Polyfluoroalkyl Derivatives of Nitrogen. Part XXXII.[1] The Kinetics and Mechanism of the Copolymerisation of Trifluoronitrosomethane and Tetrafluoroethylene

By J. D. Crabtree, R. N. Haszeldine,* A. J. Parker, K. Ridings, R. F. Simmons, and S. Smith, Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The rate of copolymerisation of trifluoronitrosomethane and tetrafluoroethylene at total concentrations of up to 0·6 mol l^{-1} in solution in fluoro-solvents such as 1,1,2-trichlorotrifluoroethane or perfluoro-n-hexane at temperatures from -36 to 80 °C is given by $k_p[CF_3NO]^{3/2}[C_2F_4]$ and, for reactions carried out in 1.1,2-trichlorotrifluoro-ethane, k_p is given by:

$$k_p(l^{3/2}\ mol^{-3/2}\ s^{-1}) = (2\cdot9 \pm 0\cdot5) \times 10^4\ exp\ -(9660 \pm 80/RT)$$

The free-radical chain process and mechanism proposed is in agreement with the experimental results. Further evidence in support of this mechanism has been obtained by studies of the e.s.r. spectra arising from reacting mixtures of CF_3NO and C_2F_4 and from solutions of CF_3NO in various solvents. Several earlier suggestions about the mechanism are discounted.

TRIFLUORONITROSOMETHANE reacts readily with tetra-fluoroethylene to give perfluoro-2-methyl-1,2-oxazetidine (I), an alternating 1 : 1 copolymer (II),[2] and a small amount of low molecular-weight compounds of possibly

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[1] Part XXXI, G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

[2] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881; *idem., Nature*, 1955, **177**, 991; D. A. Barr, R. N. Haszeldine, and C. J. Willis, *Proc. Chem. Soc.*, 1959, 230.

cyclic structure, $(CF_3NO \cdot C_2F_4)_x$,[3] $(x = 2\text{—}8)$. The ratio of copolymer to oxazetidine in the reaction products

CF$_3$N—O
| |
F$_2$C—CF$_2$

$-[N-O-CF_2-CF_2]-_n$
|
CF$_3$

(I)   (II)
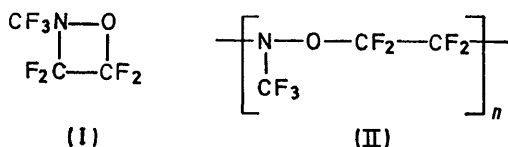
varies with reaction temperature; copolymer formation is the predominant reaction below room temperature, while the oxazetidine is the major product at higher temperatures.

The copolymerisation occurs in the dark at 0 °C, and the polarisation of the nitroso-group and the susceptibility of fluoro-olefins to nucleophilic attack would be in accord with an ionic mechanism,[2] but the results of later studies strongly suggest that a free-radical mechanism is to be preferred. Thus u.v. light accelerates the copolymerisation,[4] while small additions of hydroquinone[4] or of 1,2-diphenylpicrylhydrazyl[5] produce a retardation. The addition of small amounts of radical transfer agents reduces the molecular weight of the copolymers formed.[5] Again, the copolymerisation proceeds readily in aqueous systems and in the presence of Lewis acids,[5,6] which would be possible for a free-radical mechanism, but not for an anionic polymerisation process. Initiation by free radicals formed, for example, by the fission of the $F_3C\text{–}NO$ bond has been proposed,[7] and the triplet (or diradical) state of trifluoronitrosomethane has also been suggested as the initiating species.[4,5] Comparison with other alternating copolymerisation systems has also led to the suggestion that the copolymer is formed by addition to a growing radical chain of a 1 : 1 molecular complex of the two reactants.[7]

E.s.r. studies of reacting mixtures have shown the presence of free radical species,[8-11] but there is little kinetic information on which to base any mechanism for the copolymerisation apart from that obtained by Crawford et al.[5] These authors followed the reaction by isolating the copolymer formed, and their kinetic analysis was restricted to an examination of the initial rate of the copolymerisation process; they concluded that the orders of reaction with respect to trifluoronitrosomethane and tetrafluoroethylene were 1·3 and 0·9 respectively, although there were indications that these orders were affected by the initial concentrations of the monomers.

In the present work the kinetics of the reactions between trifluoronitrosomethane and tetrafluoroethylene have been studied in greater detail. The reactions in solution at relatively low temperatures are considered

and, since the major product under these conditions is the copolymer, the mechanism by which this is formed is examined. The e.s.r. spectra of the reacting systems have also been examined and the mechanism proposed is consistent with the kinetic and e.s.r. results. In a subsequent paper, the reaction between trifluoronitrosomethane and tetrafluoroethylene in the gas phase at temperatures above 100 °C is considered, and the mechanism by which the oxazetidine is formed in both the gas phase and liquid phase reactions is discussed.

EXPERIMENTAL

The Pyrex reaction vessels had a capillary inlet tube to minimise the dead space above the reaction mixture. The amounts of monomers and degassed solvent required to fill the vessel at the reaction temperature were introduced into the reaction vessels by condensation from expansion bulbs of known volume. The reaction vessels were then sealed in vacuo before the contents were allowed to thaw, and the vessels were placed in a thermostat in the dark. The time interval between sealing a vessel and insertion into the thermostat was never greater than 5 min. In some experiments an involatile substance was introduced into the reaction vessel in a dry box under nitrogen together with 30 cm³ of solvent, and thoroughly degassed before the monomers were introduced.

After a suitable reaction time, a vessel was removed from the thermostat and its contents were frozen by immersion in liquid nitrogen. The vessel was then attached to a vacuum line, the seal was broken in vacuo, and the volatile contents were distilled out of the reaction vessel. The residual monomers and the oxazetidine produced were separated from the solvent by fractional condensation. The solvent condensed in vacuo in traps cooled to $-76°$ and $-96°$, while the residual monomers and the oxazetidine were collected in traps cooled to $-196°$ (b.p./760 Torr:

CF$_3$NO, $-84°$; C$_2$F$_4$ $-76°$; CF$_3$·N·O·CF$_2$·CF$_2$ $-6\cdot8°$).

The residual monomers and the oxazetidine were then transferred to a bulb of known volume and the total amount was determined from the total pressure. The proportion of each component was determined by g.l.c. analysis using thermistor detectors and a 10-m glass column (4 mm i.d.) packed with Celite (80—100 mesh) coated with Kel-F oil. The column was maintained at 0 °C and oxygen-free nitrogen was used as the carrier gas. For each pure component, graphs of chromatogram area, measured by triangulation, plotted against pressure in the gas sample cell were linear, and deviations of check calibrations from the lines were always less than 1%. Analysis of synthetic gas mixtures gave reproducible results within $\pm2\cdot0\%$ of the expected values, except when the oxazetidine was less than $\sim5\%$ of the mixture. In such cases, the value for oxazetidine deviated by up to $\pm5\%$ of the true value.

The copolymer present in a reaction mixture was deter-

[3] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, unpublished results.

[4] D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 1956, 3416.

[5] G. H. Crawford, D. E. Rice, and B. F. Landrum, J. Polymer Science, 1963, A1, 565.

[6] R. E. Banks, F. Bennett, and R. N. Haszeldine, unpublished results.

[7] R. N. Haszeldine and B. J. H. Mattinson, J. Chem. Soc., 1957, 1741; D. A. Barr, R. N. Haszeldine, and C. J. Willis, J. Chem. Soc., 1961, 1351.

[8] V. A. Ginsburg, A. N. Medvedev, M. F. Lebedeva, S. S. Dubov, and A. Ya. Yakubovich, Zhur. obshchei Khim., 1965, 35, 1418.

[9] V. A. Ginsburg, A. N. Medvedev, L. L. Martynova, M. N. Vasil'eva, M. F. Lebedeva, S. S. Dubov, and A. Ya. Yakubovich, Zhur. obshchei Khim., 1965, 35, 1924.

[10] G. H. Crawford, D. E. Rice, and L. H. Piette, 2nd International Symposium on Fluorine Chemistry, 1963, 357.

[11] V. A. Ginsburg, A. N. Medvedev, S. S. Dubov, P. O. Gitel, V. V. Smolyanitshaya, and G. E. Nikolaenko, Zhur. obshchei Khim., 1969, 39, 282.

mined as the difference between the amounts of monomers initially present and the residual monomers and oxazetidine as determined by analysis. This calculated yield of co-polymer includes the small amount of low molecular-weight compounds $(CF_3NO \cdot C_2F_4)_x$ formed. A separate series of experiments in which the yield of copolymer determined in this way was compared with that actually isolated gave good agreement between the two values. In no case was the weight of copolymer isolated less than 95% of that expected from the g.l.c. analysis, and the small losses to be expected in transferring copolymer from the reaction vessel to a weighed receptacle could readily account for the difference.

Samples for study by e.s.r. were prepared as follows. A 2·5 mm i.d. silica tube was attached to a vacuum apparatus and the monomer(s) and degassed solvent vapour were condensed into the evacuated tube while it was immersed in liquid nitrogen. The tube was sealed *in vacuo* while the contents were still solid and was then stored in liquid nitrogen. The required amount of each constituent was obtained by admitting its vapour to the appropriate pressure in a bulb of known volume, the contents of which were then condensed into the tube. This was done successively so that the constituents of a sample did not mix until the sample tube was removed from the liquid nitrogen. Prolonged storage of the samples before record-ing of the e.s.r. spectrum was avoided. The time taken to thaw and mix the contents of a tube and insert the tube into the cavity of the spectrometer was never greater than 10 min, and during this time, exposure of the sample to light was minimised.

The e.s.r. spectra of samples at room temperature were recorded using a type XI spectrometer (Decca Radar Ltd.), operated at a fixed frequency of 9270 MHz, and used in conjunction with a Newport Instruments' Type D electro-magnet with 8 in diameter pole faces. The field homo-geneity was estimated to be *ca.* 100 mG over the volume of samples used. Hyperfine splittings were measured with reference to a sample of perylene dissolved in concentrated sulphuric acid.[12] Studies at temperatures other than room temperature were made using a Varian Associates' V4502 e.s.r. spectrometer in conjunction with a 12 in magnet and V4557 variable-temperature apparatus. Both spectro-meters employed 100 kHz field-modulation.

Materials.—All materials were shown by g.l.c. and i.r. to be free from impurities.

Trifluoronitrosomethane, prepared and purified as described earlier,[13] had M, 99·0—99·7 (Calc. M, 99·0) (Regnault's method).

Tetrafluoroethylene (I.C.I. Ltd.), purified by fractional condensation, followed by low-temperature fractional distillation using a Podbielniak column, had M, 99·8—100·5 (Calc. M, 100·0).

Perfluoro-2-methyl-1,2-oxazetidine was prepared by re-action of equimolar amounts of trifluoronitrosomethane and tetrafluoroethylene in a sealed tube at 100 °C, and purified by fractional condensation (Found M, 200·3; Calc. M, 199·0).

1,1,2-Trichlorotrifluoroethane (Imperial Smelting Cor-poration Ltd.), purified by shaking with sodium hydroxide pellets to remove traces of hydrogen fluoride then distilled

from sodium hydroxide, had b.p. 46·8—47·0 °C/760 Torr and M, 187·0—188·0 (Calc. M, 187·5). The vapour pressure–temperature relationship for the liquid, determined using an isoteniscope, agreed with that reported previously.[14]

Perfluoro-n-hexane was dried by refluxing it over phosphorus pentoxide followed by fractionation. The fraction b.p. 57·0—57·2/760 Torr was collected (Found M, 340; Calc. M, 338). The monomers were stored in bulbs painted black to minimise any photochemical reaction.

RESULTS

The Kinetics of the Copolymerisation.—Preliminary ex-periments confirmed quantitatively that oxazetidine, co-polymer, and the low molecular-weight compounds $(CF_3NO \cdot C_2F_4)_x$ are the only products formed by reaction of CF_3NO with C_2F_4 at temperatures in the range -23 to 60 °C, in the gas phase or in solution with either 1,1,2-trichlorotrifluoroethane or perfluoro-n-hexane. Analysis confirmed that the copolymer contained equimolar amounts of the two monomers [Found: C, 18·1; F, 66·8; N, 7·2. Calc. for $(C_3F_7NO)_n$: C, 18·1; F, 66·9; N, 7·0%]. Mass spectrometry showed that the copolymer contained a small proportion (up to 5% by weight) of the compounds $(CF_3NO \cdot C_2F_4)_x$, $(x = 3\text{—}8)$. The compound with $x = 2$ was not observed, probably because its high volatility (b.p. (100 °C/760 Torr)[3] led to its loss during isolation of the copolymer. Since all the products contain CF_3NO and C_2F_4 in equimolar proportions, the consumption of mono-mers in the reaction should always occur in equimolar amounts, irrespective of the reaction medium. This was confirmed by g.l.c. analysis of reaction mixtures.

The choice of solvents in which the homogeneous form-ation of copolymer can be studied is restricted. The co-polymer is insoluble in common solvents, but is soluble in 1,1,2-trichlorotrifluoroethane and perfluoro-n-hexane. The solubility of each monomer in these solvents, determined by Loprest's method,[15] showed that 1,1,2-trichlorotrifluoro-ethane was the most suitable solvent, but perfluoro-n-hexane was used as the solvent in some experiments. The amounts of monomers used in all experiments were less than those required to saturate the solvent at that particular temperature.

Eight reaction mixtures of identical composition were used for each kinetic experiment. Each mixture was analysed after an appropriate reaction time, and a typical set of results is shown in Figure 1. The results obtained under a given set of conditions were reproducible and did not change when different samples of monomers or solvents were used. To find the orders of the simultaneous reactions for the formation of oxazetidine (O) and copolymer (C), the values of $d[O]/dt$ and $d[C]/dt$ were determined at a series of reaction times in each kinetic experiment, by drawing tangents to the appearance curves for oxazetidine and copolymer respectively. It was found that the formation of oxazetidine was first order with respect to each reactant, and these results will be considered in detail in a subsequent paper. Figure 2 shows that plots of $d[C]/dt$ against $[CF_3NO]^{3/2}[C_2F_4]$ are linear and that the results obtained from experiments using different initial concentrations of monomers lie on a common line. The observed rate constants (k_p) obtained from the slopes of these plots are listed in Table 1 (the error limits were obtained from the

[12] A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 947.
[13] A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1675.
[14] E. G. Locke, W. R. Brode, and A. L. Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726.
[15] F. J. Loprest, *J. Phys. Chem.*, 1957, **61**, 1128.

slopes of the two extreme lines which enclosed the particular set of experimental points). The use of vessels packed with Pyrex tubes (which increased the surface : volume
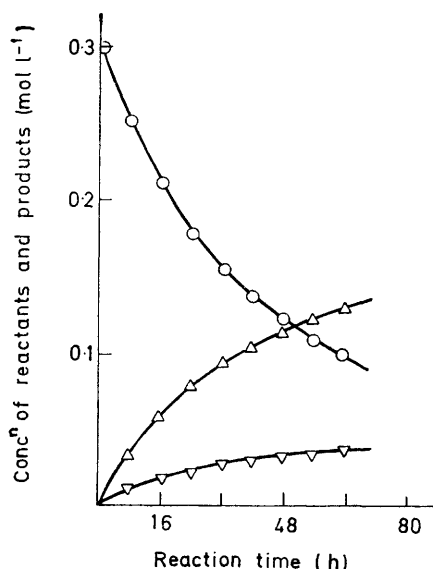

FIGURE 1 Variation in the concentrations of reactants and products during the reaction between trifluoronitrosomethane and tetrafluoroethylene. Solvent: $CF_2Cl\cdot CFCl_2$; temp. -16.5 °C; initial monomer concentration ($[CF_3NO] + [C_2F_4]$) = 0.30 mol l^{-1}; $[CF_3NO]/[C_2F_4]$ = 1.0; $\bigcirc$ residual monomers; $\triangle$ copolymer (expressed in terms of monomers consumed in its formation); $\triangledown$ oxazetidine

ratio by a factor of 7) showed that the reaction was homogeneous in character, since within experimental error the same rate constant was obtained from experiments using a packed or unpacked vessel. A similar result was also obtained when the reactants were initially in the gas phase and the surface : volume ratio of the reaction vessel was increased six-fold.

The plot of log k_p against $1/T$ is linear, with some deviation at the highest temperature used (80 °C), but the reaction at this temperature is too rapid to be followed accurately by the experimental method used. The Arrhenius equation

corresponding to the straight line (which covers the temperature range -35.5 to 60.0 °C) is:

$$k_p \ (l^{3/2} \ mol^{-3/2} \ s^{-1})$$
$$= (2.9 \pm 0.5) \times 10^4 \exp - (9660 \pm 80/RT)$$

where the error limits are the statistical 95% confidence limits. With perfluoro-n-hexane as solvent the corresponding Arrhenius parameters are $6.2 \times 10^3 \ l^{3/2} \ mol^{-3/2} \ s^{-1}$ and 9.0 kcal mol^{-1}, whilst when the polymerisation was
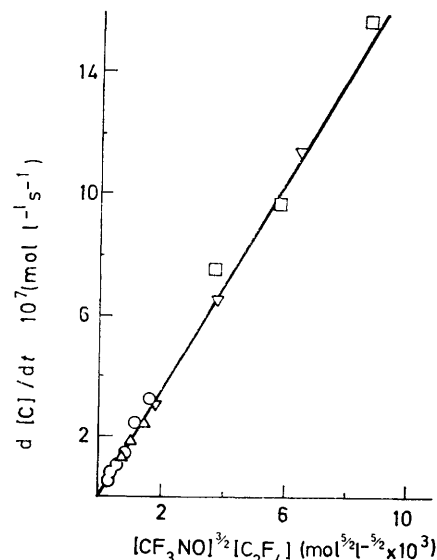

FIGURE 2 Variation in the rate of formation of copolymer with $[CF_3NO]^{3/2}[C_2F_4]$; solvent: $CF_2Cl\cdot CFCl_2$; temp. -16.5 °C

	$[CF_3NO] + [C_2F_4]$ (mol l^{-1})	$[CF_3NO]/[C_2F_4]$
$\square$	0.30	1.0
$\triangle$	0.15	1.0
$\bigcirc$	0.30	0.2
$\triangledown$	0.30	5.0

carried out with the monomers initially in the gas phase, values of $1.5 \times 10^3 \ l^{3/2} \ mol^{-3/2} \ s^{-1}$ and 9.3 kcal mol^{-1} were obtained.

TABLE 1

Observed rate constants, k_p

Reaction medium	Temp. (°C)	$\dfrac{[CF_3NO]}{[C_2F_4]}$	Total monomer concentration $[CF_3NO] + [C_2F_4]$ (mol l^{-1})	$10^5 k_p$ ($l^{3/2} \ mol^{-3/2} \ s^{-1}$)
$CF_2Cl\cdot CFCl_2$	-35.5 ± 0.5	0.2	0.3	
		1.0	0.6, 0.3, 0.13	3.5 ± 0.3
		5.0	0.3	
	-23.0 ± 0.5	0.2	0.15	
		1.0	0.6, 0.3, 0.15	11.8 ± 0.8
		5.0	0.15	
	-16.5 ± 0.5	0.2	0.3	
		1.0	0.3, 0.15	17.7 ± 0.9
		5.0	0.3	
	0.0 ± 0.2	0.2	0.3	
		1.0	0.3, 0.15	54.0 ± 2.0
		5.0	0.3	
	24.8 ± 0.1	1.0	0.15	240 ± 10
	40.2 ± 0.1	1.0	0.15	530 ± 20
	59.4 ± 0.2	1.0	0.15	1800 ± 50
	80.6 ± 0.2	1.0	0.15	2450 ± 50
$n\text{-}C_6F_{14}$	0.0 ± 0.2	1.0	0.15	41.8
	24.8 ± 0.1	1.0	0.15	167.0
Gas phase	25.0 ± 0.1	1.0	0.15	24.2
	40.0 ± 0.1	1.0	0.15	50.8

The effect on the reaction of a number of additives was examined. Water (up to 10 mol % of the total monomer concentration), an equimolar mixture of stannic chloride and water (up to 10 mol %) and carbon dioxide (up to 10 mol %), all produced less than a 10% change in the rate of formation of copolymer and had even less effect on the rate of formation of oxazetidine. 10 Mol % β-phenyl-naphthylamine reduced the rate of formation of copolymer by 25%, while 10 mol % oxygen halved the rate of copolymer formation, but in the latter case an additional product (CF_3NO_2) was formed; there was again very little effect on the rate of formation of oxazetidine. Addition of diphenylpicrylhydrazyl had a much greater effect and 0·2 mol % reduced the rate of copolymerisation by 10% but, again, had little effect on the rate of oxazetidine formation.

The addition of benzoyl peroxide (0—4 mol %) had no effect on the rate of reaction, while the same concentrations of azobisisobutyronitrile produced slight decreases in the rate of polymerisation without affecting the formation of oxazetidine. Di-isopropylperoxydicarbonate (up to 8 mol %) had no effect on the rate of reaction, and the addition of 4 mol % t-butylhydroperoxide increased the consumption of CF_3NO relative to that of C_2F_4, but all the excess of CF_3NO consumed was converted into CF_3NO_2; there was a corresponding decrease in the rate of formation of copolymer, but the formation of oxazetidine was hardly affected.

The effect of bistrifluoromethylnitroxide, which has been suggested [4] as the initiating species, was also examined. The addition of 5 and 10 mol % of this stable free radical produced an increase in the rate of polymerisation at both 25 and 60 °C, but no quantitative estimate of the effect could be made as the consumption of the two monomers was no longer equal.

E.s.r. Signals from Reacting Mixtures of CF_3NO and C_2F_4.
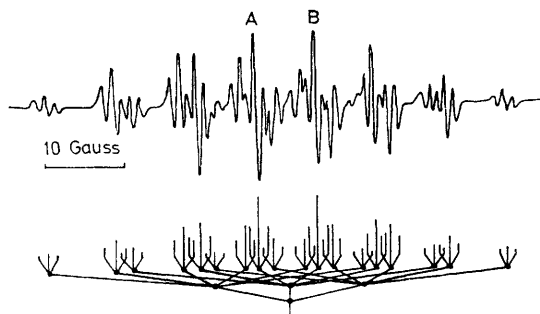—Strong e.s.r. signals were obtained in the $g = 2$ region

FIGURE 3 E.s.r. spectrum of a polymerising mixture of trifluoronitrosomethane and tetrafluoroethylene in 1,1,2-trichlorotrifluoroethane as solvent; temp. 23 °C

from an equimolar mixture of CF_3NO and C_2F_4 (0·2 mol l⁻¹ of each) in 1,1,2-trichlorotrifluoroethane at 23 °C and the spectrum obtained, together with the theoretical reconstruction, is shown in Figure 3. The structure of the spectrum is consistent with the radical species (III) where

$$-CF_2-CF_2-N-O\cdot \quad (III)$$
$$|$$
$$CF_3$$
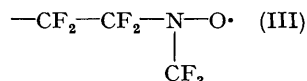
interaction with the $-N(CF_3)O\cdot$ group produces six lines of intensities 1 : 4 : 7 : 7 : 4 : 1 (assuming $a^N = a^F$).[8,10] Further

interaction with the α-CF_2 group produces the three main sets of lines (1 : 2 : 1), and interaction with the β-CF_2 group produces the small triplet splitting (1 : 2 : 1), giving a total of 54 lines which are not all resolved. Spectra of similar structures were obtained from polymerising mixtures of CF_3NO and C_2F_4 in other fluorocarbon solvents, *i.e.* perfluoro-n-hexane, hexafluorobenzene, and trichlorofluoromethane.

Spectra were also observed from solutions of CF_3NO and C_2F_4 at -30 and -60 °C. Decreasing the temperature
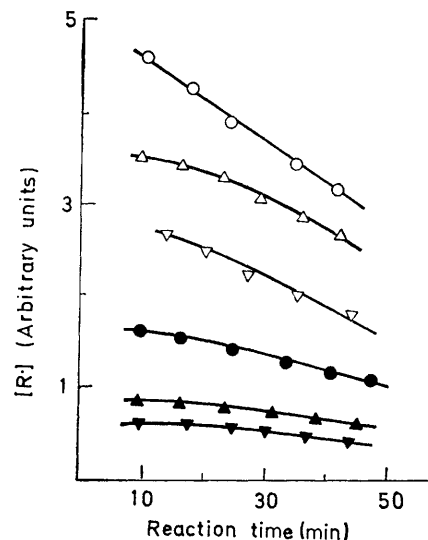

FIGURE 4 Variation in concentration of free radicals during the copolymerisation of trifluoronitrosomethane and tetrafluoroethylene. Solvent: $CF_2Cl\cdot CFCl_2$; temp. 23 °C. Initial concentration C_2F_4: 0·20 mol l⁻¹; initial concentrations CF_3NO (mol l⁻¹): ○ 0·202; △ 0·172; ▽ 0·140; ● 0·102; ▲ 0·065; ▼ 0·052

does not affect the number of lines observed, but does cause a slight change in the relative positions of some of the lines, indicating that the hyperfine splittings are temperature dependent. This effect has also been observed in the stable nitroxide $(CF_3)_2NO$.[16] The nitrogen hyperfine coupling constant has a positive temperature dependence, while that of the fluorine atoms has a negative temperature dependence. This has been explained in terms of a partial conjugation of the fluorine p orbitals with the nitrogen $2p_z$ orbital.[16]

The reaction between CF_3NO and C_2F_4 is rapid at 23 °C, and the intensities of the lines decreased slightly during the time taken to record the complete spectrum. Nevertheless, the mean heights of the two peaks A and B (Figure 3) can be used as a measure of the concentration of free radicals, in arbitrary units, at the time the spectrum was recorded, since the widths of the lines remained constant throughout the reaction. It was not possible to record the first spectrum until *ca.* 10 min after the sealed sample tube had been removed from the liquid nitrogen, and Figure 4 shows that by this time, the concentration of free radicals had reached its maximum value for a given mixture. As the reaction proceeded the concentration of radicals decreased slowly and reached zero after *ca.* 24 h, by which time the blue colour of trifluoronitrosomethane had almost disappeared.

[16] P. J. Schneidler and J. R. Bolton, *J. Amer. Chem. Soc.*, 1966, **88**, 371.

Figure 4 also shows that as the initial concentration of CF_3NO was increased, with a constant concentration of C_2F_4, the concentration of radicals formed and the rate of disappearance of radicals increased. The concentration of radicals present in each mixture after reaction times of 10 and 40 min were obtained from these results and Figure 5
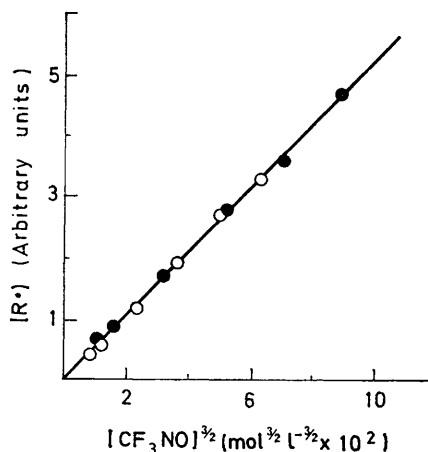

FIGURE 5 Variation with $[CF_3NO]^{\frac{3}{2}}$ of the concentration of free radicals during the copolymerisation of trifluoronitroso-methane and tetrafluoroethylene. Data from Figure 4. Radical concentrations: ● after 10 min; ○ after 40 min

shows that these concentrations were directly proportional to $[CF_3NO]^{3/2}$. In each case the corresponding concentration of CF_3NO was calculated from the initial concentrations of reactants and the rate constants for the formation of copolymer and oxazetidine. In contrast, the radical concentration was almost independent of the concentration of C_2F_4 except when CF_3NO was present in large excess.

paramagnetic species were observed when gaseous CF_3NO was scanned in the $g = 2$ and $g = 4$ regions, but preliminary experiments showed that when CF_3NO was dissolved in 1,1,2-trichlorotrifluoroethane strong absorption in the $g = 2$ region developed after 5—6 h at 25 °C in daylight. This spectrum was interpreted as two overlapping signals, an eight-line signal and a nine-line signal. In the absence of light, however, the signals observed consisted of six broad lines. The nine-line signal was very similar to the e.s.r. spectrum of bistrifluoromethylnitroxide,[17] and this can be formed in the present system photochemically from CF_3NO.[7] In subsequent experiments, therefore, exposure to light was avoided.

The essential features of the e.s.r. spectra obtained from CF_3NO in various solvents at 25 °C in the dark are summarised in Table 2, and in all cases the signal obtained consisted of six main lines. From the solutions in fluorine-containing compounds, the signals were of relatively low intensity and no further structure could be observed in each of the six broad lines. The magnitudes of the hyperfine coupling constants, and the intensity ratios observed, indicate that the signals from solutions in fluorine-containing solvents arise from a radical form of CF_3NO in which interaction of the free electron spin with a nitrogen atom ($I = +1$) and three equivalent fluorine atoms ($I = +\frac{1}{2}$) would give six lines of relative intensities $1 : 4 : 7 : 7 : 4 : 1$, assuming that the hyperfine coupling constant $a^N = a^F$.

The rates of formation and the concentrations of radicals formed depend markedly on the solvent, decreasing in the order shown in Table 2. Attempts were made to examine the kinetics of formation of the radical species, but it was not possible to use fluorocarbon solvents, because of the uncertainty as to whether the six-line signals obtained from CF_3NO in such solvents consisted of two overlapping signals. Similarly, none of the lines in the signals obtained

TABLE 2

E.s.r. spectra obtained from solutions of CF_3NO at 25 °C, $[CF_3NO] = 0.2$ mol l^{-1}

Solvent	Signal obtained	Relative intensities of the six lines	Hyperfine coupling constants (Gauss)
C_4H_8O	Complex		
C_6H_6	Sextet of triplets	$1 : 4.1 : 7.3 : 7.2 : 4.0 : 1$	11.7
$C_6H_5CH_3$	Sextet of triplets	$1 : 3.8 : 6.5 : 6.4 : 4.0 : 0.9$	11.6
n-C_6H_{14}	Sextet of doublets	$1 : 3.9 : 6.5 : 6.5 : 4.0 : 1$	11.6
C_6F_6	Six broad lines	$1 : 3.9 : 7.0 : 6.9 : 3.8 : 0.9$	11.7
$CFCl_3$	Six broad lines	$1 : 3.9 : 6.8 : 6.8 : 3.9 : 0.9$	11.6
$(C_4F_9)_3N$	Six broad lines	$1 : 3.9 : 7.0 : 6.8 : 3.9 : 0.9$	11.6
$CF_2Cl \cdot CFCl_2$	Six broad lines	$1 : 4.4 : 6.9 : 6.7 : 4.4 : 0.9$	11.5
n-C_6F_{14}	Six broad lines	$1 : 3.9 : 6.9 : 6.8 : 3.9 : 0.9$	11.6
$CHCl_3$	Six broad lines	$1 : 3.8 : 6.6 : 6.5 : 3.8 : 1$	11.6

The influence of the solvent on the rates of formation and decay of radicals during the copolymerisation at 22 °C was also investigated using 1,1,2-trichlorotrifluoroethane, perfluoro-n-hexane, hexafluorobenzene, and trichlorofluoromethane. These are all solvents for both the monomers and the copolymer, and homogeneous conditions were maintained in all cases. The time taken to reach the maximum concentration of free radicals increased in the order $C_6F_6 < CFCl_3 < CF_2Cl \cdot CFCl_2 < $ n-C_6F_{14}. Examination of the samples in the e.s.r. tubes showed that the time taken for the blue colour of CF_3NO to disappear increased in the same order, ranging from 8 h in C_6F_6 to 2 days in n-C_6F_{14}.

E.s.r. Signals from CF_3NO.—The e.s.r. spectrum from CF_3NO alone at room temperature was also examined. No

from CF_3NO in benzene, toluene, or n-hexane could be used, because their relative intensities changed noticeably with time, indicating that two radical species were present in the system. When tetrahydrofuran was used as solvent, however, each of the main lines in the e.s.r. spectrum showed further splitting and the extra resolution in the signals obtained made it possible to use the lines marked 1, 2, and 3 in the integrated first derivative spectrum (Figure 6) as a measure of radical concentration, since the structure of this spectrum did not change with time. Measurements of the intensities of these lines at various times showed that the concentration of radical species increased rapidly as soon as the contents of the sample tube

[17] W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, 1965, **87**, 802.

had thawed, and then decreased. The rate of formation of radicals at room temperature was too high to be measured accurately by e.s.r. techniques but it increased as the concentration of CF_3NO increased. Figure 7 shows that a
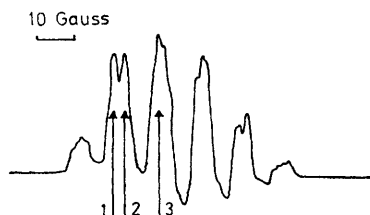
10 Gauss

FIGURE 6 Integrated first derivative e.s.r. spectrum obtained from a solution of trifluoronitrosomethane in tetrahydrofuran at 25 °C

log–log plot of the initial CF_3NO concentration against the maximum radical concentration reached in the given experiment is linear. Using the intensities of lines 1, 2, and 3 as a measure of the maximum radical concentration
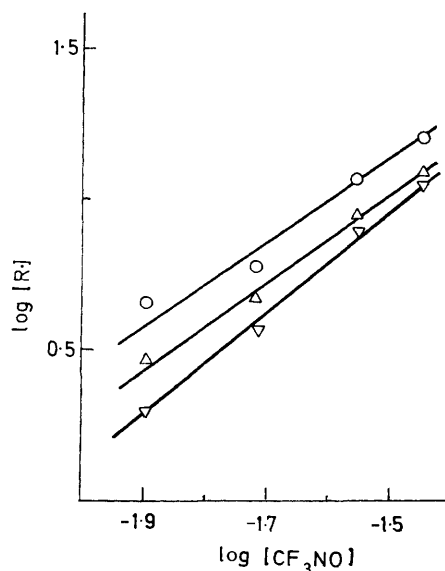
FIGURE 7 Dependence of the maximum radical concentration on the initial concentration of trifluoronitrosomethane. Solvent: tetrahydrofuran; temp. 25 °C. Concentrations obtained from ○ line 1; △ line 2; ▽ line 3 (see Figure 6)

reached gave slopes of 1·3, 1·4, and 1·65, respectively, and thus to a first approximation the maximum concentration of radicals is proportional to $[CF_3NO]^{3/2}$.

DISCUSSION

It has been shown that the rates of the reactions between CF_3NO and C_2F_4 giving oxazetidine (O) and alternating copolymer (C), are given by the equations

$$d[O]/dt = k_o[CF_3NO][C_2F_4]$$
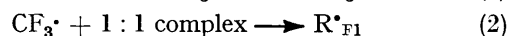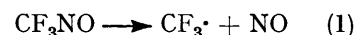$$d[C]/dt = k_p[CF_3NO]^{3/2}[C_2F_4]$$

respectively, in which k_o and k_p are observed rate constants. These equations apply to reactions carried out in the gas phase and in homogeneous solution in fluorocarbon solvents at temperatures between −36 and 80 °C, using reactant ratios of 5·0, 1·0, and 0·2, and total

initial concentrations of the two monomers in the range 0·15—0·60 mol l^{-1}. Both reactions are unaffected by changes in surface/volume ratio of the reaction vessels.
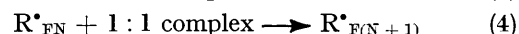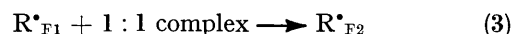
Crawford et al.[5,10] have reported that the orders of reaction with respect to CF_3NO and C_2F_4 are 1·3 and 0·9, respectively, in the polymerisation reaction, but since the polymer isolation technique was used to follow the formation of the copolymer, these values are probably approximations; they are in moderate agreement with the more accurate orders obtained in the present work. The fractional overall order of the polymerisation reaction, and the observation by e.s.r. techniques of high concentrations of radical species during the reaction, support the suggestion that the reaction proceeds by a radical chain mechanism.[4-7,10] The effects of various additives are also in accord with this suggestion.

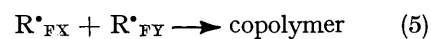If the mechanism occurs by attack of a chain centre on a 1 : 1 complex formed from the monomers:[7]

Initiation:

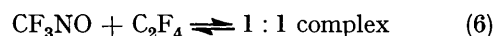$$CF_3NO \longrightarrow CF_3{\cdot} + NO \quad (1)$$
$$CF_3{\cdot} + 1 : 1 \text{ complex} \longrightarrow R^{\cdot}_{F1} \quad (2)$$

Propagation:

$$R^{\cdot}_{F1} + 1 : 1 \text{ complex} \longrightarrow R^{\cdot}_{F2} \quad (3)$$
$$R^{\cdot}_{FN} + 1 : 1 \text{ complex} \longrightarrow R^{\cdot}_{F(N+1)} \quad (4)$$

Termination:

$$R^{\cdot}_{FX} + R^{\cdot}_{FY} \longrightarrow \text{copolymer} \quad (5)$$

the stationary state approximation gives

$$\frac{d[C]}{dt} = k_4\left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} K[CF_3NO]^{3/2}[C_2F_4]$$

in which K is the equilibrium constant for the reaction:

$$CF_3NO + C_2F_4 \rightleftharpoons 1 : 1 \text{ complex} \quad (6)$$

The corresponding overall activation energy of the copolymerisation reaction (E_p) would be given by

$$E_p = E_4 + (E_1 - E_5)/2 + \Delta H_6$$

The activation energy of reaction (1) will be approximately equal to the bond dissociation energy of the C–N bond in CF_3NO, which is of the order [18] 35—50 kcal mol^{-1}. The activation energies for the propagation and termination reactions in free-radical vinyl polymerisations lie in the ranges 4—10 kcal mol^{-1} and 0—5 kcal mol^{-1} respectively.[19] If similar activation energies apply to the copolymerisation of CF_3NO and C_2F_4, then ΔH_6 lies in the range −10 to −26 kcal mol^{-1} and the complex should thus form readily at, and below, room temperature. Despite extensive investigation,[6] however, no evidence has been found for complex formation; the solubility measurements in the present work also gave no indication of any interaction. From what is
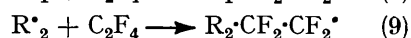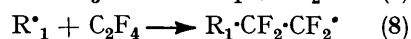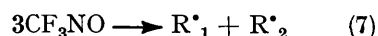
[18] J. Mason, J. Chem. Soc., 1963, 4537.
[19] C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, ' The Kinetics of Vinyl Polymerisation by Radical Mechanisms,' Butterworths, London, 1958.
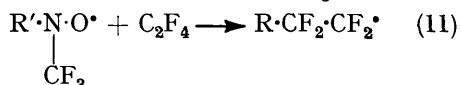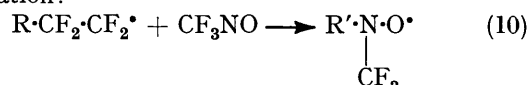
now known of the chemistry of trifluoronitrosomethane, it seems unlikely that its simple homolysis will be sufficiently fast at temperatures as low as -36 °C to initiate a measureable rate of polymerisation at that temperature. The final piece of evidence which enables the 1 : 1 complex mechanism to be rejected comes from the e.s.r. studies, which showed that the concentration of chain centres was proportional to $[CF_3NO]^{3/2}$, whereas in the above mechanism the stationary state concentration of chain centres would be proportional to $[CF_3NO]^{\frac{1}{2}}$.

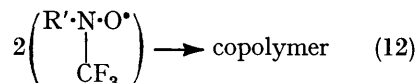An alternative reaction scheme which is consistent with all the currently available data is as follows:

Initiation:

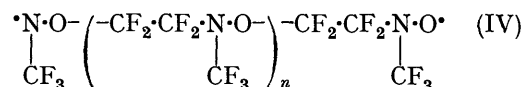$$3CF_3NO \longrightarrow R^{\bullet}_1 + R^{\bullet}_2 \qquad (7)$$

$$R^{\bullet}_1 + C_2F_4 \longrightarrow R_1{\cdot}CF_2{\cdot}CF_2{}^{\bullet} \qquad (8)$$

$$R^{\bullet}_2 + C_2F_4 \longrightarrow R_2{\cdot}CF_2{\cdot}CF_2{}^{\bullet} \qquad (9)$$

Propagation:

$$R{\cdot}CF_2{\cdot}CF_2{}^{\bullet} + CF_3NO \longrightarrow R'{\cdot}\underset{CF_3}{N}{\cdot}O^{\bullet} \qquad (10)$$

$$R'{\cdot}\underset{CF_3}{N}{\cdot}O^{\bullet} + C_2F_4 \longrightarrow R{\cdot}CF_2{\cdot}CF_2{}^{\bullet} \qquad (11)$$

Termination:

$$2\left(\begin{array}{c} R'{\cdot}N{\cdot}O^{\bullet} \\ | \\ CF_3 \end{array}\right) \longrightarrow copolymer \qquad (12)$$

If reaction (11) is much slower than reaction (10), under steady-state conditions:

$$\frac{d[C]}{dt} = k_{11}[R'\underset{CF_3}{N}{\cdot}O^{\bullet}][C_2F_4]$$

$$= k_{11}\left(\frac{k_7}{k_{12}}\right)^{\frac{1}{2}}[CF_3NO]^{3/2}[C_2F_4]$$

If the typical activation energies for propagation and termination reactions in vinyl polymerisations apply to the present case, the activation energy of the initiation reaction (7) must lie in the range 5—15 kcal mol^{-1}. Such a low activation energy is consistent with the experimental fact that the copolymerisation proceeds at a measureable rate even at -36 °C. This mechanism requires that the stationary state concentration of radicals is proportional to $[CF_3NO]^{3/2}$, as observed experimentally.

It is thus suggested that chain propagation occurs through the reaction of the radical $R'{\cdot}N(CF_3)O^{\bullet}$ [i.e. of type (III)] with tetrafluoroethylene, and the presence of this radical in the polymerising system is strongly supported by the e.s.r. spectroscopic studies reported above. The radical which results from the reaction of $R'{\cdot}N(CF_3)O^{\bullet}$ with tetrafluoroethylene must react very rapidly with trifluoronitrosomethane, since no other radical species were detected even in mixtures containing an excess of tetrafluoroethylene; reaction (11) is thus

the rate-controlling step in the propagation sequence. Ginsburg et al.[8,9,11] have suggested that a radical anion is involved in the propagation reaction and that propagation occurs by an anionic mechanism, but the results obtained in the present work show that this is most unlikely. Again, Crawford et al.[5] have suggested that propagation occurs through the successive addition of monomers to the diradical (IV), but that the free valence on the nitrogen atom is relatively inactive in the propagation. E.s.r. signals corresponding to a free valence on the nitrogen atom were not detected in the present study, however, and if such a diradical is included in the reaction mechanism the kinetic results observed cannot be explained.

$$^{\bullet}\underset{CF_3}{N}{\cdot}O^{-}\left(-CF_2{\cdot}CF_2{\cdot}\underset{CF_3}{N}{\cdot}O^{-}\right)_n -CF_2{\cdot}CF_2{\cdot}\underset{CF_3}{N}{\cdot}O^{\bullet} \quad (IV)$$

The initiation reaction proposed in the above mechanism is a third-order process in which three molecules of CF_3NO react to form two radicals, but the precise formulation of this initiation process is not clear and must await further investigation. The e.s.r. work shows that two radical species are present in a solution of trifluoronitrosomethane in benzene, toluene, or n-hexane. In addition, with tetrahydrofuran as solvent, the maximum concentration of radical species formed is proportional to $[CF_3NO]^{3/2}$, which is consistent with the radicals being formed in a third-order reaction and being removed in a second-order process. The resolution of the spectra obtained from CF_3NO in fluorine-containing solvents is not good enough to confirm that two radical species are formed in these solutions, but the general similarity of the spectra to those obtained with the other solvents indicates that this is so.

Although the structures of the radicals formed in the initiation reaction have not been determined, their rates of formation depend very markedly on the solvent used to dissolve the trifluoronitrosomethane. Similarly, the e.s.r. studies of copolymerising mixtures in a range of fluorocarbon solvents have also shown that the nature of the solvent has a marked effect on the rate of formation of radicals. If a simple homolytic process were responsible for the formation of the initiating radicals, it would be difficult to explain this marked dependence on solvent, as only small differences can arise from different extents of solvation in the initial and transition states of the initiation reaction. This indicates that a process involving electron exchange takes place and an activation energy in the range 5—15 kcal mol^{-1} is not unreasonable for such a process. It has been suggested [11] that tetrafluoroethylene is a reactant in the initiation process, but the kinetic results obtained in the present work are not consistent with this view.

In order to obtain a predicted rate equation in agreement with that found experimentally, it is necessary to assume that quadratic termination occurs. This may take place by coupling and/or disproportionation of nitroxide-type radicals, and these mechanisms are

kinetically indistinguishable. Coupling seems unlikely to occur at room temperature and above since $(CF_3)_2NO^\bullet$ exists as a stable radical under these conditions,[17] although these radicals do dimerise at lower temperatures (ΔH for the reaction is $-1\cdot8$ kcal mol^{-1}). Termination of copolymerisation is more likely to occur by disproportionation or by reaction with radicals derived by chain transfer from other substances present. In the copolymerisation of vinyl monomers, where alternating copolymers are formed, it is generally found that cross-termination, by interaction of two different radical species, predominates over other termination reactions.[20] However, the inclusion of termination reactions of this type in possible mechanisms for the present reaction leads to predicted rate equations which do not agree with those observed experimentally.

Attempts to accelerate the copolymerisation by means of conventional free-radical initiators failed. This is not necessarily contrary to the free-radical mechanism postulated, however, since the homopolymerisation of tetrafluoroethylene could not be effected by the same initiators under the experimental conditions used in the present work. Furthermore, it appears that the structure of the initiator is critical in determining its ability to initiate the polymerisation of some fluorine-containing monomers, e.g. polymers of high molecular weight can only be obtained from vinylidene fluoride when t-butyl peroxide [21] or a dialkyl peroxydicarbonate [22] is used as initiator. The fact that only bistrifluoro-methylnitroxide was effective as an initiator in the present work may indicate similar specificity in the copolymerisation of CF_3NO and C_2F_4. The results obtained in this work, therefore, provide much evidence in support of earlier suggestions that the copolymeris-ation of CF_3NO and C_2F_4 proceeds by a free-radical mechanism, but the precise nature of the initiation step has yet to be elucidated.

[20] J. C. Bevington, ' Radical Polymerisation,' Academic Press, 1961.

[21] U.S.P. 3,193,539/1965.
[22] U.S.P. 3,475,396/1969.