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

By **R. Gibbs, R. N. Haszeldine,*** and **R. F. Simmons,** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The explosive decomposition of trifluoroacetyl nitrite has been examined in the temperature range 178—232 °C. The explosion pressure is inversely proportional to the vessel diameter and a plot of log (P/T^3) against $1/T$ gives a good straight line. The corresponding activation energy is 28·7 kcal mol^{-1}, which is close to the activation energy for the slow decomposition (33·8 kcal mol^{-1}), and it is concluded that the explosion boundary is governed by self-heating.

THE thermal decomposition of trifluoroacetyl nitrite is a useful method of preparing trifluoronitrosomethane,[2] but the reaction can become explosive under certain conditions.[3] The kinetics of the slow decomposition in the gas phase have been examined [1] and the present paper reports a study of the explosion boundary. This boundary has been determined in terms of the pressure of trifluoroacetyl nitrite at which the decomposition becomes explosive at a given temperature, and the effects of vessel diameter, inert gases, and oxygen on this critical explosion pressure have been examined. It will be shown that this explosive decomposition is governed by the self-heating of the reaction.

EXPERIMENTAL

The explosive decomposition of trifluoroacetyl nitrite was studied by means of the apparatus described for the

---

[1] Part XXXIV, R. Gibbs, R. N. Haszeldine, and R. F. Simmons, *J.C.S. Perkin. II*, 1972, 773.

[2] R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 1953, 4172; R. E. Banks, 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, J. T. Brice, and R. L. Wear, *J. Org. Chem.*, 1962, **27**, 1064.

study of the slow decomposition.[1] A known pressure of reactant was admitted directly to the reaction vessel (maintained at a known temperature) and the explosion boundary determined by a bracketing technique.[4] When the explosion pressure was greater than 10 Torr, explosion could be detected by an audible click and thus the boundary was clearly defined. Below this pressure, however, the limit could only be distinguished by the very rapid increase in pressure which accompanied explosion, and since the slow reaction just below the boundary was proceeding at an appreciable rate, it was less clearly defined than at the higher pressures. The induction period prior to explosion was never more than 2—3 s and explosion was usually immediately on entry to the reaction vessel, but samples were always left in the reaction vessel for 60 s in case any unusually long induction periods occurred. In contrast to most explosions, no visible flash could be detected in the present work.

In many of the experiments the pressure of reactant in the mixing bulb exceeded the vapour pressure of the reactant at room temperature. These higher pressures were achieved by heating the mixing bulb and connecting tubing to the reaction vessel, while a nitrogen ' buffer ' was used to prevent condensation in the spoon gauge. Nevertheless, some condensation occurred in the greaseless taps on the apparatus. Direct experiments showed that this led to an error of 0·5 Torr when the pressure in the reaction vessel was 30 Torr, but at 50 Torr the error had increased to 3 Torr. At these higher pressures the explosion pressure was increasing very rapidly with decreasing temperature (see Figure 1) and thus the explosion boundary was still well defined.

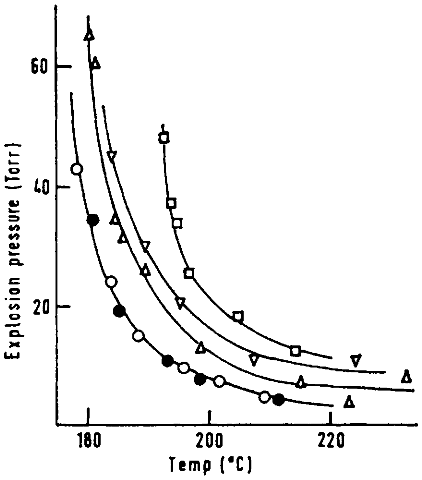

FIGURE 1 The variation in explosion pressure with temperature for the thermal decomposition of trifluoroacetyl nitrite. Vessel diameters (mm i.d.): clean Pyrex vessels; ○ 38; △ 28; ▽ 22; □ 15; clean silica vessel; ● 36

Most determinations of the ignition boundary were made using Pyrex reaction vessels, and this part of the work was completed before the slow reaction had been studied using silica vessels. Although the mixture of products obtained by reaction in Pyrex vessels was more complex than that from reaction in silica vessels,[5] Figure 1 shows that the ignition boundary was the same in both types of vessel.

Materials.—The preparation of trifluoroacetyl nitrite was described earlier.[1] Cylinder helium and argon (B.O.C.) were used directly, oxygen (B.O.C.) was passed over platinised asbestos at 360 °C and copper oxide at 700 °C, and then through a trap cooled to −78 °C, while nitrogen (B.O.C. ' white spot ') was passed over copper at 450 °C and copper oxide at 600 °C before passage through a trap cooled to −78 °C. Solid carbon dioxide was purified by fractional condensation at 2—3 Torr, followed by passage through a trap cooled to −78 °C.

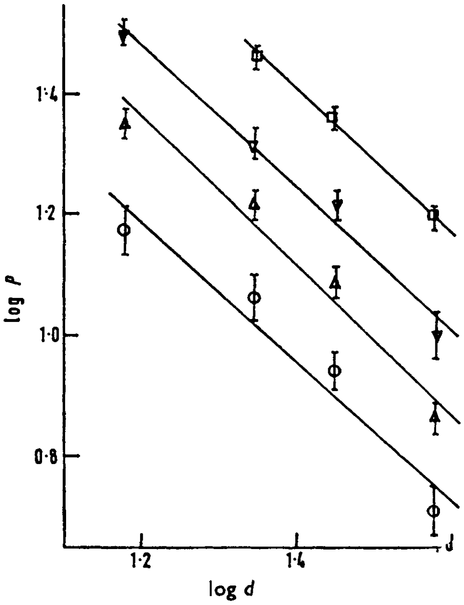

FIGURE 2 Diameter dependence of the explosion boundary of trifluoroacetyl nitrite. Temperatures (°C): ○ 207·5; △ 200; ▽ 195; □ 190

RESULTS

The spontaneous ignition boundary for trifluoroacetyl nitrite has been examined in the temperature range 178—232 °C using reaction vessels between 15 and 38 mm i.d. Figure 1 shows that the boundary approximates to a rectangular hyperbola, but the magnitude of the limit at a given temperature depends markedly on the diameter of the reaction vessel. Figure 2 is a log–log plot of the smoothed explosion pressure against the diameter of the reaction vessel for four representative temperatures. Within the experimental error, the results lie close to straight lines which are almost parallel and have a mean slope of 1·2 ± 0·2, although the lines through the actual points show some curvature. It is interesting to note, however, that where the smoothed explosion pressure is well defined, *i.e.* at 190 °C, there is little scatter in the points. Thus the explosion pressure is approximately inversely proportional to the vessel diameter.

An explosion boundary may be thermal or isothermal in character and the effect of inert gases on the boundary can be used to distinguish between the two types.[6] The effect of nitrogen, argon, helium, and carbon dioxide on the explosion boundary at 187 °C is shown in Figure 3, but the results are not of the simple type expected. Up to 15%

---

[4] C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1932, *A*138, 311.

[5] R. Gibbs, Ph.D. Thesis, University of Manchester, 1969.

[6] F. S. Dainton, *Trans. Faraday Soc.*, 1942, **38**, 227.

inert gas there is no difference between the effects of carbon dioxide, nitrogen, and helium, but at higher concentrations significant differences appear. These inert gases must have two opposing effects on the boundary; at relatively low concentrations the pressure limit increases as expected, but at higher concentrations sensitisation occurs, in that explosion occurs at a lower partial pressure of reactant. In contrast, with argon as diluent only the sensitisation effect is observed.

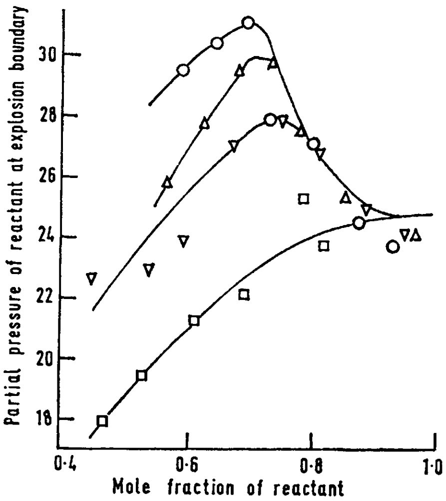

FIGURE 3 Effect of inert gases on the explosion boundary of trifluoroacetyl nitrite: ○ He; △ CO_2; ▽ N_2; □ Ar

The effect of oxygen on the explosion boundary was also examined. The partial pressure of reactant at the limit dropped from 31 to 11·7 Torr as the oxygen content was increased to 15% at 186 °C, but with higher oxygen contents the pressure limit rose again slightly. Similarly, the presence of 15% oxygen reduced the ignition boundary by 5 °C at the higher pressures (40—60 Torr) and by a rather larger amount at the lower pressures.

DISCUSSION

The rate of a chemical reaction can reach explosive proportions because of self-heating in the reaction (a thermal explosion) or because of chain-branching processes in the reaction mechanism (an isothermal explosion). It has been shown [1] that the slow decomposition of trifluoroacetyl nitrite occurs by a non-chain radical process; thus unless an entirely different mechanism is operative just below the explosion boundary, it cannot be controlled by chain-branching processes. Even if the reaction mechanism changes in this way it is difficult to visualise any mechanism for the decomposition which involves chain branching. This suggests that the observed ignition is thermal in character and thus the present results will be discussed in such terms.

The slow decomposition of trifluoroacetyl nitrite is known to be a first-order reaction and if it is assumed that there is a uniform temperature across the reaction vessel,[7] the condition for a thermal explosion is:

$$Q[\mathrm{R}]EAe^{-E/RT_0} = \chi RT_0{}^2S/V \qquad (1)$$

In equation (1) Q is the heat of reaction, A and E are the Arrhenius parameters for the decomposition, [R] the concentration of reactant, χ a heat-transfer coefficient, and T_0 the temperature of the walls of the reaction vessel of surface area S and volume V.

This is only valid if convection controls the heat loss, but Frank-Kamenetskii [8] considers that convection will be unimportant in small reaction vessels at pressures below atmospheric. Under these latter conditions the heat transfer is more likely to occur by conduction and a parabolic temperature distribution will be established within the reaction vessel. For a first-order reaction the explosion condition is then given by:

$$QEd^2[\mathrm{R}]Ae^{-E/RT_0} = 4\lambda RT_0{}^2\delta_{cr} \qquad (2)$$

where d is the vessel diameter, λ the thermal conductivity of the gas, and δ_{cr} is a dimensionless parameter which depends on the geometry of the reaction vessel ($\delta_{cr} = 2$ for an infinite cylinder). Both equations (1) and (2), however, reduce to the form:

$$\ln\,(P/T_0{}^3) = E/RT_0 + \text{Const} \qquad (3)$$

Figure 4 shows a plot of log $(P/T_0{}^3)$ against $1/T_0$ for the four reaction vessels used in the present work. Good straight lines, which are almost parallel, can be drawn through the results obtained with the 22, 28, and 38 mm i.d. vessels, but there is much more scatter in the results for the 15 mm vessel. The explosion pressures in this latter vessel were as reproducible as those obtained in the larger vessels and no simple explanation can be envisaged to explain this discrepancy. The mean activation energy from the slopes of the lines from the three largest vessels is 28·7 ± 0·2 kcal mol^{-1}, which is in reasonable agreement with the value of 33·8 kcal mol^{-1} obtained for the slow reaction.

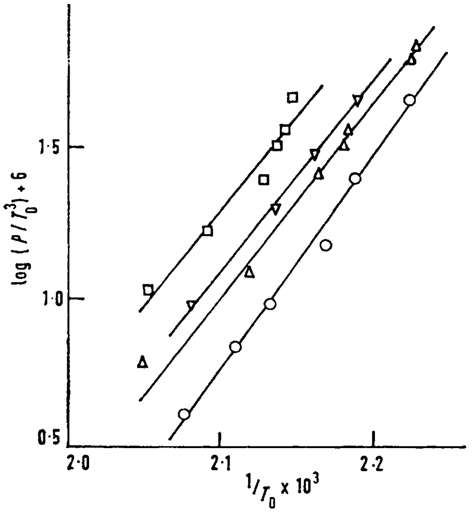

FIGURE 4 Variation of log $(P/T_0{}^3)$ with $1/T_0$. Vessel diameters (mm i.d.) of clean Pyrex vessels: ○ 38; △ 28; ▽ 22; □ 15

---

[7] N. N. Semenov, ' Some Problems of Chemical Kinetics and Reactivity,' vol. 2, transl. J. E. S. Bradley, Pergamon, London, 1959.

[8] D. A. Frank-Kamenetskii, ' Diffusion and Heat Transfer in Chemical Kinetics,' *Izvest. Akad. Nauk. S.S.S.R.*, Moscow, 1948.

It has been shown that the explosion pressure at a given temperature is approximately inversely proportional to the diameter of the reaction vessel and this is consistent with the Semenov approach [see equation (1)]. In contrast, the Frank-Kamenetskii approach predicts that the explosion pressure should be inversely proportional to the square of the vessel diameter [equation (2)]. The present results imply, therefore, that convection within the reaction vessel is the dominant mode of heat transfer at the ignition boundary of trifluoroacetyl nitrite. This is unexpected,[8] but very short induction periods are observed and, if the initial turbulence produced by the admission of the reactant is still present, there will not have been time for the parabolic temperature distribution across the vessel to be established. Under these conditions the Semenov approach would be applicable rather than that of Frank-Kamenetskii. If the plots of log P against log d are not straight lines but shallow curves, the increased diameter dependence in the larger vessels may imply the partial attainment of the parabolic temperature distribution required by the Frank-Kamenetskii approach.

The effect of inert gases on the explosion boundary is not in accord with either of the theoretical predictions. In both cases, it would be expected that the explosion pressure should rise as the thermal conductivity of the mixture is increased by the addition of inert gas, whereas a pronounced sensitisation was observed at the higher concentrations. However, a recent systematic study[9] of the heating associated with the entry of inert gases into an evacuated reaction vessel showed that the magnitude of the heating depended on both the heat capacity and the pressure of the gas. This heating was only of short duration (100—400 ms) and was small for gases with a large heat capacity; diethyl ether produced a temperature rise of only 4 °C when 5 Torr of this compound was admitted to the reaction vessel. In contrast, very large effects were observed for gases with small heat capacities. Thus a 30 °C rise was noted when 5 Torr of argon was admitted, while the temperature rose by 200 °C when 50 Torr was used.

The addition of inert gas to trifluoroacetyl nitrite not only increases the overall thermal conductivity of the mixture but also lowers the heat capacity, and these two factors will affect the explosion pressure in opposite ways. The former would make the reaction less explosive, but the heating effect from the lower heat capacity would become more and more important as the concentration of inert gas increased. Such temperature rises will be of only short duration and it is possible that above a certain partial pressure of inert gas the temperature rise is so large that the mixture explodes prematurely on admission to the reaction vessel. This occurrence would remain undetected in the present work since the induction periods were always very short.

Even the effect of inert gases on the explosion boundary, therefore, are consistent with the suggestion that the spontaneous ignition of trifluoroacetyl nitrite is governed by thermal factors, even though the results are not in complete accord with those expected from theoretical considerations. Such discrepancies, however, are not unique and further refinement of the theory is required.

[1/1970 *Received, 25th October, 1971*]

[9] D. H. Fine, P. Gray, and R. MacKinven, 12th Symposium on Combustion, p. 545, The Combustion Institute, 1969.