KINETIC MEASUREMENTS ON THE SYSTEM NO + $NO_2 \rightleftharpoons N_2O_3$ BY TIME-RESOLVED INFRARED LASER ABSORPTION

Ian W.M. SMITH and Gregory YARWOOD

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, UK

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The first direct kinetic measurements have been made on the reaction NO + $NO_2 \rightleftharpoons N_2O_3$. Equilibrium mixtures of the nitrogen oxides containing excess NO at 208 ± 3 K were perturbed by flash photolysis of a fraction of the N_2O_3. The rate of relaxation to equilibrium was monitored by observing the transmittance of a line from a cw CO laser selected to coincide with the ν_1 band in N_2O_3. At pressures up to 1000 Torr (M = He, Ar) the association reaction is third-order with $k^0(\mathrm{M = He}) = (3.6 \pm 0.15) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1} and $k^0(\mathrm{M = Ar}) = (5.5 \pm 0.8) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1}.

1. Introduction

In this paper, we report the first direct measurements on the kinetics of association and dissociation in the gas-phase system

$$\mathrm{NO} + \mathrm{NO_2} \rightleftharpoons \mathrm{N_2O_3}. \qquad (1, -1)$$

Dinitrogen trioxide is a weakly bound oxide of nitrogen, the standard change of enthalpy for reaction (1) at 298 K being $\Delta H^0_{298} \approx -40.9$ kJ mol^{-1} ‡. The reaction in the forward direction is one of radical association but is unusual in the weakness of the bond which is formed. One result of the weak N–N bond is that the N_2O_3 molecule contains vibrations of widely differing frequency, varying from the NO-stretching ν_1 vibration, which gives rise to an infrared band centred at 1829 cm^{-1}, to the torsional or hindered rotational motion around the N–N bond which has a wavenumber frequency of approximately 70 cm^{-1} [4,5]. These unusual properties suggest that it will be especially interesting to examine if the usual theories of unimolecular reaction rates can satisfactorily reproduce the kinetic behaviour in this association–dissociation system.

The measurements reported here confirm that the rates of reactions (1) and (−1) are pressure dependent at total pressures below 1000 Torr. We intend to extend our present measurements up to much higher total pressures of a wide range of third-body gases, and a comparison will then be made with theoretical calculations. In the present paper, we describe our novel experimental technique and report third-order rate constants for the association of NO and NO_2 in the presence of M = He and Ar at 208 ± 3 K.

To follow the kinetics, we employ what is essentially a "relaxation" method. The NO + $NO_2 \rightleftharpoons N_2O_3$ equilibrium is established in a low-temperature reaction cell with NO in excess over the other oxides of nitrogen. The equilibrium is then perturbed by partially flash photolysing the N_2O_3. The subsequent rate of relaxation back to equilibrium is observed by monitoring the time-dependent transmitted intensity of a cw infrared CO laser line which is selected to coincide with a strong feature in the ν_1 absorption band of N_2O_3. Time-resolved infrared laser absorption has been used relatively rarely to follow the rates of fast chemical reactions. The technique, especially as applied to transient organometallic species, has been reviewed recently by Poliakoff and Weitz [6].

2. Experimental

The main elements of the apparatus are a low-tem-

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‡ Ref. [1] gives a value of $\Delta H^0_f(N_2O_3)$ corresponding to ΔH^0_{298} for reaction (1) of −40.6 kJ mol^{-1}, ref. [2] ΔH^0_{298} = −40.9 kJ mol^{-1}, and ref. [3] ΔH^0_{298} = −41.2 kJ mol^{-1}.

perature flash photolysis system, a cw CO laser from which a single infrared line can be selected, and a fast infrared detector coupled to a transient recorder and microcomputer. A relatively brief description of the apparatus is given here, since a fuller description will be given in a future publication.

The reaction vessel was constructed from quartz tubing and was fitted with CaF_2 end windows. The central 75 cm length was jacketed with a second quartz tube and enclosed in a cooled aluminium can. Copper tubing was wound round and bonded to the aluminium container and cooled methanol was flowed through this tubing. This coolant passed through a heat exchanger immersed in a dry-ice isopropanol bath. The temperature was measured by a thermocouple which was enclosed in a thin quartz sleeve and inserted into the reaction cell. After allowing for the very small temperature rise following dissociation of the N_2O_3 (see below) and for any drift in the ambient temperature, the temperature in all the experiments that are reported here was 208 ± 3 K.

The flash lamp was 50 cm long and was mounted entirely within the cooled metal can. A 1 μF capacitor was charged to 20 kV providing a flash energy of 200 J. The profile of the light output had a width (fwhm) of 6 μs.

The liquid-N_2 cooled cw CO laser was home-built and was similar in design to the laser described by Brechignac and Martin [7]. The laser cavity consisted of a 98% reflecting, 2% transmitting output coupler and a diffraction grating with 150 lines/mm blazed at 6 μm. The grating was set so that the laser oscillated on the 11P(14) line at 1829.59 cm^{-1}, which lies close to a strong Q-branch feature in the ν_1 band of N_2O_3 [4,8].

The laser beam was directed through the reaction cell and was then focused onto a room temperature InSb detector of "labyrinth" construction (Mullard, RPY77). This detector has an intrinsic time constant of 0.1 μs but was used in conjunction with an amplifier of 300 kHz bandpass. Signals from the detector were digitised in a transient recorder (Data Laboratories, model 905, minimum channel width 0.2 μs) and then transferred to a microcomputer (Acorn, BBC model B).

Each series of experiments was performed on a single mixture of nitrogen oxides which was successively diluted to different total pressures with He or Ar. A mixture of NO_2 and NO was first prepared at room temperature and then a suitable pressure of this mixture was admitted to the cooled reaction cell. At this stage the partial pressure of NO_2 (present as NO_2, N_2O_3 or N_2O_4) was in the range 90–155 mTorr, that of NO was varied between ≈1 and 3 Torr. He or Ar was added to this mixture in the reactor, ample time being allowed for diffusive mixing after each addition. The rare gases were used directly from cylinders (He: Air Products, CP grade; Ar: Air Products, typically 2 ppm O_2) without further purification, but one series of experiments was conducted with high-purity argon (BOC Ltd., research grade, $O_2 < 1$ ppm) as diluent.

3. Results and discussion

At 208 K, the equilibrium constant K_1 for $NO + NO_2 \rightleftharpoons N_2O_3$ is 1.62 $Torr^{-1}$ or 3.5×10^{-17} cm^3 $molecule^{-1}$ [1–3]. If, for example, the partial pressure of NO is 1 Torr and the partial pressures of NO_2 and N_2O_3 are much less, $[N_2O_3]/[NO_2] = 3.5 \times 10^{-17} \times [NO] = 1.62$, and, by detailed balance, $(k_1[NO] + k_{-1})/k_1[NO] = 1 + 1/K[NO] = 1.62$.

Because the pseudo-first-order rate constants for association and dissociation are similar in magnitude, both enter into the kinetic analysis; that is, the experiments are of the classic "relaxation" type. Accordingly

$$-\mathrm{d}[\Delta N_2O_3]/\mathrm{d}t = (k_1[NO] + k_{-1})\ [\Delta N_2O_3]$$

$$= k_1[NO]\,(1 + 1/K[NO])\,[\Delta N_2O_3],$$

where $[\Delta N_2O_3]$ is the concentration of N_2O_3 at time t minus the (larger) concentration of N_2O_3 at equilibrium, that is as $t \to \infty$. Strictly, $[\Delta N_2O_3]$ is related directly to the difference in optical densities:

$$[\Delta N_2O_3]_t = [N_2O_3]_t - [N_2O_3]_e$$

$$= [\ln(I^0/I)_t - \ln(I^0/I)_e]/\sigma l = \ln(I_e/I_t)/\sigma l,$$

where σ is the effective absorption cross section and l the path length. However, in our experiments $(I/I^0)_e \approx 0.8$ and $(I/I^0)_{t=0} \approx 0.86$. Under these conditions. where the change in optical density is small, $[\Delta N_2O_3]_t$ is proportional to ΔI_t to a high degree of approximation so that $|\Delta I_t|$ should vary exponentially with time with a first-order rate constant $k_{1st} = k_1[NO]\,(1 +$

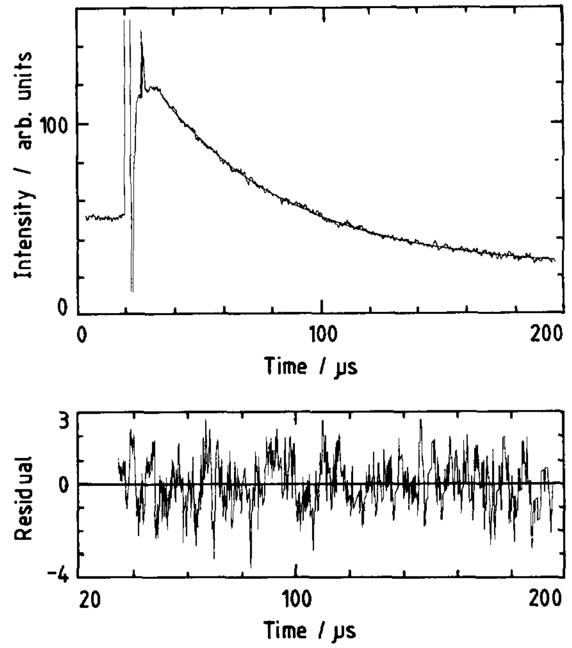

Fig. 1. Single-exponential fit to an observed experimental decay in intensity with time. The residuals of the fit are shown below. P_{NO} = 1.65 Torr, P_{He} = 803 Torr, T = 210 K.

$1/K$[NO]). Fig. 1 shows an experimental trace and its fit to a single exponential via a non-linear, least-squares procedure.

Two factors could complicate the kinetic analysis. The first is the rise in temperature which occurs because photons in the far ultraviolet are being used to break the weak N–N bond and dissociate N_2O_3. To minimise the rise in temperature, and to prevent other complications that could arise from the photo-predissociation of NO, the annular quartz jacket around the reaction cell was filled with NO. This filtered out the wavelengths capable of exciting nitric oxide but transmitted wavelengths between the NO absorption lines which can be absorbed in the strong, broad continuum of N_2O_3 centred at 215 nm. The extent of the temperature rise could be estimated in two ways. First, the proportion of N_2O_3 photolysed can be calculated from the measured change in transmitted intensity immediately after firing the flash lamp. Knowing the photon energy (approximately) and the specific heat capacity of the gas, the rise in temperature could then be calculated. Second, the main effect of any temperature jump was to modify the equilibrium concentration of N_2O_3. This was reflected in a slight difference between the asymptote of the decay traces and the pre-trigger value of the signal. Changes in temperature calculated from these two pieces of evidence were in good agreement. They were restricted to 2 K or less by only making measurements at total pressures above 160 Torr.

Although the change in temperature was slight, it was allowed for. The first-order constant derived from each trace of I versus time was divided by $(1 + 1/K[\mathrm{NO}])$ where K was the equilibrium constant which was calculated after allowing for the estimated rise above ambient temperature. This procedure yields a value of k_1[NO], a first-order rate constant for association of NO and NO_2 for the chosen third-body gas at the particular total pressure of that experiment.

A second potential complication arises because of the formation of a small concentration of N_2O_4 in the cooled gas mixtures, which is greatest when [NO]/[NO_2] in the prepared gas mixture is relatively small. The flash photolyses part of the N_2O_4, releasing NO_2 in addition to that produced by dissociation of the N_2O_3. Because, even in these mixtures [NO] $\gg$ [NO_2], the association of NO_2 with NO is much faster than the NO_2 dimerisation. As a result, when the $NO + NO_2 \rightleftharpoons N_2O_3$ system initially reaches equilibrium there can be a slightly greater concentration of N_2O_3 present than there was before the flashlamp was fired. In mixtures where [NO]/[NO_2] is relatively small and the total pressure (and therefore the heat capacity of the gas) is large so that the temperature jump is insignificant, the signals of transmitted intensity are seen to return to below their pre-trigger value, confirming this effect. The signals then return to their original equilibrium value on a much longer time scale as the $2\,NO_2 \rightleftharpoons N_2O_4$ equilibrium is established. These observations, and extensive computer modelling of the system, confirm that the interpretation of the traces of ΔI_t versus time at short delays is not significantly affected by the effects of N_2O_4 dissociation and reformation.

Fig. 2 shows a plot of values of the observed first-order decay constants against the pressure of added helium in a series of experiments with a constant partial pressure of NO. Clearly, the rate constants vary linearly with pressure. This correlation has been confirmed in several series of experiments and show that the reaction is in its third-order regime at pressures of He or Ar up to 1000 Torr. The conditions in these experiments, and

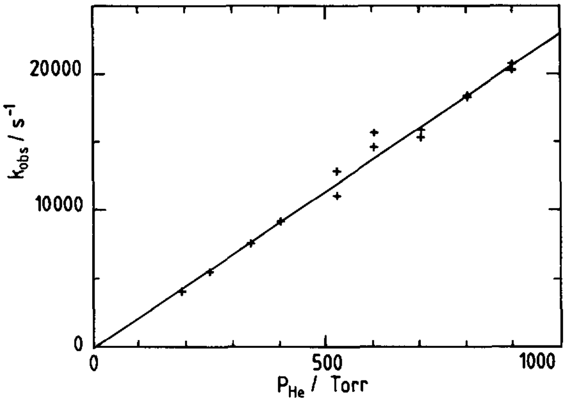

Fig. 2. Plot of the observed first-order decay constant against the pressure of helium added. P_{NO} = 1.65 Torr, T = 209–210 K.

the results of them, are summarised in table 1. The average values of the third-order rate constants (in cm^6 $molecule^{-2}$ s^{-1}) at 208 K are

$$k_1^0(M = He) = (3.6 \pm 0.15) \times 10^{-33},$$

$$k_1^0(M = Ar) = (5.5 \pm 0.8) \times 10^{-33}.$$

When unimolecular dissociation reactions, or the reverse association reactions, are studied over only a limited range of pressure, great care has to be taken to establish if the reaction is truly in its third-order regime, since curvature over a small part of the fall-off region can be very slight. Three subsidiary pieces of evidence support our assertion that the $NO + NO_2$ association is a third-order reaction with M = He or Ar at total pressures up to 1000 Torr. Firstly, plots of k_1 [NO] versus [M], like that in fig. 2, pass, within experimental error, through the origin. Put another way, values of the third-order rate constants derived from individual experiments by calculating $k_1/[M]$ show no significant variation with [M].

Secondly, the measured value of k_1 can be compared with the rate constants obtained for similar association reactions like $OH + NO_2 \rightarrow HONO_2$ and $ClO + NO_2 \rightarrow ClONO_2$ [9]. These reactions are appreciably more exothermic than $NO + NO_2 \rightarrow N_2O_3$ (ΔH^0_{298} = −207 and −109 kJ mol^{-1}, respectively), so their third constants are much larger. However, the shape of the fall-off curves should be very similar, with those for different reactions merely being displaced along the [M]

Table 1
Experimental results and the conditions in each series of experiments

	P_{NO} (Torr)	P_M (Torr)	Number of experiments	T (K)	k_1^0 (cm^6 $molecule^{-2}$ s^{-1})
(i) M = He	2.92	190–600	12	208–211	$(3.69 \pm 0.15)^{a)} \times 10^{-33}$
	1.65	190–900	16	209–210	$(3.49 \pm 0.12) \times 10^{-33}$
	0.93	400–960	11	209–213	$(3.55 \pm 0.14) \times 10^{-33}$
	0.93	400–970	21	206–209	$(3.65 \pm 0.16) \times 10^{-33}$
				mean	$(3.6 \pm 0.15)^{b)} \times 10^{-33}$
(ii) M = Ar	2.44 c)	200–500	15	207–208	$(5.44 \pm 0.22)^{a)} \times 10^{-33}$
	2.46	200–660	15	207–209	$(5.10 \pm 0.14) \times 10^{-33}$
	1.67	190–500	10	206–207	$(6.38 \pm 0.19) \times 10^{-33}$
	0.93	190–375	9	206	$(5.83 \pm 0.50) \times 10^{-33}$
				mean	$(5.5 \pm 0.8)^{b)} \times 10^{-33}$

a) Errors in each individual result correspond to two standard deviations.

b) Result quoted is the weighted mean of the individual results; the error quoted is twice the average deviation of the individual results from this weighted mean.

c) Obtained using high-purity argon.

axis [10]. This comparison also supports the view that the rates of reactions (1) and (−1) are directly proportional to [He] or [Ar] through the pressure range examined in our experiments.

Finally, we note that the highest second-order rate constant that was measured in the current investigation was 3.0×10^{-13} cm^3 molecule^{-1} s^{-1}. It is (1/250)th of the value estimated [11] for the limiting high-pressure rate constant for reaction (1) using the maximum free-energy model of Quack and Troe [12].

The values of k_1^0 for M = He and M = Ar can be used to calculate the relative collisional efficiencies of these two cases at removing energy from the NO + NO_2 energised collision complex. Using the usual expression for the rate constant for bimolecular collisions, i.e. $Z^0 = \pi\sigma^2 \bar{c}\, \Omega^*$, where Ω^* is the collision integral, we find

$$\beta_c(M = He)/\beta_c(M = Ar) = 0.47.$$

This value is rather smaller than is usually found for the relative efficiencies of these two third-body gases [9]. A possible cause might have been oxygen impurity in the argon. Oxygen is thought to form a quite strongly bound species with NO [13] which could provide a bound-complex type mechanism [14] for rapid NO + NO_2 association. However, a series of experiments performed with high-purity argon gave the same result as those using normal research grade gas, confirming that any effects due to O_2 were insignificant. Experiments extending the pressure range and the variety of third-body gases are now under way.

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