $\lambda \ll 1$, we obtain values of k_5 of λ (2-5×10⁸) sec⁻¹ using the data for acetone, HFA and cyclo-C₆F₁₂ acting as quenchers. Thus the life of the CH₃CF₃^{**} molecule is $\geq 2 \times 10^{-9}$ sec.

VARIATION OF $R_{CH,CF}/R_{CH,=CF}$, WITH TEMPERATURE

The variation of θ with temperature is illustrated in fig. 5. Using constant pressures of 60 mm acetone and 10 mm HFA over the temperature range 23-240°C we have

$$\theta = [0.2 \pm 0.03] \exp [1880 \pm 120]/RT.$$

Thus as the temperature increases, the elimination reaction (5) is favoured at the expense of the stabilization reaction, (4); apparently reaction (5) has a greater "activation energy" than reaction (4) although the meaning of this phrase when



FIG. 5.—Variation of θ with temperature.

applied to a hot molecule is obscure. Although the temperature variation of θ gives the apparent result that $E_5 - E_4 = 1.9$ kcal mole⁻¹, this must be corrected for the fact that our experiments were done at constant pressures so that as the temperature varied the concentrations of third bodies in eqn. (17) also varied. This is corrected for by subtracting *RT* from the observed activation energy so that $E_5 - E_4$ (corrected) = 1.1 kcal mole⁻¹. Pritchard and co-workers observed a similar temperature dependence of $R_{CH_2FCH_2F}/R_{CH_2=CHF}$ in their study of the reactions of CH₂F radicals but the data did not fit an Arrhenius plot. They pointed out that

1435

the collision number Z increases slightly with temperature and as $k_4 = \lambda Z$, this would favour ethane at the expense of olefine whereas the opposite effect is observed. A similar temperature dependence has been observed in the system

$$\operatorname{CH}_3 + \operatorname{CH}_3 \rightleftharpoons C_2 \operatorname{H}_6^* \xrightarrow{M}_c C_2 \operatorname{H}_6.$$

Thus, Dodd and Steacie ¹⁸ found that the ratio k_b/k_c increased with temperature and that $E_b - E_c \sim 2$ kcal mole⁻¹. Toby and Weiss ²¹ have confirmed this. Other examples of an apparent temperature dependence of the decomposition of a hot molecule are also known.^{4, 22} Presumably even a molecule such as $CH_3CF_3^*$ with excess energy of 88 kcal mole⁻¹ at, say room temperature, will have somewhat more energy at higher temperatures by virtue of the increased thermal energy of the reactants and may thus have a shorter life (i.e., because $D(CH_3 - CF_3)$, which is the excess energy, increases with temperature). The observed activation energy difference of $E_5 - E_4$ is indeed of the order of the changes in thermal energies involved. There is, however, an alternative explanation. Pritchard and co-workers suggest that the efficiency of energy transfer increases with temperature which would therefore increase k_4 contrary to observation. However, the work of Rabinovitch's school ²⁰ provides convincing experimental evidence that energy transfer is less efficient at higher temperatures; this would reduce k_4 and decrease θ as observed.

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APPENDIX

Our analyses for $CH_2 = CF_2$ could be in error if there were a significant contribution by the reaction

$$CF_3 + CH_2 = CF_2 \rightarrow CF_3 - (CH_2 - CF_2) -$$
(18)

(we neglect the corresponding reaction involving CH_3 as it is expected to be much slower). Reactions similar to (18) have been studied by Pearson and Szwarc 23 using various olefines including $CH_2 = CHF$ but not $CH_2 = CF_2$. For the reactions

$$CF_3 + CH_2 = CHF \rightarrow CF_3 - (CH_2 - CHF) -$$
(19)

$$CF_3 + (CH_3)_2 CHCH(CH_3)_2 \rightarrow CF_3H + (CH_3)_2 CHC(CH_3)_2$$
(20)

they obtained $k_{19}/k_{20} = 1.55 \exp(1020/RT)$. From the work of Ayscough and Steacie ²⁴ on the reactions of CF₃ radicals with isobutane, we estimate that $k_{20} = 3 \times 10^{11}$ $\exp(-5000/RT)$ cm³ mole⁻¹ sec⁻¹ allowing for the fact that the hydrocarbon in eqn. (20) has 2 tertiary H (the work of ref. (23) also indicates that $E_{20} > 4.4$ kcal mole⁻¹). Hence $k_{19} = 4.5 \times 10^{11} \exp(-4000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. If a similar equation applies to $CH_2=CF_2$, then reaction (18) could remove some of the $CH_2=CF_2$ produced in our experiments. We have tested this as follows.

Mixtures of acetone and HFA were photolyzed with various percentage conversions with the results given in table 4. Increasing the photolysis time decreases the ratio CH_2 = CF_2/CH_3CF_3 presumably because reaction (18) becomes more important as $CH_2=CF_2$ accumulates. Some photolyses of mixtures of HFA and $CH_2 = CF_2$ were also performed in an attempt to measure k_{18}/k_{2}^{3} . Accurate results could not be obtained because, in order to obtain measurable yields of C_2F_6 , it was necessary to use low pressures of $CH_2=CF_2$ most of which was consumed during the reaction. Nevertheless, the results roughly confirmed the above equation for k_{18} .

If $CH_2 = CF_2$ is formed by reaction (5) and consumed by reaction (18), then if photolysis is prolonged until a steady-state concentration of $CH_2 = CF_2$ is reached,

$$[CH_2 = CF_2]_{ss} = k_{1a} R_{C_2H_6}^{\frac{1}{2}} / k_2^{\frac{1}{2}} k_{18} (1 + k_4 [M] / k_5)$$

Inserting appropriate values of the various rate constants, at 23°C and 155°C, $(CH_2=CF_2)_{ss}$ has the values $1\cdot3\times10^{-9}$ and $1\cdot7\times10^{-9}$ mole cm⁻³ respectively. Since our reaction vessel had a volume of 160 ml the corresponding maximum amounts of $CH_2=CF_2$ in the products would be 2×10^{-7} and $2\cdot8\times10^{-7}$ mole respectively. These agree tolerably well with observed results for the longest photolyses in table 4 although the calculated values are somewhat low; probably our values of k_{18} used above were too large.

TABLE 4.—THE EFFECT OF PHOTOLYZING MIXTURES OF ACETONE AND HEXAFLUOROACETONE FOR VARIOUS TIMES

temp., t °C	time,	HFA	acetone	products, mole × 107			$CH_2 = CF_2$
	sec	mm	mm	CO	CH 3CF3	$CH_2 = CF_2$	CH ₃ CF ₃
23	3905	6.9	43.6	9.79	2.56	0.52	0.20
38	39000	9.7	43.6	147	36.4	2.90	0.08
157	225	10.8	63.7	23.1	3.55	2.4	0 .68
154	450	10.8	63.7	43·2	7.43	4·2	0.57
155	660	13.9	59·2	74.3	9.87	4.6	0.47

In view of the importance of reaction (18) our photolyses were always as short as possible. The average concentration of the $CH_2=CF_2$ during the run did not exceed about 10 % of the steady-state value and was frequently less. However, it is necessary to produce $\sim 5 \times 10^{-8}$ mole of $CH_2=CF_2$ for reasonable accuracy in the gas analysis and this fixed the lower limit of the percentage decomposition. We believe therefore that the $CH_2=CF_2$ analyses are accurate to within 10 %.

Reaction (18) has been discussed in some detail because, in a system where the products include olefines, such reactions must not be neglected. In principle, the addition to the olefine could be so fast as to make it impossible to obtain accurate olefine analyses at all.

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