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Kinetic Study of the Gas-phase Decomposition of the Trifluoroacetyl Radical

Effects of Temperature and Pressure upon the Rate Constants

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The kinetics and pressure dependence of the decomposition of the trifluoroacetyl radical:

$$CF_3CO+M \rightarrow CF_3+CO+M \qquad (5')$$

have been studied by generating the radicals from the selective photolysis of azomethane in the presence of 1,1,1-trifluoroacetaldehyde over the temperature range 338–417 K. The rate constants of the decomposition reaction ($k_{5'}$) have been measured relative to the radical combination reactions:

$$CH_3+CF_3CO \rightarrow CF_3COCH_3 \qquad (6)$$

$$2CH_3 \rightarrow C_2H_6. \qquad (2)$$

The rate constants ($k_{5'}$), were found to be pressure-dependent over the pressure range 50–740 Torr, with SF_6 as a bath gas.

The A factor of the radical decomposition reaction has been calculated from transition-state theory to be $A_{5'}^{\infty} \approx 2.2\times10^{13}\ s^{-1}$. Treatment of the pressure dependence of the rate constants ($k_{5'}$), according to the RRKM theory of unimolecular reactions, yielded a high-pressure limiting activation energy $E_{5'}^{\infty} = 83.1$ kJ mol^{-1}.

Thus the present data are consistent with a high-pressure limiting Arrhenius expression:

$$\log(k_{5'}^{\infty}/s^{-1}) = (13.34\pm0.8)-[(10000\pm1000)/2.303T]$$

where the error limits are estimates of the accuracies of the Arrhenius parameters.

The results are discussed in relation to existing data on the CF_3CO radical and are compared with kinetic data on the decomposition reactions of the CH_3CO and C_2H_5CO radicals.

Kinetic and thermochemical data on acyl radicals are important in their own right and have become increasingly in demand as the need for information on radical reactions grows with the development of kinetic modelling of complex systems such as combustions and atmospheric chemistry. Quantitative information on the decomposition reactions of acyl radicals is fragmentary and has a history of controversy.[1-4] While the rate constants for the decompositions of the acetyl[5-7] and propionyl[8-10] radicals appear to be reasonably well established and in line with current theories of chemical kinetics, for other acyl radicals few rate constants have been confirmed. The trifluoroacetyl radical is a case in point, where the sole quantitative study[11] reports an A factor approximately three powers of ten lower than the minimum A factor required by transition-state theory. In addition the observed rate constants[11] were found to be independent of pressure up to a total pressure of *ca.* 600 Torr,† in

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† 1 Torr = 101 325/760 Pa.

contrast to the predictions of unimolecular reaction rate theory and the observed pressure dependences of the CH_3CO and C_2H_5CO radical decomposition reactions.

Here we report a further investigation of the kinetics of the decomposition of the CF_3CO radical by a method which has yielded consistent data for the CH_3CO[12] and C_2H_5CO[8] radicals.

EXPERIMENTAL

APPARATUS AND PROCEDURE

Runs were carried out in a 159 cm^3 cylindrical quartz reaction vessel contained in an electrically heated furnace and controlled to better than ± 1 K. Reactant pressures were measured with a mercury manometer attached directly to the cell. Radiation of wavelength centred around 366 nm was isolated from a 250 W medium-pressure mercury arc by means of Corning filters no. 7-37 and 0-52. Under these conditions there was no photolysis of the trifluoroacetaldehyde.

ANALYSIS

CH_4, CO and N_2 were pumped off at liquid-air temperature with a Töpler pump and analysed by gas chromatography. The column consisted of 2.25 m of 30–60 mesh 5 Å molecular sieve and the carrier gas was H_2 with a thermal-conductivity detector. Temperature programming was carried out with the column initially at 323 K for 4 min followed by an increase of 30 K min^{-1} to 383 K. Under these conditions CO had a retention time of 6 min.

C_2H_6 was pumped off at 123 K from a Ward still *via* the Töpler pump. Gas-chromatographic analysis was carried out on a 1.75 m column packed with 100–120 mesh Porapak T and operated isothermally at 353 K with flame ionization detection.

The remainder of the products and reactants were then condensed into the injection loop of the gas chromatograph and analysed on the same column as for C_2H_6 but this time with temperature programming and flame ionization detection. The column was operated at room temperature for 4 min followed by a temperature rise of 35 K min^{-1} to 458 K. The retention time of 1,1,1-trifluoroacetone was 23 min.

Quantitative calibrations for the products CO, C_2H_6 and CF_3COCH_3 were carried out with authentic samples of these materials.

MATERIALS

Azomethane was prepared from *sym*-dimethylhydrazine dihydrochloride (Aldrich Chemical Co.) by the method described by Renaud and Leitch.[13] 1,1,1-Trifluoroacetaldehyde was obtained as the hydrate (Lancaster Syntheses Ltd) and dehydrated with a stirred mixture of P_2O_5 and concentrated H_2SO_4 maintained at 363 K. SF_6 (Cambrian Gases, C.P. grade) was used without further purification.

RESULTS

The proposed mechanism, to account for the formation of the products N_2, CH_4, CO, C_2H_6 and CF_3COCH_3 formed by the selective photolysis of $CH_3N{=}NCH_3$ in the presence of CF_3CHO, is as follows:

$$CH_3N{=}NCH_3 + h\nu \rightarrow 2CH_3 + N_2 \tag{1}$$

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

$$CH_3 + CF_3CHO \rightarrow CH_4 + CF_3CO \tag{3}$$

$$CF_3CO + M \rightleftarrows CF_3CO^* + M \tag{4, -4}$$

$$CF_3CO^* \rightarrow CF_3 + CO \tag{5}$$

$$CH_3 + CF_3CO \rightarrow CF_3COCH_3 \qquad (6)$$

$$CH_3 + CH_3N{=}NCH_3 \rightarrow CH_4 + CH_2N{=}NCH_3 \qquad (7)$$

$$\rightarrow (CH_3)_2NNCH_3 \qquad (8)$$

$$CH_2N{=}NCH_3 + R \rightarrow RCH_2N{=}NCH_3 \qquad (9)$$

$$(CH_3)_2NNCH_3 + R \rightarrow (CH_3)_2NN(CH_3)R. \qquad (10)$$

A steady-state treatment of the activated CF_3CO^* radicals gives

$$d[CH_3CO^*]/dt = k_4[CF_3CO][M] - k_{-4}[CF_3CO^*][M] - k_5[CF_3CO^*] = 0. \qquad (I)$$

We can also write the rate equations:

$$R_{CF_3COCH_3} = k_6[CH_3][CF_3CO]$$

$$R_{CO} = k_5[CF_3CO^*]$$

$$R_{C_2H_6} = k_2[CH_3]^2$$

where R_X is the rate of formation of product X. Substitution of these three rate equations into eqn (I) and rearranging yields

$$R_{CF_3COCH_3}/(R_{CO}R^{\frac{1}{2}}{}_{C_2H_6}) = F = (k_{-4}k_6)/(k_5k_4k_2^{\frac{1}{2}}) + k_6/(k_4k_2^{\frac{1}{2}}[M]). \qquad (II)$$

Thus a plot of the rate function, F, against $1/[M]$, a classical Hinshelwood–Lindemann plot, should be linear. In this treatment [M] is taken to be the initial total concentration of all reactants, on the basis that the reactions proceed to low percentage conversions. From eqn (II) it follows that as $[M] \rightarrow \infty$, *i.e.* $1/[M] \rightarrow 0$

$$F = (k_{-4}k_6)/(k_5k_4k_2^{\frac{1}{2}}) = k_6/(k_{5'}^{\infty}k_2^{\frac{1}{2}})$$

and that $k_6/(k_{5'}^{\infty}k_2^{\frac{1}{2}})$ can be calculated from the intercept of the plot of F against $1/[M]$, where $k_{5'}^{\infty}$ is the high-pressure limit of the decomposition reaction

$$CF_3CO + M \rightarrow CF_3 + CO + M. \qquad (5')$$

Absolute values of $k_{5'}^{\infty}$ were obtained by taking $k_2 = 2.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} independent of temperature[14] and by making the reasonable assumption that $k_2 = k_6$.

The experimental results for the temperatures 338, 377, 395 and 417 K are shown in table 1. The first point to note is that F displays distinct pressure dependence, for instance at 395 K, F decreases by a factor of 3.3 over the pressure range 26–658 Torr. This is good evidence for the pressure dependence of the CF_3CO decomposition reaction. It was not possible to carry out experiments below 338 K owing to the ready polymerization of the aldehyde.[15] At the same time the temperature range could not be extended beyond 417 K as the yields of CF_3COCH_3 became too small for accurate measurement. The apparatus was not designed to operate at total pressures exceeding 1 atm. The range of experimental conditions, which we recognize to be limited, was the maximum obtainable with the present system.

The Hinshelwood–Lindemann plots of the experimental data are reasonably good straight lines, which by least-mean-squares analyses yield the following values of $k_{5'}^{\infty}$:

T/K	338	377	395	417
$k_{5'}^{\infty}$/s^{-1}	4.05	42.8	117	376.

These in turn correspond to the following Arrhenius equation:

$$k_{5'}^{\infty} = 1.0 \times 10^{11} \exp(-8080/T) \text{ s}^{-1}.$$

Table 1. Rate data from the photolysis of azomethane in the presence of trifluoroacetaldehyde

$p_{(CH_3N)_2}$ /Torr	p_{CF_3CHO} /Torr	p_{total} /Torr^a	R_{CO} /10^{-8} mol dm^{-3} s^{-1}	$R_{C_2H_6}$ /10^{-8} mol dm^{-3} s^{-1}	$R_{CF_3COCH_3}$ /10^{-8} mol dm^{-3} s^{-1}	$F = \frac{R_{CF_3COCH_3}}{R_{CO} R^{\frac{1}{2}}_{C_2H_6}}$ /10^3 mol$^{-\frac{1}{2}}$ dm$^{\frac{3}{2}}$ s$^{\frac{1}{2}}$
			$T = 338$ K			
10	17	27	0.28	0.26	0.75	52.5
14	23	37	0.54	0.56	2.06	51.0
17	20	37	0.30	2.60	2.39	49.4
20	30	50	0.83	0.31	2.22	48.0
29	44	73	1.30	1.35	6.85	45.4
27	42	107	0.87	0.77	3.43	44.9
22	39	197	0.65	0.84	2.46	41.3
27	27	287	1.15	1.09	4.57	38.1
24	32	324	1.10	0.84	3.57	35.4
21	35	380	1.42	0.28	2.62	34.9
30	41	527	1.29	0.87	4.44	36.9
34	35	624	1.78	0.80	5.37	33.7
			$T = 377$ K			
10	16	26	0.47	0.82	0.35	8.22
12	22	34	0.70	2.36	0.80	7.44
10	20	42	0.71	0.63	0.41	7.28
18	28	46	1.03	3.01	1.09	6.10
13	25	48	0.49	1.42	0.41	7.02
18	36	54	1.24	2.38	1.20	6.27
27	40	67	1.82	2.08	1.60	6.10
30	44	74	1.96	1.98	1.61	5.83
31	47	78	1.82	6.23	2.68	5.90
30	41	105	1.55	1.18	0.89	5.29
28	42	154	1.36	8.18	1.71	4.40
27	41	208	1.58	2.95	1.09	4.02
26	35	254	1.19	2.04	0.71	4.18
32	40	318	1.91	0.68	0.63	3.99
32	42	378	1.26	7.63	1.29	3.71
34	55	497	0.63	7.95	0.64	3.60
31	56	613	1.02	6.73	9.31	3.52
29	44	739	0.94	3.52	6.28	3.56

			$T = 395$ K			
10	16	26	0.89	0.33	0.20	3.91
11	19	30	0.72	0.32	0.14	3.43
13	20	33	0.69	0.51	0.17	3.45
14	23	37	0.97	0.70	0.25	3.08
18	32	50	1.44	1.04	0.38	2.58
20	30	50	1.76	0.62	0.40	2.89
27	44	71	2.89	0.55	0.54	2.52
27	58	85	3.08	0.43	0.46	2.23
37	40	112	2.28	0.98	0.45	1.99
30	35	171	1.18	0.65	0.17	1.79
29	40	171	0.71	1.07	0.11	1.50
25	33	217	1.26	2.89	0.28	1.31
39	55	354	0.82	2.38	0.16	1.26
17	22	389	1.10	2.47	0.27	1.56
25	48	497	0.90	4.53	0.24	1.25
36	68	528	1.12	2.55	0.27	1.51
17	31	658	0.74	3.86	0.17	1.17
			$T = 417$ K			
9	18	27	0.68	1.79	0.23	2.53
10	20	30	0.79	3.34	0.34	2.35
12	30	42	1.07	1.30	0.23	1.88
18	24	42	1.02	0.65	0.14	1.70
15	35	50	1.15	3.26	0.31	1.49
24	45	69	1.81	3.40	0.43	1.29
39	40	79	1.80	0.75	0.20	1.28
20	41	128	1.29	1.45	0.14	0.901
26	40	181	1.15	5.28	0.17	0.643
40	61	279	1.32	3.23	0.14	0.590
36	48	316	1.21	5.22	0.20	0.724
38	47	434	0.98	3.63	0.10	0.536
46	48	478	2.22	5.80	0.23	0.430
44	52	624	1.90	2.49	0.11	0.367

[a] $p_{\text{total}} = p_{(\text{CH}_3\text{N})_2} + p_{\text{CF}_3\text{CHO}} + p_{\text{SF}_6}$.

At the mean temperature of these experiments the universal frequency factor for a unimolecular reaction (*ekT*/***h***) corresponds to 1.9×10^{13} s^{-1} and consequently the derived value of $A_5^\infty = 1.0 \times 10^{11}$ s^{-1} imples a large negative entropy of activation. Similarly low *A* factors were originally reported for the CH_3CO decompositions but these have been shown to be wrong. The problem in studies of the present type is that the experimental rate constants have been measured too far from the high-pressure limiting conditions and accurate extrapolations are difficult to make.

Two alternative extrapolation techniques were applied.[16] In the first a plot of $1/k$ against $1/P^{\frac{1}{2}}$ was made and again the intercept yields a value of k^∞, which often corresponds to an overestimate.[16] The present data for temperatures of 338, 377 and 395 K were treated in this way but the data for 417 K gave a negative intercept and were therefore neglected. The derived values of k^∞ are as follows:

T/K	338	377	395
$k_5^\infty/\mathrm{s}^{-1}$	4.8	68.6	273

corresponding to the Arrhenius equation

$$k_5^\infty = 4.3 \times 10^{12} \exp(-9320/T)\ \mathrm{s}^{-1}.$$

The second extrapolation procedure involves plotting $1/k$ against $1/p^\alpha$, where α is an adjustable parameter with a value between 0 and 1. α is optimised to give the best straight-line fit of the data. From the data of table 1, k_5^∞ values derived in this way are as follows:

T/K	338	377	395	417
α	0.5	0.6	0.7	0.8
$k_5^\infty/\mathrm{s}^{-1}$	4.8	58.6	155	582.

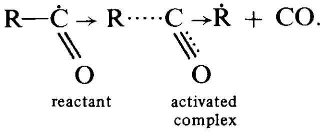
These yield the following Arrhenius equation, when treated by a least-mean-squares analysis:

$$k_5^\infty = 4.0 \times 10^{11} \exp(-8520/T)\ \mathrm{s}^{-1}.$$

It is clear that while these alternative extrapolations offer some improvement on the Hinshelwood–Lindemann procedure, none of the treatments yields an acceptable value of the *A* factor for the radical decomposition reaction. Accordingly a different approach was applied.

The high-pressure limiting *A* factor for the radical decomposition reaction was calculated from transition-state theory, and the pressure dependence of the rate constants was treated by the RRKM theory of unimolecular reactions to derive the high-pressure limiting activation energy.

For the CH_3CO and C_2H_5CO radical decomposition reactions the experimental *A*-factors[5–10] are close to the value of (*ekT*/***h***) indicating that the structure of the activated complex is close to that of the reactant radical. These structures can be represented as



$$\mathrm{R{-}\dot{C}{=}O \rightarrow R\cdots C{=}O \rightarrow \dot{R} + CO.}$$

The main structural changes contributing to $\Delta S^\ddagger$ in this case involve changes in the vibrational modes. The vibrational assignments for the CF_3CO radical have been made from the experimental frequencies[17] in the aldehyde CF_3CHO. The activated complex was assumed to involve a loosening of the C—C=O bending frequency and

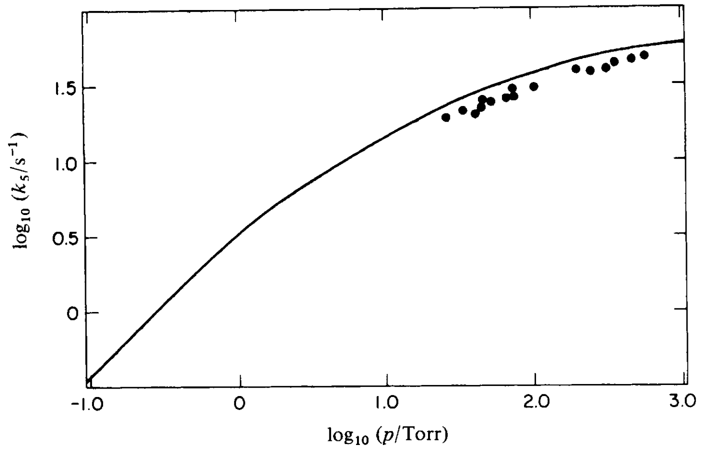


Fig. 1. (—) Calculated RRKM fall-off curve (Forst program) optimized to experimental rate constants at 377 K (●).

a slight tightening of the C=O stretching frequency, in accord with the structures proposed above. The assigned vibrational frequencies are listed in the Appendix.

The A factor for reaction (5′) was then calculated from the transition-state theory equation

$$\log(A_{5'}/\text{s}^{-1}) = \log(ek/h)+\log(T/\text{K})+\Delta S^{\ddagger}/2.303R$$

in which the entropy of activation, $\Delta S^{\ddagger} = 0.29$ J mol^{-1} K^{-1}, was calculated from the changes in vibrational frequencies and the tabulation of assigned entropies,[3] and the other terms have their usual meaning. For the mean temperature of these experiments, 337 K, this corresponds to $A_{5'} = 2.2\times10^{13}$ s^{-1}.

The development and application of the RRKM theory of unimolecular reactions have been described in detail by Robinson and Holbrook.[3] The calculations are most readily achieved with the aid of computer programs. For the present purposes two such programs were applied, a Forst program and a Marcus program. The Forst program requires a knowledge of the Arrhenius parameters for the reaction as well as the usual molecular properties. The Marcus program on the other hand, calculates the A factor from the vibrational assignments of the reactant and activation complex. The input data required for the computer program are listed in the Appendix.

Taking the previously calculated value $A_{5'} = 2.2\times10^{13}$ s^{-1}, the activation energy was optimised to the fall-off data at the experimental mid-point temperature of 377 K by the use of the Forst program. This resulted in a value of $E_{5'} = 83.1$ kJ mol^{-1}. The derived pressure fall-off curve is compared with the experimental data in fig. 1.

The Marcus program was then used to treat the data at all four temperatures and the corresponding fall-off curves are shown in fig. 2 and 3. The best fits were obtained at 377 and 395 K. At 338 and 417 K the calculated curves were an underestimate and overestimate, respectively, in relation to the experimental data, which could be interpreted as indicating a systematic error. Better fits of the data could be derived by adjustments to the estimated A factor, but this hardly seems justified.

We conclude that the present data for reaction (5′) are consistent with the Arrhenius equation

$$\log(k_{5'}^{\infty}/\text{s}^{-1}) = (13.34\pm0.8)-[(10000\pm1000)/2.303T]$$

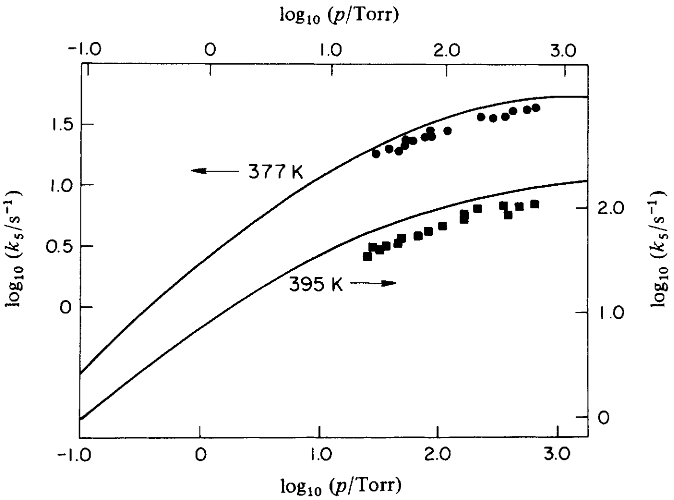


Fig. 2. (—) Calculated RRKM fall-off curves (Marcus program) compared with experimental rate constants at 377 (●) and 395 (■) K.

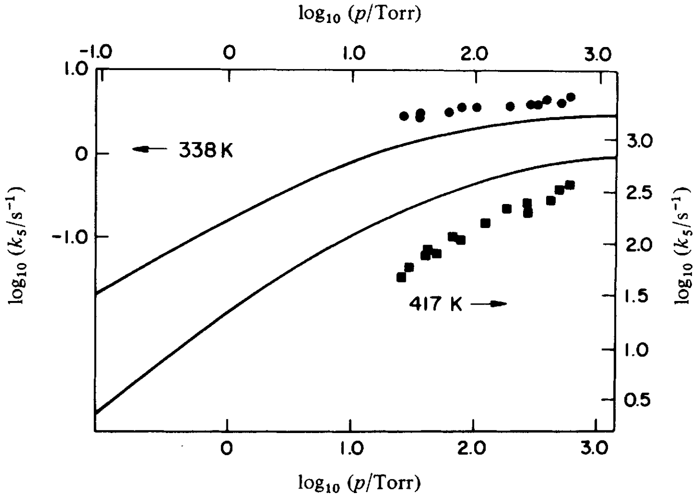


Fig. 3. (—) Calculated RRKM fall-off curves (Marcus program) compared with experimental rate constants at 338 (●) and 417 (■) K.

in which the error limits are estimates of the overall accuracies of the derived *A* factor and temperature coefficient and reflect the problems inherent in the interpretation of data obtained in the pressure fall-off region.

DISCUSSION

KINETIC STUDIES OF THE CF_3CO DECOMPOSITION REACTION

Amphlett and Whittle[11] obtained kinetic data on the CF_3CO decomposition reaction

$$CF_3CO \rightarrow CF_3 + CO \qquad (5)$$

relative to the reactions

$$CF_3CO + X_2 \rightarrow CF_3COX + X \qquad (11)$$

where $X_2 = Cl_2$ or Br_2, by photolysing the halogen in the presence of CF_3CHO. Over the temperature range 300–443 K they determined

$$\log(k_5/s^{-1}) = 10.42 - (5030/2.303T)$$

and in view of their assumed values of k_{11} it was recommended that A_5 and E_5 be regarded as upper and lower limits, respectively. This paper also incorporates some earlier data of Tucker and Whittle[18] on reaction (5), derived from the photolysis of $(CF_3)_2CO$ in the presence of Cl_2.

A comparison of the rate constants at 377 K reveals a value of $k_5 = 4.2 \times 10^4\ s^{-1}$ as measured by Amphlett and Whittle[11] and a value of $k_5^{\infty} = 66.5\ s^{-1}$ from the present data. At present we have no explanations of this very large discrepancy between the two studies. One could argue that the values of the rate constants (k_{11}) of the reference reactions assumed by Amphlett and Whittle might be too high, but it seems unlikely that any discrepancy in the k_{11} values would amount to as much as a factor of 600.

The abnormally low A factor reported by Amphlett and Whittle was at the time of publication compatible with the existing literature value of the A factor for the CH_3CO radical decomposition, which was subsequently shown to be much closer to (ekT/h). Amphlett and Whittle considered the possibility that their rate constants (k_5) had been measured in the pressure fall-off region. The bulk of their experiments, performed over the pressure range 20–80 Torr, showed no variation with pressure, as did a reaction carried out in the presence of 550 Torr of added N_2. In view of the established pressure dependences of the CH_3CO and C_2H_5CO decompositions, together with the present finding of a distinct pressure dependence of the CF_3CO decomposition reaction, the lack of such an effect in the experiments of Amphlett and Whittle is puzzling.

McIntosh and Porter[19] attempted to determine the kinetic stability of the CF_3CO radical from flash photolysis of $(CF_3)_2CO$ alone and in the presence of Br_2. Their derived data for reaction (5) were inconclusive, however, owing to the likely generation of excited CF_3CO radicals from the primary photochemical dissociation.

One other set of relevant experiments involving CF_3CHO have been reported by Loucks *et al.*,[20] who pyrolysed di-t-butyl peroxide in the presence of the aldehyde over the temperature range 390–441 K. CF_3COCH_3 was observed as a product and was ascribed to the following reaction sequence:

$$CH_3 + CF_3CHO \rightarrow CH_3(CF_3)CH\dot{O} \qquad (12)$$

$$CH_3(CF_3)CH\dot{O} \rightarrow CF_3COCH_3 + H. \qquad (13)$$

The occurrence of the reaction

$$CH_3 + CF_3CO \rightarrow CF_3COCH_3 \qquad (6)$$

in this system was discounted on the grounds of the lack of thermal stability of the CF_3CO radical at these temperatures. Small amounts of the alcohol $CH_3(CF_3)CHOH$ were detected, which is good evidence for the occurrence of reaction (12) followed by

$$CH_3(CF_3)CH\dot{O} + CF_3CHO \rightarrow CH_3(CF_3)CHOH + CF_3CO.$$

The exclusive decomposition of the alkoxy radical according to reaction (13) in preference to the alternative processes

$$\mathrm{CH_3(CF_3)CH\dot{O}} \rightarrow \mathrm{CH_3 + CF_3CHO}$$
$$\rightarrow \mathrm{CF_3 + CH_3CHO}$$

is questionable on thermochemical grounds. In addition, recent studies[21, 22] of the decompositions of the analogous alkoxy radicals, $\mathrm{CH_3(CF_3)_2C\dot{O}}$ and $\mathrm{CF_3(CH_3)_2C\dot{O}}$, have shown that decomposition in each case occurs exclusively *via* CF_3 loss. A further argument against reactions (12) and (13) forming the exclusive route to CF_3COCH_3 formation in the Loucks *et al.*[20] system comes from their observation that the yields of this product were 4–5 times larger than the yields of H_2. The latter would be expected to be the major product of the H atoms in the presence of the labile CH of the parent aldehyde. Even if reaction (12) did occur to some extent, the lack of equality between CF_3COCH_3 and H_2 implies an additional source of CF_3COCH_3 in this system, which we contend is reaction (6). The Arrhenius parameters obtained by Loucks *et al.*[20] for the proposed reaction (12)

$$k_{12} = 5.0 \times 10^6 \exp(-2010/T)\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

are highly suspect. Both the A factor and the activation energy would appear to be seriously underestimated on the basis of transition-state theory and in relation to recent related data for alkyl-radical additions to carbonyl groups.[22]

Unfortunately Loucks *et al.*[20] provide no analytical data on the rates of formation of CO in their study, which would have enabled a test of their system in terms of a mechanism involving reactions (5) and (6). It is possible, however, to treat our data according to a mechanism containing reactions (12) and (13). This kinetic analysis is similar to those which we have recently used for CH_3 additions to CF_3COCF_3[21] and to CF_3COCH_3.[22] If reactions (12) and (13) are the only sources of CF_3COCH_3 formation then for a fixed temperature a plot of $R_{CF_3COCH_3}/R^{\frac{1}{2}}_{C_2H_6}$ against $[CF_3COCH_3]$ should be linear and pass through the origin. When treated in this fashion, the present data do not show such linear dependence. While this does not rule out the formation of some of the CF_3COCH_3 by reactions (12) and (13), it disproves the carbonyl-addition mechanism as the exclusive route to this product.

COMPARISON OF CF_3CO, CH_3CO AND C_2H_5CO DECOMPOSITIONS

It is interesting to compare the present results for the decomposition of the CF_3CO radical with data for the related CH_3CO and C_2H_5CO radical reactions. As seen from table 2 the rate constants at 377 K reveal that the sequence of kinetic stabilities runs $CF_3CO > CH_3CO > C_2H_5CO$, which is a reflection of the activation energies for the decomposition reactions since the A factors are effectively equal. On the other hand, in its pressure fall-off behaviour the CF_3CO radical is much closer to C_2H_5CO than to CH_3CO, as shown by the $P_{\frac{1}{2}}$ values, which are the pressures at which k_∞ falls to one-half of its high-pressure value.

$P_{\frac{1}{2}}$ values are determined by the critical energy of the reaction together with the number of effective oscillators of the molecule. Thus the large difference between the $P_{\frac{1}{2}}$ values for CH_3CO and CF_3CO is accounted for by the increased number of effective oscillators arising from the F atoms in CF_3CO, together with the larger E^∞ for CF_3CO. In the case of C_2H_5CO and CF_3CO the greater number of effective oscillators for C_2H_5CO compared with CF_3CO is offset by the smaller activation energy for the decomposition of C_2H_5CO compared with CF_3CO.

Table 2. Comparison of the kinetics of the decompositions of the radicals CF_3CO, CH_3CO and C_2H_5CO

radical	E^∞/kJ mol^{-1}	log (A^∞/s^{-1})	k^∞/s$^{-1\,a}$	$p_{\frac{1}{2}}$/Torr^a
CF_3CO	83.1	13.3	6.0×10^1	56
CH_3CO	72.0	13.5	3.3×10^3	1135^b
C_2H_5CO	61.5	13.3	6.0×10^4	216^c

^{a} At 377 K. ^{b} Extrapolated from the data of Watkins and Word[7] and of O'Neal and Benson.[23] ^{c} Extrapolated from the data of Watkins and Thompson[10] and of Kerr and Lloyd.[8]

CONCLUSIONS

The present kinetic study of the CF_3CO decomposition reaction suggests a rate constant given by

$$k_5^\infty \approx 2.2\times10^{13}\exp(-10000/T)\ \mathrm{s}^{-1}.$$

This result is consistent with literature data for the kinetics of the CH_3CO and C_2H_5CO decomposition reactions but is seriously at variance with previously published data,[11] which indicate rate constants *ca.* 600 times greater than those corresponding to the above Arrhenius equation.

In view of this large unexplained discrepancy, it would be desirable to obtain further data on reaction (5′) by an independent study. We are presently attempting to investigate the kinetics of the system

$$CF_3+CO+M \rightleftharpoons CF_3CO+M$$

by generating CF_3 from the photolysis of $CF_3N{=}NCF_3$ in the presence of CO.

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APPENDIX TABLE

Vibrational assignments[a]

	$\bar{\nu}$/cm^{-1}		
	CF_3CHO	CF_3CO	$CF_3CO^\ddagger$
C=O str.	1770	2100	2100
C—F str.	1305	1305	1305
C—F str.	1200	1200	1200
C—F str.	1140	1140	1140
C—C str.	957	370	rc[b]
CF_3 def.	840	840	840
CF_3 def.	710	710	710
CF_3 def.	530	530	530
C—C=O bend	430	220	100
CF_3 rock	320	215	215
CF_3 rock	265	180	180
torsion	184	150	150

[a] Collision diameter of SF_6, $\sigma = 5 \times 10^{-8}$ cm; collision efficiency of $SF_6 = 0.5$. [b] Reaction coordinate.