Kinetics and Enthalpy Change of the Addition Reaction between Bistrifluoromethyl Nitroxide Radical and Tetrafluoroethylene

By Philip E. Coles, Robert N. Haszeldine,* Anthony J. Owen, Peter J. Robinson, and Brian J. Tyler
(*Chemistry Department, University of Manchester Institute of Science and Technology, Manchester* M60 1QD)

Summary Rate constants and Arrhenius parameters have been measured for the addition of the bistrifluoromethyl nitroxide radical to tetrafluoroethylene [reaction (2)], and ΔH° for the overall reaction (1) has been determined.

The organic chemistry of the stable bistrifluoromethyl nitroxide radical has been studied extensively but little work has been done on its physical aspects. In this work the overall reaction (1)[1] was followed using three techniques

$$2(CF_3)_2N{\cdot}O{\cdot} + C_2F_4 \rightarrow (CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}O{\cdot}N(CF_3)_2 \qquad (1)$$

—total pressure measurement, photometry of the radical at 540 nm, and quantitative g.l.c. analysis. The concentrations of reactants and products measured by the three methods were in close agreement. The rate of reaction was measured at 295—355 K, with total reactant pressures of 10—108 mmHg† and radical–olefin ratios from 4 : 1 to 1 : 9. Although tetrafluoroethylene is readily telomerised, only one significant product, the 2 : 1 adduct, was observed. Even when the olefin–nitroxide ratio exceeded 100, only a trace of a second product was observed (unidentified, but even if it is the 2 : 2 adduct its maximum concentration is *ca.* 2 p.p.m.), demonstrating the excellent radical-scavenging ability of the nitroxide. Integrated second-order function plots (first-order in each reactant) were linear up to *ca.* 75% reaction, with slopes independent of the reactant pressures at a given temperature. These kinetics strongly suggest that the reaction mechanism is as shown in equations (2) and (3). The Arrhenius plot was a good straight line, corresponding to $\log_{10}(A_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 7{\cdot}61 \pm 0{\cdot}05$

$$(CF_3)_2N{\cdot}O{\cdot} + C_2F_4 \rightarrow (CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot} \qquad (2)$$

$$(CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot} + (CF_3)_2N{\cdot}O{\cdot} \rightarrow (CF_3)_2N{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}O{\cdot}N(CF_3)_2 \qquad (3)$$

and $E_2 = 44{\cdot}6 \pm 0{\cdot}4$ kJ mol^{-1} (error limits here and below are standard deviations). A 12-fold increase in surface–volume ratio had only a slight effect on the observed rate constant (decrease of 8—25%).

A considerable self-heating effect during reaction (1) has been reported,[2] and we have measured the heat release in

---

† 1 mmHg = 133·322 Pa.

order to assess the thermochemistry and magnitude of consequent errors in the rate constants. The rise in temperature at the centre of a spherical reaction vessel (120 cm^3) was measured using a 0·001 in diameter, silica-coated Pt–13% Rh/Pt thermocouple, at 355—412 K and total pressures of 21—28 mmHg, using near-stoicheiometric mixtures. The heat release calculated[3] using measured temperature rises, which were of the order of 4—10 K, and the directly measured reaction rates was 240 ± 6 kJ per mole of reaction (1), corresponding to $\Delta H^\circ_1 = -246 \pm 6$ kJ mol^{-1} at the reaction temperatures. The exothermicity of this reaction is low compared with those estimated by approximate group-additivity calculations for the addition of most other radicals to tetrafluoroethylene (*e.g.* ΔH° for addition of 2 H, −670; 2 Pr^i, −494; and 2 EtO, −420 kJ mol^{-1}), indicating the relative weakness of the $(CF_3)_2N{\cdot}O{-}CF_2R$ bonds formed.

During the heating experiments, the rates of reaction were simultaneously measured by pressure change, with g.l.c. check on the final stoicheiometry. The second-order integrated function plots were linear up to at least 50% reaction and gave $\log_{10}(A_2/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = 7{\cdot}3 \pm 0{\cdot}5$ and $E_2 = 44 \pm 4$ kJ mol^{-1}, in good agreement with the previous results. The discrepancies are probably attributable to the large dead-space (*ca.* 25%) in the second system,[4] despite corrections having been made.

Corrections for the heating effect were made to the first set of rate-constants (rejecting points, about one third of the data, for which the correction was uncertain owing to probable convection);[3] the corrected parameters differ insignificantly from the original data, the resulting Arrhenius equation being (4). The A-factor is normal,[5] and the activation energy high relative to reactive radicals

$$\log_{10}(k_2/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = (7{\cdot}56 \pm 0{\cdot}05) - (44{\cdot}4 \pm 0{\cdot}3)\ \text{kJ mol}^{-1}/2{\cdot}303\,\boldsymbol{R}T \qquad (4)$$

such as $CH_3{\cdot}$ or $CF_3{\cdot}$ [*cf.* rate constants for addition at 298 K/dm^3 mol^{-1} s^{-1}: H, 10^9; CF_3, 3×10^6; Me, 2×10^4; CCl_3, 8×10^2; $(CF_3)_2N{\cdot}O{\cdot}$, 0·6],[5] and reflecting the relative weakness of the bonds being formed.

(*Received*, 30*th December* 1974; *Com.* 1564.)

[1] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1966, 901.
[2] A. V. Mel'nikova, M. K. Baranaev, S. P. Makarov, and M. A. Englin, *J. Gen. Chem.* (*U.S.S.R.*), 1970, **40**, 350.
[3] T. Boddington, P. Gray, and B. J. Tyler, *Internat. J. Chem. Kinetics*, 1974, **6**, 531.
[4] P. J. Robinson, *Trans. Faraday Soc.*, 1967, **63**, 2668.
[5] J. A. Kerr and M. J. Parsonage, 'Evaluated Kinetic Data on Gas-Phase Addition Reactions,' Butterworth, London, 1972.