Short Communication

Quenching rate constant for $O(^1S)+NO$*

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The quenching of $O(^1S)$ by NO has been investigated. The rate constant is found to be $(5.7 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} at 291 K and $(5.0 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} at 201 K, in good agreement with previous measurements. The half-quenching density is $(2.3 \pm 0.3) \times 10^9$ molecule cm^{-3}, which suggests that NO is the dominant quencher in NO-rich auroral forms.

Introduction

The concentration of NO in the unperturbed atmosphere (Barth[1,2], Meira[3], Norton and Barth[4], Pearce[5], and Strobel[6]) is too low to be of any importance in $O(^1S)$ quenching. However, recent rocket-borne mass-spectrometric measurements (Zipf, Borst and Donahue[7] of the composition of neutrals in aurorae have indicated that large amounts of NO can be present in some auroral forms at altitudes of 100 to about 130 km (Shemansky, Zipf and Donahue[8]). NO was found to be the second most abundant constituent in these events. If the quenching rate constants previously measured are correct (Table 1) (Black *et al.*[9] and Filseth *et al.*[10] the lifetime of $O(^1S)$ in bright aurorae would be largely determined by NO, rather than by O or O_2. Because of the importance in aurorae we have reinvestigated the $O(^1S)$–NO quenching. As the mean atmospheric temperature

TABLE 1

$O(^1S)+NO$ QUENCHING RATE CONSTANTS

$k_{NO} \times 10^{10}$ (cm^3 molecule^{-1} sec^{-1})	Temperature	Ref.
5.5	Room temp.	9
8.0	Room temp.	10
5.7 ± 0.6	291 ± 1 K	This work
5.0 ± 0.6	201 ± 1 K	This work

at those altitudes is well below room temperature, measurements have been made at 201 K as well as at 291 K.

Experimental

As in previous experiments in this laboratory[10-12], $O(^1S)$ atoms were generated by the pulsed vacuum ultra-violet photolysis of CO_2 and the $O(^1S)$ concentration was measured as a function of time after the flash by observation of the $^1S \rightarrow {}^1D$ emission at 5577 Å. Rate constants were derived directly from the decay of the 5577 Å emission. Diffusive removal of $O(^1S)$ atoms out of the fluorescence viewing zone of the reaction vessel was of no concern because of the fast decays observed. A buffer gas (Ar or N_2) was nevertheless added in order to ensure isothermal conditions. Signals were measured by pulse counting and accumulated by a multichannel scaler with a time resolution of 20 μsec channel width. Decay curves covered at least 3 half-lifetimes of $O(^1S)$.

Quenching by transient photolysis products (*e.g.* O, N, CO) from CO_2 and NO was certainly negligible because of the very low flash energy used ($\sim$1 joule/discharge) and also the large efficiency of NO itself. Calibrated mixtures of (1.08 $\pm$ 0.02)% CO_2 in Ar and (0.0096 $\pm$ 0.0002)% NO in N_2 were used. The certified purities were $\geqslant$99.998%, except for NO which was $\geqslant$99.0%. The gases were passed through cooled traps ($-78°$C and $-160°$C) and Linde molecular sieve type 3A traps before entering the reaction vessel.

Results

Quenching by Ar and N_2 was found to be negligible in comparison to that by CO_2 and NO at the pressures and temperatures used, in agreement with previous work[12]. The decay of the $O(^1S)$ concentration is therefore given by

$$\frac{S_0}{S} = \exp\{[A + k_{CO_2}(T)\{CO_2\} + K_{NO}(T)\{NO\}](t-t_0)\} \tag{1}$$

where S_0 and S are the signals of the 5577 Å emission at times t_0 and t, respectively. The radiative decay rate, $A = 1.31 \pm 0.05$ sec^{-1} (Corney and Williams[13]), could be neglected in all cases as the collisional deactivation rates were orders of magnitude faster. $k_{CO_2}(T)$ and $k_{NO}(T)$ are the deactivation rate constants at temperature T and $\{CO_2\}$, $\{NO\}$ are the concentrations of CO_2 and NO, respectively.

Exponential decay of the signal was observed in all experiments. Rate constants, $k_{NO}(T)$, were thus derived according to eqn. (1) from the slopes of plots of the decay rate, defined as $R = (t-t_0)^{-1} \ln S_0/S$, against the NO concentration at constant CO_2 concentration. Figure 1 shows plots of R against the NO concentration for the two temperatures, 291 and 201 K. The intercepts at zero NO concentration correspond to the CO_2 quenching rates at the two temperatures.
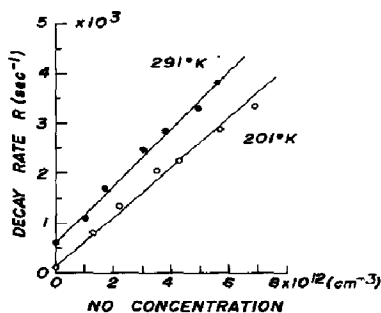
Fig. 1. Decay rate of the 5577 Å intensity *versus* NO concentration at constant CO_2 concentrations at 291 K and 201 K.

The absence of NO fluorescence was established by flashing NO alone, in which case no signal was observed. Also, no chmiluminescence of NO_2, produced by O + NO recombination, was detected. The NO_2 chemiluminescence has been previously observed in the flash photolysis of NO (Stuhl and Niki[14]); however, in the latter experiments NO pressures were orders of magnitude higher than in the present experiments.

The values of k_{NO} (T) derived from the slopes of the plots in Fig. 1 are $(5.7 \pm 0.6) \times 10^{-10}$ cm³ molecule⁻¹ sec⁻¹ at 291 ± 1 K and $(5.0 \pm 0.6) \times 10^{-10}$ cm³ molecule⁻¹ sec⁻¹ at 201 ± 1 K, in good agreement with the previous measurements (Table 1). The indicated error limits include the least square standard deviations of the slopes of Fig. 1 as well as the estimated accuracy limits of the measurements of other parameters such as pressure and NO concentration. The activation energy is zero within the experimental errors. The NO quenching efficiency corresponds to a half-quenching number density for NO of $(2.3 \pm 0.3) \times 10^9$ molecule cm⁻³ at 291 K.

The half quenching number density is that concentration of NO which leads to quenching and radiative loss of O(1S) being equal. That is, k_{NO} [NO]$^{\frac{1}{2}}$ = A. This suggests that NO will be the main quenching gas for O(^{1}S) at altitudes up to about 130 km in those NO-rich auroral forms previously reported. For the concentrations of NO in the model atmosphere of the auroral form given by Shemansky, Zipf and Donahue[8], for instance, the effective O(^{1}S) lifetime at an altitude of 100 km would be reduced by a factor of about 400 in comparison to the NO-free atmosphere. Even at 130 km the reduction amounts to a factor of about 4.3.

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