

LIF detection of NO₃ radical after pulsed excitation of NO₂ vapor at 436.45 nm

S.A. Nizkorodov^{a,1}, V.I. Makarov^{a,2}, I.V. Khmelinskii^a, S.A. Kotschubei^b, K.A. Amosov^b

^a Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk 630090, Russian Federation

^b Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russian Federation

Received 4 August 1993; in final form 17 February 1994

Abstract

Single-photon excitation of gaseous NO₂ at 436.45 nm at 10⁻³–10¹ Torr pressure range has been shown to produce NO₃ as an intermediate of NO₂ under threshold photolysis. Serious kinetic evidence has been obtained that the formation of NO₃ can proceed through the reaction of electronically excited NO₂ species with ground state NO₂ molecules.

1. Introduction

Though the mechanism for the photolysis of gaseous nitrogen dioxide has been thoroughly studied in the past [1–6] the question of whether reactions of electronically excited NO₂ (NO₂^{*}) with ground state NO₂ molecules may significantly contribute to the photodissociation yield in the threshold spectral region ($\lambda_{\text{ex}} > 397.8$ nm) has not yet been resolved. The possible existence of such reactions was first considered by experimentalists after they discovered secondary products of NO₂ photolysis after optical excitation of NO₂ with λ_{ex} up to ≈ 600 nm [7–16] under single-photon absorption conditions. The contributions to the NO₂^{*} internal energy, required for dissociation, from collisions and internal rotational and vibrational degrees of freedom account for a non-zero photodissociation yield only up to $\lambda_{\text{ex}} \approx 430$ nm un-

der normal conditions [13]. At higher excitation wavelengths photolysis is believed to proceed via some photoinitiated reactive process. Norrish [8] and Dickinson and Baxter [7] suggested the reaction



Jones and Bayes [13] found experimentally that some proportion of NO₂^{*} is indeed quenched reactively but they could not distinguish between mechanism (1) and the alternative route,



From kinetic considerations that did not include reaction (2) it was found that $k_1/k_q \approx 2.7 \times 10^{-3}$ [17] where k_q is the fluorescence self-quenching rate constant for NO₂^{*}. Neither NO₃ nor any other intermediate of NO₂ under threshold photolysis has been experimentally detected yet. To gain more insight into the problem we have searched for NO₃ radical using the time-resolved LIF technique.

¹ Present address: Institute of Physical Chemistry, Basel University, CH-4056 Basel, Switzerland.

² Present address: RIKEN, Hirosawa 2-1, Wako-shi, Saitama 351-01, Japan.

2. Experimental

In the experiments the NO_3^* species were prepared by a dye-laser pulse (0.15 cm^{-1} fwhm, 10 ns pulse duration, 3–5 mJ/pulse, 3 mm beam diameter) and the NO_3 concentration was probed by LIF excited with a conventional He–Ne laser (2 mW, 3 mm beam diameter). The experiments were carried out with samples of pure gaseous NO_2 or NO_2/NO mixtures at 10^{-3} – 10^1 Torr in a cylindrical stainless-steel gas cell ($\varnothing=40$ mm; $L=100$ mm) equipped with six quartz windows ($\varnothing=10$ mm). Both laser beams were counter-propagated along the diameter of the cell. The fluorescence, filtered with a 700 nm interference filter, was observed perpendicular to the direction of the exciting and probing beams. About 8% of the fluorescent photons were collected.

Fluorescence from the cell was time-resolved with the help of two multichannel analyzers. A fast multichannel analyzer was used to record the rising part of the fluorescence. The delayed part of the fluorescence was sampled separately by another analyzer with smaller operational frequency. The extraction of the LIF signal of NO_3 was accomplished using the standard probing laser off/on scheme. The corresponding experiment with an empty cell gave no background. Radiation from the He–Ne laser alone produced no fluorescence. The dye laser was pulsed with a frequency of about 1 Hz or less to let the NO_3 molecules disappear completely. After 10–100 pulses the NO_2 in the cell was refreshed to avoid the accumulation of photolysis products. Unfiltered time-averaged luminescence spectra of our system were obtained using a spectrograph with a typical resolution of $15 \text{ cm}^{-1}/\text{mm}$. The line positions were calibrated against the emission lines of Ne. The NO_2 used in our experiments was obtained by thermal decomposition of $\text{Pb}(\text{NO}_3)_2$ and purified by vacuum trap-to-trap distillation to remove the traces of NO and O_2 . NO was synthesized as described in ref. [18].

3. Results

Fig. 1 shows microdensitograms of plates of some luminescence spectra of pure NO_2 vapour irradiated with a pumping dye laser at $\lambda=436.45$ nm and a probing He–Ne laser at $P=P_{\text{NO}_2}=2.8$ Torr. The

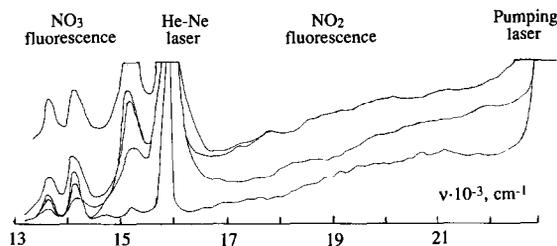


Fig. 1. Typical low-resolution luminescence spectra of pure NO_2 at 2.8 Torr pressure irradiated with pumping dye laser at $\lambda=436.45$ nm and probing He–Ne laser. Labeling of the X axis is approximate. Line positions were calibrated against Ne emissions. Three lines at the red of the He–Ne laser correspond to the strongest emission features of NO_3 radical (see text).

spectra were obtained with different spectrograph resolution. The spectra include two strong lines due to the exciting and probing light, a broad unresolved fluorescence of NO_2 and three lines at ≈ 13600 , 14100 and 15100 cm^{-1} ($\pm 20 \text{ cm}^{-1}$) corresponding to the luminescence of NO_3 radical [19–22]. The reported positions of the strongest fluorescent lines of NO_3 radical are 15108 cm^{-1} (ν_1-0 transition), 14057 cm^{-1} (ν_2-0 transition) and 13619 cm^{-1} (ν_3-0 transition) [21]. The intensity distribution is 2:2:1 in that order for excitation at 661.9 nm [21] and $\approx 3:2:1$ at 604.4 nm [22]. One can see that the intensity pattern and line positions of the three lines observed at 633 nm excitation are similar to those reported. Moreover, in some of our spectra a fourth intense line at about 14750 cm^{-1} could be seen (lower trace in Fig. 1). This line corresponds to the NO_3 14748 cm^{-1} emission which is about 3 times less intense than the 14057 cm^{-1} line [21]. Other weaker lines ($\approx 10\%$ of 14057 cm^{-1} line intensity [21]) were not apparent in our low-resolution spectra. Since no other nitrogen compound or any conceivable impurity possesses strong fluorescence at this spectral range with the pattern shown in Fig. 1 we can unambiguously assign it to fluorescence of the NO_3 radical.

Fig. 2 shows the decaying part of the difference between the total fluorescence signal (excited with both the He–Ne laser and the dye laser) and the NO_2 fluorescence decay excited with only the pulsed dye laser. The difference signal was in fact biexponential consisting of a sharp rise and a much longer tail. The magnitude of the signal depended linearly on the pumping laser power. The rise time of the signal was coincident to within 10%–20% with the lifetime of

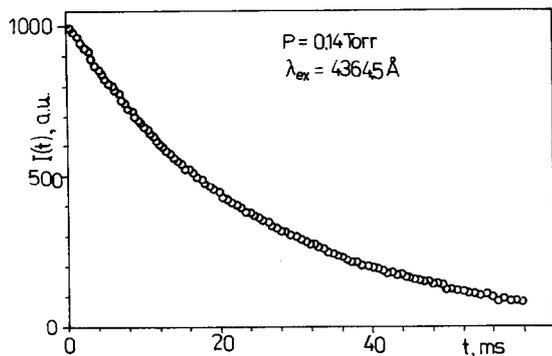


Fig. 2. A typical decay of NO_3 LIF signal at 0.14 Torr.

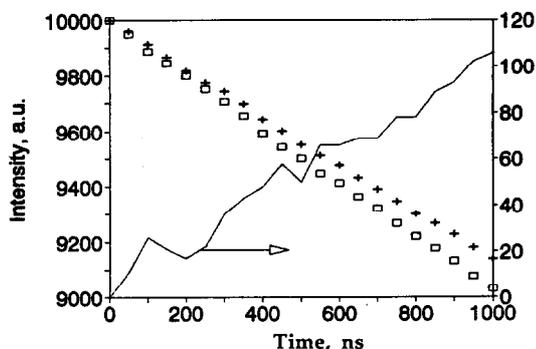


Fig. 3. Rising part of NO_3 LIF signal at 0.14 Torr. (\square) Fluorescence; (+) LIF + fluorescence; (—) LIF.

the NO_2 fluorescence recorded under the same conditions and was much shorter than the characteristic time of the decay (denoted hereafter by τ_{ph}). An example of the rising part of the NO_3 fluorescence is shown in Fig. 3. Note the worse signal-to-noise ratio due to the strong background of NO_2 fluorescence.

Fig. 4 shows how $(\tau_{\text{ph}})^{-1}$ changes with NO_2 pressure (P). The dependence shown is a second-order polynomial with $C_2 = 2.0 \times 10^3 \text{ Torr}^{-2} \text{ s}^{-1}$. Small additions of NO substantially reduced the magnitude of τ_{ph} . The linear dependence of $(\tau_{\text{ph}})^{-1}$ on the partial pressure of added NO (P_{NO}) at $P = 2.7$ Torr is also shown in Fig. 4.

4. Discussion

We advance the following arguments in favor of the statement that the difference in fluorescence signals recorded with and without a probing laser corresponds to the LIF of NO_3 radical excited by a He–Ne

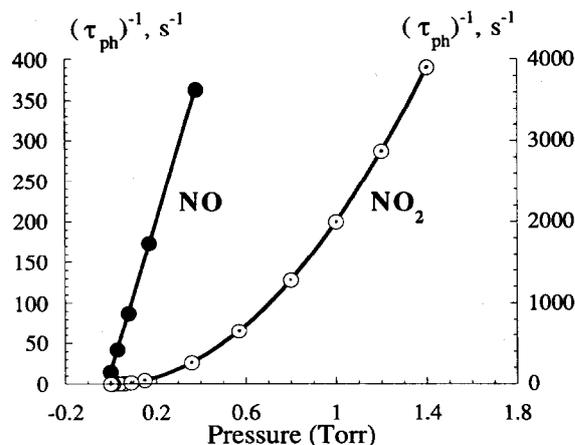


Fig. 4. (a) Filled circles, left Y axes: NO_3 fluorescence decay rate in mixture of NO and NO_2 versus pressure of added NO (X axis). Pressure of nitrogen dioxide is fixed at 2.7 Torr. (b) Dotted circles, right Y axes: NO_3 fluorescence decay rate in pure gaseous NO_2 versus pressure of NO_2 (X axes). No admixture of NO .

laser. Firstly, peaks attributable to the fluorescence of NO_3 appeared in the luminescence spectrum (Fig. 1) only when the He–Ne laser was on. This indicates that the NO_3 emission was not a chemiluminescence of some kind but rather that it must have been excited by the He–Ne laser. Secondly, the intensity of these peaks in the spectrum decreased substantially when a small amount of NO was added to the mixture. The time of decay of the NO_3 fluorescence dropped as well. This can be explained by the known fact that nitrogen oxide reacts with NO_3 to produce NO_2 with gas-kinetic speed. Thirdly, estimations show that the He–Ne laser is capable of producing $> 10^6$ photons per dye-laser pulse under our experimental conditions if we assume that reaction pathway (2) exists and is $\approx 10^3$ – 10^4 less efficient than the NO_2 fluorescence self-quenching in collisions (as recommended in ref. [17]). The estimation is based on the facts that: (a) the absorption cross section for NO_3 at 632.82 nm is as high as $\approx 3 \times 10^{-18} \text{ cm}^2$ since the He–Ne laser emission falls within a strong quasi-continuous absorption band of NO_3 which peaks at ≈ 624 nm [23], (b) the yield of the NO_3 fluorescence at 632.82 nm excitation is close to unity [24], (c) the He–Ne laser does not excite NO_2 fluorescence (no continuous background). Thus, the observation of NO_3 must be relatively straightforward and we be-

lieve that the difference signal is in fact NO_3 fluorescence.

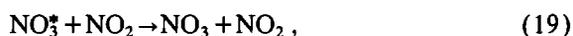
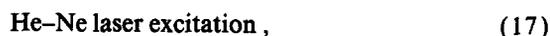
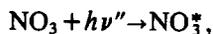
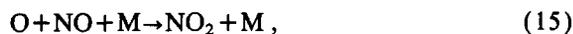
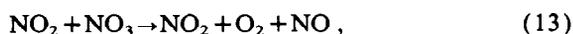
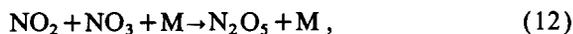
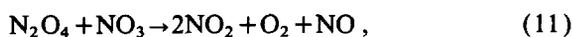
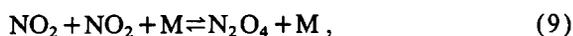
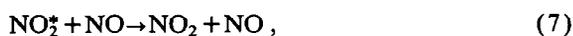
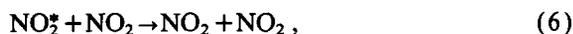
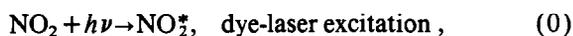
Since NO_3 fluorescence rises synchronously with the decay of the NO_2 fluorescence it is natural to think that electronically excited nitrogen dioxide NO_2^* is a precursor of NO_3 . There are two feasible reaction pathways from NO_2^* to NO_3 . The first (i) assumes that reaction (2) occurs with non-zero probability. The second (ii) comprises of the three-body association of O with NO_2 , the two-photon dissociation of NO_2 with the dye laser being the source of oxygen atoms,



Besides, the molecule of NO_2 may be excited internally prior to the optical excitation so that the NO_2^* formed can undergo first-order or second-order fragmentation, though the probability of that at 436.45 nm excitation and at room temperature is vanishing,



In order to assist in distinguishing mechanisms (i) and (iia, iib, iic) a kinetic analysis must be done. Other important processes that can take place in the given system are



The physical quenching of the fluorescence of NO_2^* and NO_3^* by N_2O_4 is thought to be as efficient as that by NO_2 so the NO_2 in reactions (6) and (19) must be assumed to be in both monomer and dimer forms. We assume that the partial pressures of stable molecules such as NO_2 (P), NO (P_{NO}) (if it was deliberately added to the mixture) do not change appreciably with time because under our experimental conditions less than 1% of NO_2 is initially excited. Consequently, the partial pressures of N_2O_4 (P_2) and M ($P_{\text{M}} = P_{\text{NO}} + P + P_2$) may be considered to be constant as well. Then the solution of the kinetic equations for reactions (0)–(20) is straightforward. The time-dependent fluorescence of NO_2^* excited with a He-Ne laser for mechanism (i) can be written as

$$I_{\text{LIF}} = k_{17} \frac{k_2 P C_0}{A - D} \left(\frac{1}{A - E} [\exp(-At) - \exp(-Et)] + \frac{1}{E - D} [\exp(-Dt) - \exp(-Et)] \right). \quad (21)$$

The solution for mechanism (iia) has exactly the same form but parameter A in (21) and (22) (see below) is replaced by parameter B throughout and the product $k_2 P C_0$ is replaced by $k_4 P P_{\text{M}} C'_0$. Here A , B , D , E are effective rate constants for the decay of, respectively, NO_2^* , O, NO_3 and NO_3^* , C_0 and C'_0 are the partial pressures of NO_2^* and O at $t=0$,

$$A = k_5 + k_6(P + P_2) + k_7 P_{\text{NO}} + \text{minor terms}, \quad (22)$$

$$B = k_4 P P_{\text{M}} + k_{14} P + k_{15} P_{\text{NO}} P_{\text{M}}, \quad (23)$$

$$D = k_8 P_{\text{NO}} + (k_{10} + k_{11}) P_2 + k_{12} P P_{\text{M}} + k_{13} P + k_{16}, \quad (24)$$

$$E = k_{18} + k_{19}(P + P_2) + k_{20} P_{\text{NO}}. \quad (25)$$

Mechanisms (iib) and (iic) have 6-exponential solutions which contain the same exponential factors. Now, with expressions (21)–(25) at hand we can decide which of the mechanisms can better account for our experimental results. The strongest argument

against mechanism (iia) may be advanced on the basis of the power-dependence of the yield of the NO_3 fluorescence which should be quadratic in that case since the oxygen atoms are prepared in a two-photon process. No square or polynomial dependence of the NO_3 yield on pump laser power was observed; therefore, we believe that the formation of the oxygen atom in reaction (3a) is not important at our excitation wavelength. Further evidence comes from measurements of the risetime of the NO_3 fluorescence. The evaluation of Eqs. (22)–(25) with rate constants taken from refs. [20,22,25,26] showed that (21) can be approximated by a biexponential solution for a broad range of pressures. The biexponential solution corresponds to a simplified steady-state treatment for the NO_3^* species which gives values A^{-1} for mechanism (i) and B^{-1} for mechanisms (iia)–(iic) for the rise time of the NO_3 fluorescence. The experiment showed that, within our experimental precision, the rise time was equal to the lifetime of the NO_2 fluorescence $\tau_{\text{rise}} = (A^{-1})$ in the 10^{-3} – 10^1 pressure range. Since the A/B ratio changes from about 3 at 1 Torr to 10^2 at 10^{-3} Torr ($P_{\text{NO}} = 0$), i.e. A^{-1} is not of the same order of magnitude as B^{-1} , τ_{rise} is hardly equal to B^{-1} . This suggests that mechanism (i) must be operative. The evidence is not entirely conclusive, however, because the difference between A^{-1} and B^{-1} is not really great and may be affected by uncertainties in the values of accepted rate constants.

At times $t > A^{-1}$ the fluorescence of NO_3 must be essentially monoexponential and proportional to $\exp(-Dt)$, and parameter D should be equal to the experimentally determined $(\tau_{\text{ph}})^{-1}$ whatever the mechanism. From expression (24) one can see that at a fixed pressure of NO_2 $(\tau_{\text{ph}})^{-1}$ should depend linearly on the pressure of NO . A least-squares fit of this dependence provides us with $k_8 = (3.0 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ which is in good agreement with the recommended value of $2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [20]. In pure NO_2 vapour ($P_{\text{M}} = P + P_2$) the decay rate parameter $(\tau_{\text{ph}})^{-1}$ should be polynomial in the pressure of NO_2 . Since the equilibrium constant K_9 is as small as $8 \times 10^{-3} \text{ Torr}^{-1}$ the relative abundance of the dimer at pressures below 1 Torr is less than 1% of that of the monomer. Therefore, we can approximate P_{M} by P and P_2 by $P^2 K_9$, and simplify (24) by

$$D \approx P^2 [(k_{10} + k_{11})K_9 + k_{12}] + k_{13}P + k_{16}. \quad (26)$$

Fitting this expression to the experimental points at $P < 1$ Torr allows one to obtain numerical values for $(k_{10} + k_{11})K_9 + k_{12} = (1.8 \pm 0.2) \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ and for $k_{13} = (3.0 \pm 0.6) \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. The rate constant k_{13} agrees with a recently measured value of $7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ [20] to within an order of magnitude. The author of ref. [26] has tabulated the value of k_{12} as $1.5 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$. The processes in reactions (10) and (11) have not been studied experimentally yet but if we compare k_{12} from ref. [26] with the value of $(k_{10} + k_{11})K_9 + k_{12}$ obtained in our work we can see that $(k_{10} + k_{11})K_9$ must be small. This gives an upper limit for $k_{10} + k_{11}$ equal to $\approx 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. As a result we have derived from our consideration three kinetic rate constants k_8 , k_{12} and k_{13} which agree satisfactorily with known values. This fact supports our proposition about the formation of NO_3 under our experimental conditions. From the zeroth-order term in (24) it was possible to estimate crudely an upper limit for the efficiency of quenching of NO_3 on the surface of the walls as 10^{-5} . Thus NO_3 surface decay was not significant in our case.

5. Conclusions

The fluorescence of NO_3 radical which was formed after the irradiation of pure NO_2 vapour at 436.45 nm was temporally resolved. Spectroscopic analysis and rate constants derived from the fluorescence decay rate confirmed the identity of a fluorescence carrier. Further examination of the time profile and power-dependence of the fluorescence gave evidence that NO_3 is a product of the photoinitiated reaction (2).

References

- [1] W. Schneider, G.K. Moortgat, G.S. Tyndall and J.P. Burrows, *J. Photochem. Photobiol. A* 40 (1987) 195.
- [2] J.C.D. Brand, W.H. Chan and J.L. Hardwick, *J. Mol. Spectry.* 56 (1975) 309.
- [3] N. Sugimoto, *J. Mol. Spectry.* 106 (1984) 307.
- [4] J.C.D. Brand and P.H. Chiu, *J. Mol. Spectry.* 75 (1979) 1.
- [5] H.S. Johnston and R. Graham, *Can. J. Chem.* 52 (1974) 1415.
- [6] N. Sugimoto, S. Takezawa and N. Takeuchi, *J. Mol. Spectry.* 102 (1983) 372.

- [7] R.G. Dickinson and W.P. Baxter, *J. Am. Chem. Soc.* 50 (1928) 774.
- [8] R.G.W. Norrish, *J. Chem. Soc.* (1929) 1158, 1611.
- [9] H.H. Holmes and F. Daniels, *J. Am. Chem. Soc.* 56 (1934) 630.
- [10] H.W. Ford and S. Jaffe, *J. Chem. Phys.* 38 (1963) 2935.
- [11] J.N. Pitts, J.H. Sharp and S.J. Chan, *J. Chem. Phys.* 40 (1964) 3655.
- [12] F.E. Blacet, T.C. Hall and P.A. Leighton, *J. Am. Chem. Soc.* 84 (1962) 4011.
- [13] I.T.N. Jones and K.D. Bayes, *J. Chem. Phys.* 59 (1973) 4836.
- [14] V.I. Makarov, *Intern. J. Chem. Kinetics* 22 (1990) 1.
- [15] A.B. Harker, W. Ho and J.J. Ratto, *Chem. Phys. Letters* 50 (1977) 394.
- [16] C.L. Creel and J. Ross, *J. Chem. Phys.* 64 (1976) 3560.
- [17] S.M. Kostikov, V.P. Balahnin, V.P. Bulatov and O.M. Sarkisov, *Khim. Phys.* 3 (1984) 234 (in Russian).
- [18] F.M. Rappoport and A.A. Ilijinskaya, *Methods of synthesis of pure gases* (Goschimizdat, Moscow, 1963) p. 193 (in Russian).
- [19] M.W. Malko and J. Troe, *Intern. J. Chem. Kinetics* 14 (1982) 399.
- [20] R.P. Wayne, I. Barnes, P. Biggs, J.P. Burrows, C.E. Canosa-Mas, J. Hjorth, G. Le Bras, G.K. Moortgat, D. Perner, G. Poulet, G. Restelli and H. Sidebottom, *The nitrite radical: physics, chemistry and the atmosphere (Special Issue)*, *Atm. Environ.* 25 A (1991) 1.
- [21] H.H. Nelson, L. Pasternack and J.R. McDonald, *J. Phys. Chem.* 87 (1983) 1286.
- [22] T. Ishiwata, I. Fujiwara, Y. Nagure, K. Obi and I. Tanaka, *J. Phys. Chem.* 87 (1983) 1349.
- [23] J.P. Burrows, G.S. Tyndall and G.K. Moortgat, *J. Phys. Chem.* 89 (1985) 4848.
- [24] J.J. Orlando, G.S. Tyndall, G.K. Moortgat and J.G. Calvert, *J. Phys. Chem.* 97 (1993) 10996.
- [25] S.A. Nizkorodov, V.I. Makarov, I.V. Khmelinskii, S.A. Kotschubei and K.N. Amosov, *Chem. Phys. Letters* 215 (1993) 662.
- [26] W.B. Demore, J.J. Margitan, M.J. Molina, R.T. Watson, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard and A.R. Ravishankara, *Chemical kinetics and photochemical data for use in stratospheric modeling*, JPL Publication (1987).