Polyfluoroalkyl Derivatives of Nitrogen. Part XXXIV.[1] The Kinetics of the Gas-phase Thermal Decomposition of Trifluoroacetyl Nitrite. The Slow Reaction

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The kinetics of the gas-phase thermal decomposition of trifluoroacetyl nitrite have been studied over the temperature range 119—172 °C. The formation of CO_2 is quantitative and the decomposition is first order in reactant. The rate constant for the decomposition:

$$\log k\ (s^{-1}) = (14{\cdot}26 \pm 0{\cdot}23) - (33{,}800 \pm 440)/4{\cdot}576\ T$$

is independent of the initial pressure of reactant from 7·7—22·2 Torr and independent of the surface:volume ratio of the reaction vessel; it is also unaffected by the presence of nitric oxide, propene, trifluoronitrosomethane, and carbon dioxide. The formation of trifluoronitrosomethane is inhibited by propene and by any trifluoronitrosomethane initially present, but is enhanced by the presence of nitric oxide. It is concluded that the reaction occurs by a homogeneous radical non-chain process, in which the initial rate-determining step is the cleavage of the O–NO bond to produce nitric oxide and the trifluoroacetoxyl radical.

THE thermal decomposition of trifluoroacetyl nitrite is a very useful route for the preparation of trifluoronitrosomethane [2-4] $CF_3{\cdot}CO_2NO \longrightarrow CF_3NO + CO_2$ and a continuous process based on these earlier results has been developed [5] in which the decarboxylation is carried out in a fluorocarbon solvent. These early studies of the pyrolysis were concerned mainly with the nature and quantities of the products formed in the decomposition.[2] When the reactant is entrained in a stream of nitrogen and pyrolysed in a platinum reaction vessel at 190°, carbon dioxide is formed quantitatively but the yield of trifluoronitrosomethane (expressed in terms of the reactant decomposed) decreased as the residence time increased. This indicates that trifluoronitrosomethane is removed by secondary reactions, and the identification of *O*-nitrosobistrifluoromethylhydroxylamine and tristrifluoromethylhydroxylamine supports this suggestion.[2] The thermal decomposition of trifluoroacetyl nitrite also can become explosive if the concentration of reactant becomes too high.[3] The present paper reports a kinetic study of the slow reaction; the kinetics of the explosive decomposition will be considered in a subsequent paper.

EXPERIMENTAL

Apparatus.—The silica reaction vessel (20 × 3·5 cm i.d.) was enclosed in an electric furnace and connected to a conventional vacuum system by a ground-glass joint. The furnace was controlled by a Sunvic RT2 temperature controller with a platinum resistance thermometer, while the temperature was measured with a calibrated Chromel–Alumel thermocouple. The temperature variation along the reaction vessel was only ±0·5°, while the fluctuation in temperature at a given point was never more than ±0·2° during an experiment.

The reactant is a liquid of low volatility at room temperature, which is readily adsorbed on tap grease and reacts with mercury. Thus greaseless taps (Springham diaphragm taps with Viton A diaphragms) were used wherever adsorption of reactant on tap grease might affect the kinetic results, and all pressure measurements involving the reactant were made with Bourdon gauges similar to that of Foord.[6] The reactant was stored in the liquid state in an ampoule and this ampoule and the 1 litre mixing bulb were enclosed in an air thermostat. The tubing connecting the reaction vessel to the mixing bulb was also heated electrically to avoid any condensation. The initial pressure in the reaction vessel was obtained from the known pressure in the mixing bulb and the expansion ratio for the mixing bulb and reaction vessel, while the pressure during the reaction was obtained from the analysis of reaction mixtures. After the required reaction time, the contents of the reaction vessel were condensed into the analysis train and, when the sample had warmed to room temperature, its pressure in a known volume was measured. The corresponding pressure in the reaction vessel could then be obtained from the known volume ratios for the apparatus. To obtain detailed kinetic data about the course of the reaction, mixtures which had undergone varying degrees of reaction were analysed. The experiments for a given set of experimental conditions were carried out in a random order and some duplicate experiments were made also, as a check, but these were always in good agreement. When the pressure of reactant in the mixing bulb exceeded the vapour pressure at room temperature (*ca.* 15 Torr), nitrogen was admitted to the spoon of the gauge as a ' buffer ', but the pressure of reaction mixtures for analysis were always measured in a sufficiently large volume to keep the total pressure below this value.

Materials.—Trifluoroacetic anhydride and dinitrogen trioxide were condensed in an ampoule cooled in liquid nitrogen. The mixture was then allowed to warm to room temperature, and the product, purified by distillation under reduced pressure, had physical and spectroscopic data identical to those of pure trifluoroacetyl nitrite. Dinitrogen trioxide was prepared by condensing equimolar quantities of nitric oxide and nitrogen dioxide in a trap cooled to

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[1] Part XXXIII, J. D. Crabtree, R. N. Haszeldine, K. Ridings, R. F. Simmons, and S. Smith, *J.C.S. Perkins II*, 1972, 119.

[2] R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 1953, 4172; R. E. Ranks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 1961, 64; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.* (*C*), 1966, 1350.

[3] C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, 1962, **27**, 1064.

[4] J. D. Park, R. W. Rosser, and J. R. Lacher, *J. Org. Chem.*, 1962, **27**, 1462.

[5] U.S.P. 3,162,692/1964.

[6] S. G. Foord, *J. Sci. Instr.*, 1934, **11**, 126.

$-196°$. Nitric oxide was prepared by the reduction of sodium nitrite with acidified ferrous sulphate solution, and purified by passage through 30% sodium hydroxide solution and conc. sulphuric acid. The nitrogen dioxide was prepared by the reaction of stoicheiometric quantities of nitric oxide and oxygen. Trifluoronitrosomethane [7] was spectroscopically and analytically pure. Samples of pure *O*-nitrosobistrifluoromethylhydroxylamine and tristrifluoromethylhydroxylamine were available for the calibration of the gas chromatography columns.

Analysis of Reaction Mixtures.—Preliminary experiments showed that the products of the decomposition were carbon dioxide, trifluoronitrosomethane, nitric oxide, tristrifluoromethylhydroxylamine, and *O*-nitrosobistrifluoromethylhydroxylamine. A wide range of chromatographic columns was used in an attempt to separate these products from each other and from the reactant, but no single column gave the required analytical data, and an analytical method based on fractional condensation and gas chromatography was finally adopted. After the pressure of the reaction mixture in a known volume had been determined, the mixture was cooled to $-196°$ and allowed to distil at a pressure of 1—2 Torr through two U-tubes, cooled to -72 and $-182°$ respectively, into a trap cooled to $-196°$. The $-72°$ fraction was pure reactant, while the most volatile fraction was pure nitric oxide, and the pressures were measured for each of these components in a suitable volume. After the $-182°$ fraction had been allowed to warm up to room temperature and mix for at least 5 min (to ensure that the mixture was homogeneous), samples were analysed with either a 2-m column of silica gel or an 8-m column of Kel–F 3 oil on Celite. The former column gave an analysis for carbon dioxide and trifluoronitrosomethane, while the other column analysed the tristrifluoromethylhydroxylamine and *O*-nitrosobistrifluoromethylhydroxylamine. Since the initial pressure of reactant was always low (<25 Torr), however, there was insufficient material to obtain both analyses from the same reaction mixture and thus duplicate experiments were required for a complete analysis. The analysis of synthetic mixtures similar in composition to the reaction mixtures showed that this procedure enabled each component to be estimated with an error of $<2\%$, while the typical analytical results given in Table 1 show that the recovery was quantitative within the experimental error. Complete analyses were only performed, however, at the extremes of the temperature range and, at the intermediate temperatures, the analyses were restricted to reactant, carbon dioxide, and trifluoronitrosomethane.

TABLE 1

Analytical data for the thermal decomposition of trifluoroacetyl nitrite

Temp. (°C)	Initial pressure $CF_3{\cdot}CO_2NO$ (Torr)	Pressure $CF_3{\cdot}CO_2NO$ reacted	Partial pressures of products (Torr)						Analytical recovery (%)
			CO_2	NO (x)	CF_3NO (y)	$(CF_3)_2NOCF_3$ (z)	$(CF_3)_2NONO$	$x + y + z$	
172	9·3	1·71	1·70	0·49	0·97	0·14		1·60	99·6
		2·96	2·82	0·41	1·61	0·30		2·32	95·1
		4·48	4·32	1·18	2·66	0·49	0·01	4·33	98·2
		6·25	6·30	1·81	3·67	0·80	0·01	6·28	99·8
		7·61	7·71	2·50	4·36	0·83	0·02	7·69	100·0
125	10·4	0·29	0·41	0·25	0·02	0·09		0·36	96·4
		0·81	0·85	0·49	0·14	0·18		0·81	97·1
		1·31	1·26	0·40	0·63	0·22		1·25	99·6
		1·60	1·74	0·41	1·10	0·26		1·77	101·1

RESULTS

The kinetics of the thermal decomposition of trifluoroacetyl nitrite have been examined at seven temperatures within the range 119—172°. The initial pressure of reactant was restricted to 7·7—22·2 Torr because of the low vapour pressure of the reactant but, at a given temperature, the reaction has been examined at three different initial pressures at least. The analytical results showed that in every case carbon dioxide was formed quantitatively and that the major part of the nitrogen appeared as trifluoronitrosomethane and nitric oxide (see Table 1). Significant amounts of tristrifluoromethylhydroxylamine were formed also but the amount of *O*-nitrosobistrifluoromethylhydroxylamine was always negligible ($\leqslant 0{\cdot}2$ Torr). Table 1 also shows that the carbon dioxide formed in the decomposition was equal to the combined amounts of nitric oxide, trifluoronitrosomethane, and tristrifluoromethylhydroxylamine. Each of these latter three compounds contain one nitrogen atom in the molecule and thus the decomposition can be represented by the equation:

$$nCF_3CO_2NO = nCO_2 + xNO + yCF_3NO + z(CF_3)_2NOCF_3$$

where the sum $(x + y + z) = n$.

An examination of the initial rates of removal of reactant and plots of log (partial pressure of reactant) against time showed that the reaction is first order in trifluoroacetyl nitrite. To obtain reliable first-order rate constants for the decomposition, however, it is necessary to allow for the ' dead space ' in the apparatus. The above stoicheiometric equation shows that the pressure should double during the reaction in the absence of any ' dead space ' and thus the integrated first-order rate equation becomes: [8]

$$\ln\,[P_0/(2^aP_0 - P)] = kt$$

where P_0 is the initial pressure, P the total pressure of the reaction mixture at time t, and $a = (1 + V_cT_h/V_hT_c)^{-1}$. In this latter expression V_c and T_c are the volume and temperature of the ' dead space ' and V_h and T_h are the volume and temperature of the reaction vessel respectively. Figure 1 shows that plots of log $(2^aP_0 - P)$ against time gave good straight lines which extended up to 85% reaction. The rate constants obtained from the slopes of these lines are summarised in Table 2 and it can be seen that they are effectively independent of the initial pressure of reactant.

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[7] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881.

[8] P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655.

A plot of log (rate constant) against $1/T$ (K) gave a good straight line which corresponds to the Arrhenius equation:

$$\log k\ (\mathrm{s}^{-1}) = (14{\cdot}26 \pm 0{\cdot}23) - (33{,}800 \pm 440)/4{\cdot}576T$$

Several kinetic experiments were carried out using a reaction vessel in which the surface : volume ratio had been increased approximately seven times by packing it with silica tubing. The decomposition was still first order in reactant and the first-order rate constants are compared in Table 3 with those obtained with the unpacked vessel. The agreement between the two sets of values is very satisfactory and thus the reactant is consumed in an homogeneous process. In addition, the appearance of carbon dioxide and trifluoronitrosomethane were unaffected by this increase in the surface : volume ratio of the reaction vessel.

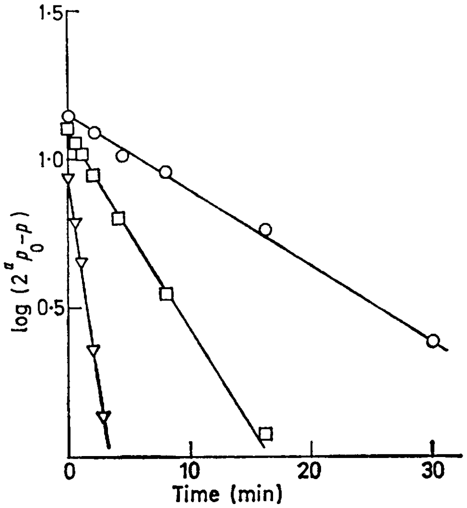

FIGURE 1 First order function plots for the disappearance of trifluoroacetyl nitrite. Temperature: ○ 145°; □ 157°; ▽ 172 °C

TABLE 2

Variation of rate constant for decomposition with temperature

Temp. (°C)	Initial pressure (Torr)	$k \times 10^5$ (s^{-1})	Temp. (°C)	Initial pressure (Torr)	$k \times 10^5$ (s^{-1})
119	10·6	2·9	157	9·1	117
	14·9	3·2		9·7	120
	19·3	3·0		14·0	117
129	10·2	7·5		18·0	123
	11·1	8·5		22·2	122
	18·6	8·7	161	7·7	228
	22·4	9·0		9·6	230
133	8·1	12·0		13·4	225
	10·2	13·1		17·2	234
	14·5	14·8	172	7·7	426
	19·1	13·2		9·6	444
145	10·4	40·0		13·4	448
	14·7	42·0		17·3	433
	19·2	42·0			
	24·0	41·0			

TABLE 3

Effect of surface:volume ratio of reaction vessel on the rate constant for the decomposition

Temp. (°C)	Initial pressure (Torr)	$k \times 10^5$ (s^{-1}) Packed vessel	Unpacked (average)
145	6·8	39·6	41·2
	9·3	39·2	
	12·0	46·6	
157	9·4	118	120·5
	11·7	122	

Two distinct reaction mechanisms can be visualised which are in accord with these kinetic results. The first involves an initial fission of the weakest bond in the reactant molecule to give two radical fragments, followed by their subsequent rapid reaction, while the second involves a molecular decomposition followed by further reaction of the initial products. In an attempt to obtain further information about the precise reaction mechanism, therefore, the effect of a number of additives on the reaction has been examined. Table 4 shows that none of the additives used had any effect on the first-order rate constant for the consumption of reactant, which strongly suggests that trifluoroacetyl nitrite is not removed from the system by any radical chain process. In contrast, however, the formation of trifluoronitrosomethane was affected by the initial addition of propene, nitric oxide, and trifluoronitrosomethane itself. None of these additives had any effect on the formation of carbon dioxide and the addition of carbon dioxide showed that this product had no effect at all on the course of the reaction.

TABLE 4

Effect of additives on the rate constant for the decomposition

Temp. (°C)	Initial pressure CF_3CO_2NO (Torr)	Additive	Mole % additive	$k \times 10^3$ (s^{-1})
157	9·1	None		1·17
	9·0	CO_2	50	1·20
	12·0	CF_3NO	50	1·14
	9·1	NO	54	1·19
	9·1	NO	15	1·13
	8·6	NO	40	1·17
	8·6	NO	71	1·12
172	13·4	None		4·48
	12·8	C_3H_6	52	4·56
129	11·1	None		0·085
	10·2	C_3H_6	54	0·084

The addition of an equimolar quantity of trifluoronitrosomethane reduced the initial rate of formation of this product by a factor of 2 and the yield later in the reaction was reduced by *ca.* 30%. Separate experiments showed that no significant decomposition of trifluoronitrosomethane occurs under the present reaction conditions and thus this reduction in rate must arise from a specific effect of trifluoronitrosomethane itself. Figure 2 shows that increasing amounts of nitric oxide favours the formation of trifluoronitrosomethane. A linear relation exists between the quantity of trifluoronitrosomethane formed and the amount of reactant decomposed, and the slope of these lines represents the number of moles of trifluoronitrosomethane formed for each mole of reactant which decomposes. For the reactant itself the slope of this line was only 0·63, but when the initial ratio of reactant : nitric oxide was 1 : 2·43 the slope of the line was almost 0·9, so that the formation of trifluoronitrosomethane was almost quantitative under these conditions.

Figure 3 shows that the addition of propene had no effect on the consumption of reactant or on the appearance of carbon dioxide, but the formation of trifluoronitrosomethane was affected quite markedly. First, there was an induction period for the formation of this product, whereas in the absence of propene there was no induction period at the higher temperatures. At the lowest temperature used in the present work, however, there was a suggestion that trifluoronitrosomethane was not formed from the very start of the reaction. In addition, Figure 3 shows that propene also reduces the absolute amount of trifluoronitrosomethane formed in the reaction. These observations on the effect of additives on the formation of trifluoronitrosomethane, therefore, suggest that this product is not formed in a simple molecular process.

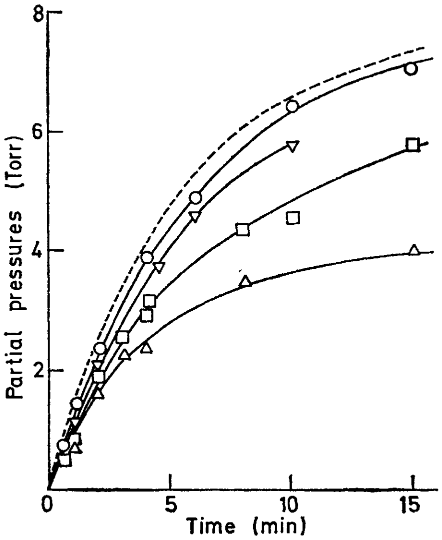

FIGURE 2 Effect of nitric oxide on the formation of trifluoronitrosomethane. Temperature 157 °C. Nitric oxide added: △ none; □ 15 mol %; ▽ 40 mol %; ○ 71 mol %. ---- Formation of CO_2

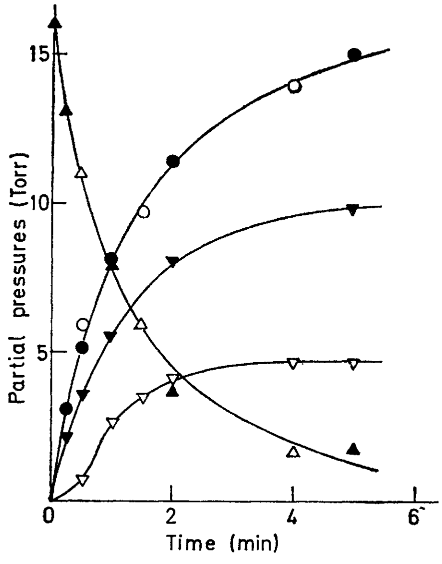

FIGURE 3 Effect of propene on the decomposition of trifluoroacetyl nitrite. Temperature 172 °C. △, ▲ $CF_3{\cdot}CO_2NO$; ○, ● CO_2; ▽, ▼ CF_3NO. Open symbols no added C_3H_6; full symbols added C_3H_6

DISCUSSION

The above results show that the gas-phase thermal decomposition of trifluoroacetyl nitrite is first order in reactant between 119 and 172° from 7·7 to 22·2 Torr. The reaction is homogeneous and the consumption of reactant is unaffected by nitric oxide and propene. In contrast, the appearance of trifluoronitrosomethane is affected by both these additives and by the addition of trifluoronitrosomethane itself. In general, the kinetics of the thermal decomposition of gaseous organic compounds can be explained in terms of one of three distinct mechanisms, namely radical chain, radical non-chain, and molecular processes. In the present case, however, a radical chain mechanism can be rejected since the disappearance of trifluoroacetyl nitrite is unaffected by additives which are well known to be powerful inhibitors of radical-chain processes. In addition, the rate equation predicted by any plausible reaction mechanism of this type is not in accord with the experimental results. A molecular mechanism similar to that suggested by Park *et al.*[4] can be rejected, since such a mechanism requires quantitative yields of both carbon dioxide and trifluoronitrosomethane. To explain the present results in terms of such a mechanism it would be necessary to invoke secondary reactions of trifluoronitrosomethane, but direct experiments show that the required decomposition reactions do not occur under the present reaction conditions.

If the thermal decomposition of trifluoroacetyl nitrite occurs by a radical non-chain mechanism, the first step in the reaction must involve the fission of the weakest bond in the reactant molecule. A consideration of known bond-dissociation energies in other compounds[9] suggests strongly that this will be the O–NO bond. The strength of the corresponding bond in alkyl nitrites[9] is close to 37 kcal mol^{-1}. It follows that reaction (1) is the most likely first step in the reaction mechanism. The subsequent decomposition of the trifluoroacetoxyl radical by reaction (2) gives carbon dioxide and trifluoromethyl radicals and, if there is no alternative reaction for the former species, the quantitative yield of carbon dioxide can be explained. The kinetics of the decomposition of alkyl nitrites have generally been discussed in terms of a mechanism similar to that proposed[10] for the decomposition of ethyl nitrite. An analogous reaction scheme cannot be devised for the thermal decomposition of trifluoroacetyl nitrite, however, because the corresponding abstraction reactions would involve cleavage of a C–F bond. This is energetically unfavourable at the temperatures used in this study, but an alternative radical non-chain mechanism can be envisaged which can explain the present results, namely:

$$CF_3{\cdot}CO_2NO \longrightarrow CF_3CO_2{\cdot} + NO \quad (1)$$
$$CF_3{\cdot}CO_2{\cdot} \longrightarrow CF_3{\cdot} + CO_2 \quad (2)$$
$$CF_3{\cdot} + NO \longrightarrow CF_3NO \quad (3)$$
$$CF_3NO + CF_3{\cdot} \longrightarrow (CF_3)_2N{\cdot}O{\cdot} \quad (4)$$
$$(CF_3)_2N{\cdot}O{\cdot} + CF_3{\cdot} \longrightarrow (CF_3)_2NOCF_3 \quad (5)$$
$$(CF_3)_2N{\cdot}O{\cdot} + NO \longrightarrow (CF_3)_2NONO \quad (6)$$

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[9] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 1958.

[10] J. B. Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801; 1956, **78**, 1780.

This mechanism predicts that the rate of decomposition of trifluoroacetyl nitrite is $-\mathrm{d}[CF_3{\cdot}CO_2NO]/\mathrm{d}t = k_1[CF_3{\cdot}CO_2NO]$ and, applying the steady-state approximation to the trifluoroacetoxyl radical, the same rate equation is predicted for the formation of carbon dioxide. Both these predictions are in accord with the experimental observations. The expected rate of formation of trifluoronitrosomethane can be derived by applying the steady-state treatment to the trifluoromethyl radical.

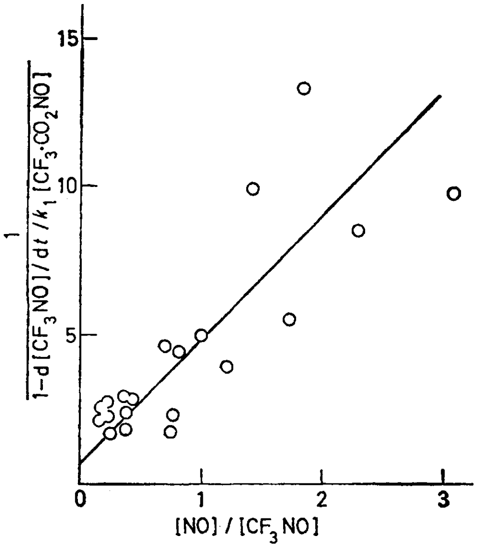

FIGURE 4 Variation of $1/(1 - \mathrm{d}[CF_3NO]/\mathrm{d}t/k_1[CF_3{\cdot}CO_2NO])$ with $[NO]/[CF_3NO]$. Temperature 157 °C

Table 1 shows that the yield of tristrifluoromethylhydroxylamine is at least 40 times greater than that of *O*-nitrosobistrifluoromethylhydroxylamine, so that the rate of reaction (6) is small compared with that of reaction (5). Reaction (6) might have been expected to have been fast compared with reaction (5) since the nitric oxide concentration is very much greater than the concentration of trifluoromethyl radicals. Reaction (6) is known to be reversible under certain photochemical conditions,[11] but this only provides an explanation of the observed data if the equilibrium lies well to the left.

The rate of formation of trifluoronitrosomethane is thus:

$$\mathrm{d}[CF_3NO]/\mathrm{d}t = k_1[CF_3{\cdot}CO_2NO]\{1 - 3k_4[CF_3NO]/(2k_4[CF_3NO] + k_3[NO])\}$$

The addition of nitric oxide should increase the rate of formation of trifluoronitrosomethane, as observed experimentally. Rearranging the last equation gives:

$$\frac{1}{1 - \mathrm{d}[CF_3NO]/\mathrm{d}t/k_1[CF_3{\cdot}CO_2NO]} = \frac{2}{3} + \frac{k_3[NO]}{3k_4[CF_3NO]}$$

This relationship can be examined quantitatively and the result is shown in Figure 4. The points show a fair scatter around the mean straight line through the points, but this must be expected since corresponding values of $\mathrm{d}[CF_3NO]/\mathrm{d}t$ and $k_1[CF_3{\cdot}CO_2NO]$ have similar magnitudes. In addition, the former quantity was obtained from the slope of the partial pressure against time plot for trifluoronitrosomethane. The intercept in Figure 4 must be very close to the expected value of 0·67.

Applying the steady-state treatment to the trifluoromethyl radical gives the following rate equations for the formation of nitric oxide and tristrifluoromethylhydroxylamine:

$$\mathrm{d}[NO]/\mathrm{d}t = 2k_1k_4[CF_3{\cdot}CO_2NO][CF_3NO]/(k_3[NO] + 2k_4[CF_3NO])$$

$$\mathrm{d}[(CF_3)_2NOCF_3]/\mathrm{d}t = k_1k_4[CF_3{\cdot}CO_2NO][CF_3NO]/(k_3[NO] + 2k_4[CF_3NO])$$

These expressions are too complex to compare directly with the experimental results, but a comparison of the two equations shows that the rates of formation of these two compounds should be in the ratio 2 : 1. Experimentally this ratio was 2·1 : 1 and this provides further support for the above radical non-chain mechanism.

All the reactions in the proposed mechanism involve a radical intermediate, except for the initial decomposition of the reactant. Thus the rate of this latter reaction should be unaffected by added propene, as observed experimentally, but the rate of formation of carbon dioxide was also unaffected. Again, the kinetic evidence showed no indication of the occurrence of reaction (—1), even when nitric oxide was added to the reaction mixture. It appears, therefore, that the trifluoroacetoxyl radical is unstable and that its stationary-state concentration is negligibly small.

TABLE 5

Arrhenius parameters for the decomposition of alkyl nitrites

Compound	log *A*	*E* (kcal mol^{-1})	Ref.
CH_3ONO	13·3	36	12
C_2H_5ONO	14·2	38	13, 14
C_3H_7ONO	14·5	38	15
$(CH_3)_2CH{\cdot}ONO$	14·2	37	16
C_4H_9ONO	14·0	36	17

The fission of the O–NO bond is also the rate-determining step in the decomposition of a number of alkyl nitrites, and the corresponding activation energies and pre-exponential factors are summarised in Table 5.

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[11] A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1175.

[12] E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.*, 1934, *A*, **146**, 388.

[13] E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, 1934, **2**, 345.

[14] J. B. Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 1780.

[15] E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, 1935, **3**, 344.

[16] E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.*, 1935, *A*, **151**, 685.

[17] E. W. R. Steacie and W. MacF. Smith, *J. Chem. Phys.*, 1936, **4** 504.

The pre-exponential factor from the present study is very close to the values for the alkyl nitrites, but the present activation energy is slightly lower. One possible explanation of this difference is that the O–NO bond in trifluoroacetyl nitrite is weakened by the presence of the adjacent electrophile group, relative to that in the alkyl nitrites.

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