Polyfluoroalkyl Derivatives of Nitrogen. Part XXXIII.[1] The Kinetics of the Reaction between Trifluoronitrosomethane and Tetrafluoroethylene to form Perfluoro-2-methyl-1,2-oxazetidine

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The kinetics of the reaction between trifluoronitrosomethane and tetrafluoroethylene to give perfluoro-2-methyl-1.2-oxazetidine have been studied for both the gaseous and liquid phase reactions. with mixture compositions in the range 1 :5 to 5 :1 trifluoronitrosomethane : tetrafluoroethylene. The gas-phase reaction has been studied at temperatures between 110 and 150° with total initial pressures in the range 125—500 Torr and, with 1.1.2-trichlorotrifluoroethane as solvent. the liquid-phase reaction has been examined between −35 and 80° over a four-fold variation in the initial total concentration of reactants. The reaction is a homogeneous bimolecular reaction in both phases, and the respective second-order rate constants are given by the Arrhenius equations:

$$k(\mathrm{l\ mol^{-1}\ s^{-1}}) = (3{\cdot}85 \pm 0{\cdot}78) \times 10^{7} \exp - (16.200 \pm 250/RT)$$
$$k(\mathrm{l\ mol^{-1}\ s^{-1}}) = (3{\cdot}27 \pm 0{\cdot}54) \times 10^{6} \exp - (13{,}215 \pm 90/RT)$$

It is suggested that the abnormally low pre-exponential factors obtained reflect the formation of the transition state in a specifically orientated collision process, and that the nature of this transition state is similar to those obtained in Diels–Alder addition reactions.

THE kinetics of the reaction between trifluoronitrosomethane and tetrafluoroethylene to form a 1 : 1-copolymer were examined earlier;[1] the present paper considers the kinetics of the formation of perfluoro-2-methyl-1,2-oxazetidine. In the liquid-phase reaction below 0° the oxazetidine is a minor product of the reaction, but its importance increases with temperature, and in the gas phase reaction above 100° it is the only product.[2] The present kinetic study, therefore, covers both the gaseous and liquid-phase reactions using 1,1,2-trichlorotrifluoroethane as solvent.

EXPERIMENTAL

Apparatus. The gas-phase reaction was examined in a Pyrex reaction vessel (20 × 3·6 cm. i.d.) enclosed in an electric furnace and connected to a conventional vacuum system by a ground-glass joint. The premixed gases were admitted from a 1-l expansion bulb and the pressure change during the reaction was followed with a null-point manometer. The dead space between the reaction vessel and manometer was kept to a minimum by the use of capillary tubing. The furnace was controlled by a Sunvic RT2

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[1] Part XXXII, J. D. Crabtree, R. N. Haszeldine, A. J. Parker, K. Ridings, R. F. Simmons, and S. Smith, preceding paper.

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

temperature controller and platinum resistance thermometer, and the temperature was measured with a calibrated Chromel–Alumel thermocouple. The temperature of the furnace was constant within 0·75° along the length of the reaction vessel and did not vary by more than ±0·2° during an experiment.

A mixture was removed from the reaction vessel for g.l.c. analysis *via* a cold finger cooled to −196°. It was then transferred to a 150 cm^3 bulb and kept at room temperature for 15 min, to ensure that representative samples were analysed by g.l.c. Details of this analysis were given earlier,[1] together with the experimental method by which the reaction in solution was followed.

Materials.—Details of the preparation and/or purification of the reactants were given earlier.[1] Cyclohexene, purified by fractionation from sodium wire, had b.p. 82·8° [lit., 82·7—83·2°], and no impurities could be detected by i.r. spectroscopy or g.l.c.

RESULTS

Gas-phase Reaction.—The variation in pressure during the reaction was always reproducible, and no deposits were apparent on the surface of the reaction vessel even after many experiments. During the course of preliminary experiments using equimolar mixtures of trifluoronitrosomethane and tetrafluoroethylene, it was found that the ratio of the initial and final pressures was 1·95, and i.r. and g.l.c. analysis of reaction mixtures showed that only unchanged reactants and perfluoro-2-methyl-1,2-oxazetidine were present at any particular time. The direct analysis of reaction mixtures by g.l.c. showed that the two reactants were always consumed in equal amounts, and that the equivalent amount of oxazetidine had been formed. In addition, Figure 1 shows that the extent of reaction obtained by analysis was in excellent agreement with that calculated from the pressure change. A similar result was obtained with mixtures containing an excess of tetrafluoroethylene, but when trifluoronitrosomethane was in large excess a minor side-reaction to form *O*-nitrosobistrifluoromethylhydroxylamine (the dimer of trifluoronitrosomethane) became apparent at the high temperatures. Nevertheless, the results show that the reaction to form the oxazetidine is essentially simple, and justify the use of pressure measurements to follow the course of the reaction.

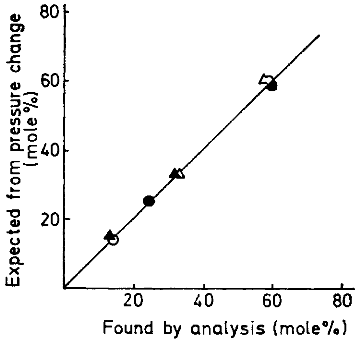

FIGURE 1 Comparison of the amount of perfluoro-2-methyl-1,2-oxazetidine found by analysis with that calculated from pressure changes: reaction temperatures: ○, △ 110°; ●, ▲ 150°; initial pressures: ○, ● 500 Torr; △, ▲ 125 Torr

Figure 2 shows that the reaction was second order overall, and separate experiments using unequal amounts of the two reactants showed that the reaction was first order with respect to each reactant. The reaction was examined over the pressure range 125—500 Torr and the observed rate constants were independent of the initial total pressure of reactants. Table 1 shows that the observed rate constants were also independent of the initial composition of the reaction mixture, except at the higher temperatures when trifluoronitrosomethane was in large excess. Under these latter conditions, however, the interpretation of the pressure measurements in terms of the formation of the oxazetidine is complicated by the dimer formation mentioned above. The analytical results for the 5 : 1 mixture of trifluoronitrosomethane and tetrafluoroethylene gave a value of 0·146 l mol^{-1} s^{-1} for the rate constant for the formation of the oxazetidine at 150°, which is in good agreement with those obtained from pressure measurements for the other mixture compositions.

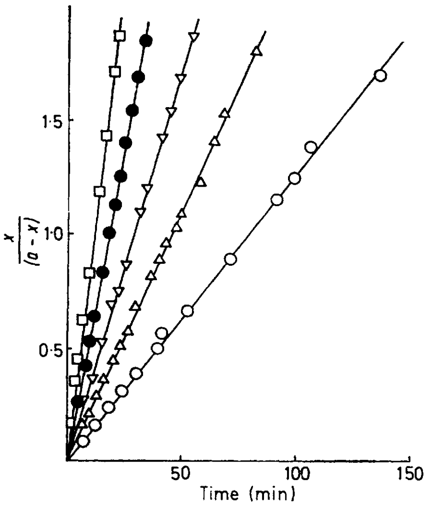

FIGURE 2 Second-order function plots for the gas-phase reaction between trifluoronitrosomethene and tetrafluoroethylene. $CF_3NO : C_2F_4$ = 1 : 1; initial pressure 500 Torr; temperature: ○ 110°, △ 120°, ▽ 130°, ● 140°, □ 150°

TABLE 1

Variation of the second-order rate constants with mixture composition and temperature for the gas-phase reaction

	Gaseous composition; $C_2F_4 : CF_3NO$		
Temp. (°C)	5 : 1	1 : 1	1 : 5
	$k \times 10^2$ (l mol^{-1} s^{-1})		
110	1·98	1·98	2·11
120	3·40	3·47	3·85
130	5·64	5·66	6·65
140	9·50	9·51	11·2
150	14·9	15·0	18·6

If the rate constants from mixtures containing a large excess of trifluoronitrosomethane are neglected, the plot of log (rate constant) against $1/T$ (K) is accurately linear and corresponds to the Arrhenius equation:

$$k(\text{l mol}^{-1}\text{ s}^{-1}) = (3{\cdot}85 \pm 0{\cdot}78) \times 10^7 \exp -(16{,}200 \pm 250/RT)$$

When the surface : volume ratio of the reaction vessel was increased by a factor of 11, by packing the reaction vessel with Pyrex tubes, the reaction was still first order with respect to each reactant. Table 2 shows a comparison of the rate constants obtained in the packed and unpacked vessels and it will be seen that the rate constants were effectively independent of the surface : volume ratio of the reaction vessel. The effect of varying amounts of cyclohexene on the reaction was also examined using an equimolar mixture of reactants with an initial total pressure of 250 Torr. The comparison of the rate constants in Table 3 shows that the presence of this additive had essentially no effect on the rate of the reaction.

TABLE 2

Comparison of rate constants for the gas-phase reaction in packed and unpacked vessels

Total initial pressure of reactants: 500 Torr.

		$k \times 10^2$ (l mol^{-1} s^{-1})	
Temp. (°C)	$C_2F_4 : CF_3NO$	Packed vessel	Unpacked vessel
110	1 : 1	2·05	1·98
	5 : 1	1·98	1·98
	1 : 5	2·20	2·11
150	1 : 1	15·0	15·0
	5 : 1	14·2	14·9
	1 : 5	17·8	18·6

TABLE 3

Comparison of rate constants for the gas-phase reaction in the presence and absence of cyclohexene

$C_2F_4 : CF_3NO = 1 : 1$; Total initial pressure 250 Torr.

	$k \times 10^2$ (l mol^{-1} s^{-1})		
Temp. (°C)	Concentration of cyclohexene (mol %)		
	0	0·5	1·0
110	1·98	2·01	2·01
130	5·66	5·52	5·59
150	15·0	14·2	13·5

Reaction in Solution.—Perfluoro-2-methyl-1,2-oxazetidine is a minor product of the reaction between trifluoronitrosomethane and tetrafluoroethylene when the reaction occurs in solution at temperatures below 0°.[1] The rate of formation of oxazetidine (d[O]/d*t*) under a given set of experimental conditions was determined from the corresponding slope of the appearance curve for the oxazetidine (see Figure 1 of earlier paper), and the results in Figure 3 show that the reaction is still first order in each reactant under these conditions. Again, the results from experiments at a given temperature, in which the initial concentrations of the reactants were varied, all lie on a common line, the slope of which gives the corresponding rate constant.

With 1,1,2-trichlorotrifluoroethane as the solvent, the reaction was examined over the temperature range −35 to 80°, and the rate constants obtained are given in Table 4. A plot of log (rate constant) against $1/T$ (K) was again accurately linear and the corresponding Arrhenius equation is:

$$k(\text{l mol}^{-1}\,\text{s}^{-1}) = (3{\cdot}27 \pm 0{\cdot}54) \times 10^{6} \exp -(13{,}215 \pm 90/RT)$$

where the error limits are the statistical 95% confidence limits. The reaction was also followed with the reactants in perfluoro-n-hexane as solvent at 0 and 25°, and these results gave a pre-exponential factor of $2{\cdot}0 \times 10^5$ l mol^{-1} s^{-1} and an activation energy of 11·4 kcal mol^{-1}.

The formation of the oxazetidine in 1,1,2-trichlorotrifluoroethane is unaffected by changes in the surface : volume ratio of the reaction vessel or by the presence of additives expected to affect the rate of a reaction proceeding by a radical chain mechanism.[1]

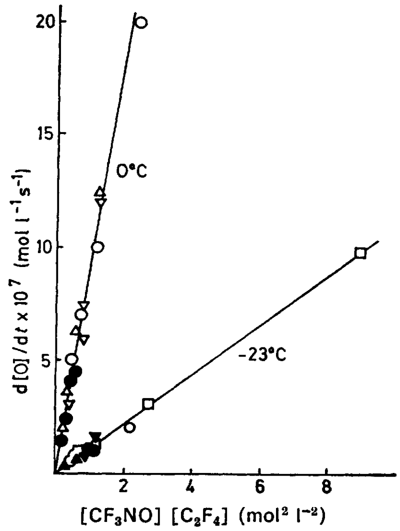

FIGURE 3 Variation in the rate of formation of oxazetidine with the product of the reactant concentrations. Solvent: 1,1,2-trichlorotrifluoroethane

	$CF_3NO : C_2F_4$	Total initial conc. (mol l^{-1})
□	1 : 1	0·60
○	1 : 1	0·30
●	1 : 1	0·15
△	1 : 5	0·30
▽	5 : 1	0·30
▲	1 : 5	0·15
▼	5 : 1	0·15

TABLE 4

Variation in the second-order rate constant with temperature for the liquid-phase reaction

Solvent: $CF_2Cl{\cdot}CFCl_2$

Temp. (°C)	$k \times 10^6$ (l mol^{-1} s^{-1})
−35·5	1·65 ± 0·10
−23·0	11·0 ± 1·5
−16·5	20·5 ± 1·5
0·2	103 ± 7·0
24·8	780 ± 40
40·2	1780 ± 80
59·4	6500 ± 400
80·6	20,500 ± 1500

DISCUSSION

The above results show that the reaction between trifluoronitrosomethane and tetrafluoroethylene to form perfluoro-2-methyl-1,2-oxazetidine is a homogeneous non-chain process in the gas phase and in solution. The reaction has been found to be first order in each reactant under all the conditions examined, and this is consistent with a simple bimolecular reaction step. Such reactions normally have pre-exponential factors in the range 10^9—10^{11} l mol^{-1} s^{-1}, and the low value obtained for the formation of the oxazetidine implies that the reaction has a low steric factor. These are usually explained in terms of an abnormally negative entropy of activation for the formation of the transition state, and are expected for reactions in which translational and rotational degrees of freedom of the reactants are converted into vibrational degrees of freedom in the transition state. In such cases the transition state is formed in a rather specific collision process in which the orientations of the colliding molecules are exactly right, and it is not unreasonable that the reaction between trifluoronitrosomethane and tetrafluoroethylene falls into this category.

There are very few reactions which have been studied in both the gaseous phase and in solution, but the available information shows that the Arrhenius parameters can vary substantially with the reaction medium. For example, the pre-exponential factor for the dimerisation of cyclopentadiene [3] changes by a factor of 100 when the reaction is carried out in paraffin, in comparison with the reaction in the gaseous phase. It is striking that in the formation of the oxazetidine the changes in the Arrhenius parameters with reaction medium tend to compensate for each other. Thus, as the activation energy decreases there is a corresponding decrease in the pre-exponential factor. This suggests that in solution the activated complex for the formation of the oxazetidine is significantly solvated, which reduces both the activation energy and pre-exponential factor in comparison with the gas-phase reaction.

Although this is the only reaction between trifluoronitrosomethane and a fluoro-olefin that has been studied kinetically, the similar reaction with other fluoro-olefins has been studied qualitatively. As a generalisation the formation of an oxazetidine requires, or proceeds most readily with, an olefin that contains a $CF_2=$ group, and does not occur, or occurs only reluctantly, when the fluoro-olefin contains more than one hydrogen atom on the doubly bonded carbon atoms.[4] A similar generalisation may be made for the dimerisation of fluoro-olefins to form fluoro-cyclobutanes. A few of these simple dimerisation reactions have been studied kinetically in the gaseous phase,[5] and the pre-exponential factors obtained (10^7—10^8 l mol^{-1} s^{-1}) are similar to that for the formation of perfluoro-2-methyl-1,2-oxazetidine. The activation energies for the dimerisation of the fluoro-olefin, however, are *ca.* 26 kcal mol^{-1}, which is 10 kcal mol^{-1} larger than that for the oxazetidine formation. A lower value must be expected for the latter reaction, however, since none of the tetrafluoroethylene dimerised to give perfluorocyclobutane under the conditions used in the present study.

It was originally suggested [6] that the formation of an oxazetidine is preceded by the initial formation of a 1 : 1 complex between the olefin and the nitroso-compound, in a manner similar to that postulated for the transition state of a Diels–Alder reaction, but no direct evidence has so far been obtained to support this suggestion. The results of the present kinetic study are consistent with those expected for a reaction with a four-centre transition state, but they do not enable a distinction to be made between a concerted mechanism or a transition state with some ionic character. Nevertheless, the suggestion that the formation of perfluoro-2-methyl-1,2-oxazetidine occurs by a Diels–Alder type of reaction still seems reasonable, since there is a striking similarity between the present kinetic results and those obtained for most Diels–Alder addition reactions.[7] The latter type of reaction has been the subject of many studies, both in the gaseous and liquid phases, and in all cases the reaction has been found to be bimolecular. Again, the pre-exponential factors all lie in the range 10^6—10^7 l mol^{-1} s^{-1} and the activation energies are in the range 16—23 kcal mol^{-1}.

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