

DETERMINATION OF THE $\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$ RATE CONSTANT BY IR TDL AND FT SPECTROSCOPY

J. Hjorth, F. Cappellani, C. Nielsen* and G. Restelli
 Commission of the European Communities
 Joint Research Centre - Ispra Establishment
 21020 Ispra (Va) - Italy

*on leave from the University of Oslo, Dept. of Chemistry
 Blindern - Norway

1. INTRODUCTION

One of the reactions which destroy NO_3 in the troposphere at night is:



This reaction is not the most important sink for NO_3 ; however, it is not negligible. The first attempt to evaluate its rate constant k_1 was made by Schott and Davidson (1958) in the study of the irreversible decomposition of N_2O_5 in the temperature range 750 - 934 K. Different expressions were obtained for k_1 as a function of T, according to different analyses of the experimental data, which give ^{at} $T = 296 \text{ K}$ $k_1 = 1.29 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $k_1 = 2.35 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, respectively. Graham and Johnston (1978) took advantage of their determination of the equilibrium constant K for reactions (2)



to derive k_1 from the data measured for the product ($k_1 \times K$) by Johnston and Tao (1951) in the temperature range 338 - 396 K. Their expression for k_1 leads to a value at 296 K equal to $3.92 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. These studies were recently analysed by Johnston et al. (1986) and the discrepancies among the results accounted for by introducing the contribution of the unimolecular thermal decomposition of NO_3



with a rate constant $k_3 = 2.5 \times 10^6 \exp(-6100/T) \text{ s}^{-1}$. The expression for k_1 as derived from the data of Johnston and Tao (1951) can be written as a function of K as $k_1 = \sqrt{2.05 \times 10^{13} \exp(-12400/T)} \times K$.

In the present study k_1 was evaluated from a simultaneous determination of $\overline{[NO]}$ and $\overline{[NO_2]}$ in a steady state situation after mixing excess NO_2 and N_2O_5 in zero air in a large reaction chamber at 296 K. NO is generated by reactions (1) and (3) and disappears by the reaction with NO_3



The steady state equation is given by

$$k_3 \overline{[NO_3]} + k_1 \overline{[NO_3]} \overline{[NO_2]} = k_4 \overline{[NO]} \overline{[NO_3]} \quad (a)$$

Experimental conditions were selected in order to obtain in eq.(a), k_3 negligible with respect to the product $k_1 \overline{[NO_2]}$; assuming for k_1 a value of $5 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The rate constant k_1 could then be derived from

$$k_1 = k_4 \frac{\overline{[NO]}}{\overline{[NO_2]}} \quad (b)$$

The evaluation of k_1 appears independent of the concentration of N_2O_5 in the experiment; which, however, influences the relaxation time needed to reach the steady state situation. Simulations using the FACSIMILE computer programme (Chance et al., 1977) showed that the equilibrium situation was reached in few minutes for the experimental conditions used.

2. EXPERIMENTAL TECHNIQUES

The experiments were performed in a 480L glass Teflon reaction chamber, 60 cm diameter, 150 cm long under dark conditions at 296 K. A three-mirror White type multiple reflection system with a path length set for the experiments at 80 m was coupled to a Bruker IFS 113 V interferometer (FTS) or by a remotely operated flip mirror to an IR tunable diode laser spectrometer (TDL). The FTS was used to measure the concentrations of NO_2 , N_2O_5 and HNO_3 from spectra recorded at 1 cm^{-1} instrumental resolution; the TDL operated in second harmonic absorption mode (2f) (Reid et al., 1978) to measure the NO concentration. $\overline{[NO_2]}$ and $\overline{[N_2O_5]}$ were evaluated from the integrated absorption of their bands centred at 2906 cm^{-1} ($\nu_1 + \nu_3$) and 1245 cm^{-1} , respectively. $\overline{[NO]}$ was determined from the 2f signal of its $3/2_Q$ (1,5) line at $1875.8132 \text{ cm}^{-1}$. This spectral feature was selected according to the laser emission and mode structure in conjunction with the absence of interfering absorption from other molecules (Figure 1).

High specificity and sensitivity were obtained by recording the 2f spectra with the gas sample in the reaction chamber at reduced pressure (15-50 Torr).

Calibration curves were constructed from standard gas mixtures of NO₂ and NO in N₂ recording the spectra under the same conditions, temperature, pressure, instrumental resolution, as in the experiments.

The NO₂, N₂O₅ and NO concentrations were measured in the range (1-5) × 10¹⁵, (0.5-3) × 10¹⁴ and (2-11) × 10¹⁰ molecules cm⁻³, respectively.

3. RESULTS AND DISCUSSION

Experiments were carried out at 15 as well as at 50 Torr total pressure, but no significant pressure dependence could be observed. k_1 was then evaluated by the use of Eq.(b) as an average of all the individual determinations. The combined effect of random and systematic errors led to the expression:

$$k_1 = (1.54 \pm 0.28) \times 10^{-26} / k_4 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

Inserting the value for k_4 at 296 K given in the last JPL compilation (Demore et al., 1987) $k_4 = (3.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$,

k_1 is found as

$$k_1 = (5.12 \pm 1.79) \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

If k_1 is calculated at 296 K as a function of K from the expression by Johnston et al. (1986) using for the equilibrium constant K the value recommended in the JPL compilation, it results equal to $4.61 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The agreement is good if one considers that the two values were obtained from two different approaches.

The value of the equilibrium constant K for reactions (2) is still an unsettled question as determinations in the literature vary within a factor two. Using the k_1 value of this study and the expression for $k_1 \times K$ given by Johnston et al. (1986), the equilibrium constant K can now be calculated. When this procedure is applied, a value for K equal to $2.56 \times 10^{10} \text{ molec. cm}^{-3}$ is obtained. This value compares favourably with that given in the JPL compilation, equal to $2.85 \times 10^{10} \text{ molec. cm}^{-3}$, and shows a better agreement with the values determined by Tuazon et al. (1984)

and Kircher et al. (1984) than with the previous values of Graham and Johnston (1978) and Malko and Troe (1982). Unfortunately the uncertainty in k_4 which, in turn, determines the uncertainty in the value for k_1 used, precludes any definitive conclusion.

The hypothesis of a heterogeneously catalyzed decay of NO_3 to $\text{NO} + \text{O}_2$ on the reactor walls was taken into consideration, in particular because the experiments were carried out at reduced pressure. There is, however, some evidence against the relevance of this hypothesis.

(i) Johnston et al. (1986) in their study of the homogeneous thermal decay of NO_3 to $\text{NO} + \text{O}_2$, exclude any significant contribution from heterogeneous reactions. This conclusion was based on a comparison of kinetic data for experiments performed at atmospheric pressure in reaction chambers of volumes ranging over a hundred fold range (37 to 3700 L).

(ii) In the present study, a dependence of the k_1 value on the ratio of $\overline{[\text{NO}_2]}$ to $\overline{[\text{N}_2\text{O}_5]}$ should appear, which was not observed.

(iii) Finally, an attempt was made to estimate an upper limit for this heterogeneous contribution to NO formation by measuring the formation of NO_2 during the decay of N_2O_5 , as NO would react rapidly with NO_3 to form NO_2 . Measurements were performed on the formation of NO_2 at 50 Torr and 296 K in the usual experimental set-up but with a much smaller NO_2 to N_2O_5 ratio. It was found that this reaction would contribute less than 10% to the production of NO at the experimental conditions applied by the determination of k_1 . With the higher $\overline{[\text{NO}_2]}$ to $\overline{[\text{N}_2\text{O}_5]}$ ratio used for the determination of k_1 , this contribution, if due to NO_3 wall decay, would be further reduced. Note that also the heterogeneous decay of HNO_3 (Svensson and Ljungstrom, 1988), which is formed from N_2O_5 might contribute to the formation of NO_2 as suggested by an observed correlation between the rate of NO_2 formation and the build-up of HNO_3 in the reactor.

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