Short Communication

Temperature-dependent $N_2(A^3\Sigma^+_u)$ quenching rate coefficients

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In this note, we report results of measurements of the temperature-dependence of certain N_2 ($A^3\Sigma^+_u$) reactions. Except for electronic energy transfer with Hg, NO and CO, little is known about the products of N_2 (A) quenching reactions, and it is hoped that these new data may eventually be of some value in indicating the types of interactions taking place.

We have found that a convenient way of generating N_2 (A) is to photolyze N_2O at 1470 Å or shorter wavelengths[1]. At 1470 Å, the quantum yield is $\sim 8\%$. The N_2 (A) molecules are detected by the chemiluminescence following NO addition:

$$N_2 (A^3\Sigma^+_u) + NO \rightarrow N_2 + NO (A^2\Sigma^!) \tag{1}$$
$$\downarrow$$
$$NO + h\nu \; [NO (\gamma) \text{ bands}]$$
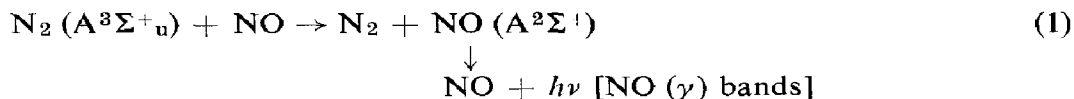
An EMI 9558Q photomultiplier tube in combination with a 200 Å FWHM interference filter centered at 2540 Å was used to detect the NO (γ) radiation. The 1 s lifetime of the N_2 (A $\rightarrow$ X) transition precludes direct observation of N_2(A) in this system.

N_2(A) is generated periodically by pulsing the exciting 1470 Å lamp, and the decay of the NO(γ)-band signal while the lamp is off gives a measure of the N_2(A) loss rate in the reaction cell. The resulting increase in signal decay rate following addition of quenching gases then establishes a quenching coefficient for the added gas. The technique and apparatus have been thoroughly described in earlier publications[2-5]. All measurements were made in the presence of 1.6×10^{14} cm^{-3} N_2O, 1.6×10^{13} cm^{-3} NO, and 1.6×10^{17} cm^{-3} Ar as a buffer gas.

Of the six quenching gases studied, perhaps the most important is O_2, as its interactions with N_2(A) may be of importance both in flames and in the upper atmosphere. Figure 1 shows a plot of decay time constant *vs.* [O_2] for different temperatures; the slopes of these lines are the rate coefficients. Figure 2 shows Arrhenius plots ($\log_{10} k$ vs. T^{-1}) for all the gases measured. The signals are strong and there is little scatter in the data over the temperature range measured

(240–370 K). Table 1 presents the activation energy, the $\log_{10}$ of the pre-exponential factors, and the 300 K rate coefficients for the six reactions. The error limits are based on an assigned error range of $\pm 10\%$ for each decay time-constant measurement. The hard sphere collision frequency corresponds approximately to a rate coefficient of $\log_{10} k = -9.5$ (cm^3 molecule^{-1} s^{-1}), so that for the reactants less active at 300 K (H_2, CH_4, C_2H_6) reaction proceeds with a probability of 0.4–0.8 once the activation barrier is crossed, whereas for the more active reactants (O_2, CO, N_2O) the reaction probability is only 0.02–0.13, although the activation barrier is lower.

$N_2(A)$ has an excitation energy of 6.2 eV, and is thus capable of dissociating all of the molecules investigated except CO, but, as mentioned above, the only known products of $N_2(A)$ interaction are represented by reaction (1), with NO, and the analogous reactions[6] with CO and Hg. The relatively low pre-exponential factors for O_2 and N_2O may be an indication that the interaction involves bond dissociation, and that the $N_2(A)$ must approach along the internuclear axis of the target molecule to transfer its energy into bond vibration.

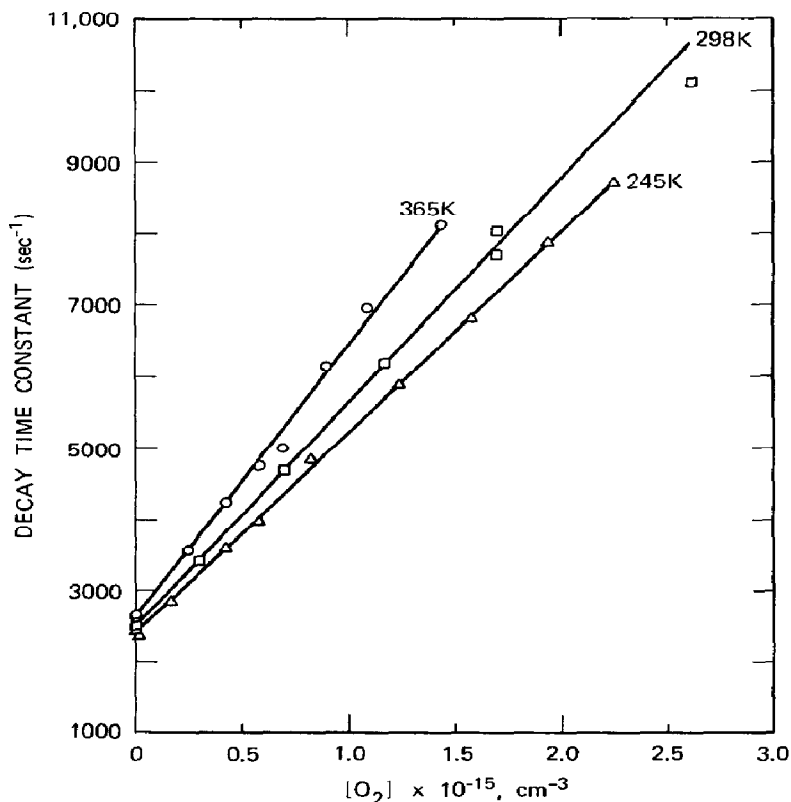Fig. 1. Decay time constant vs. $[O_2]$. $[N_2O] = 1.6 \times 10^{14}$ cm^{-3}; $[NO] = 1.6 \times 10^{13}$ cm^{-3}; $[Ar] = 1.6 \times 10^{17}$ cm^{-3}.
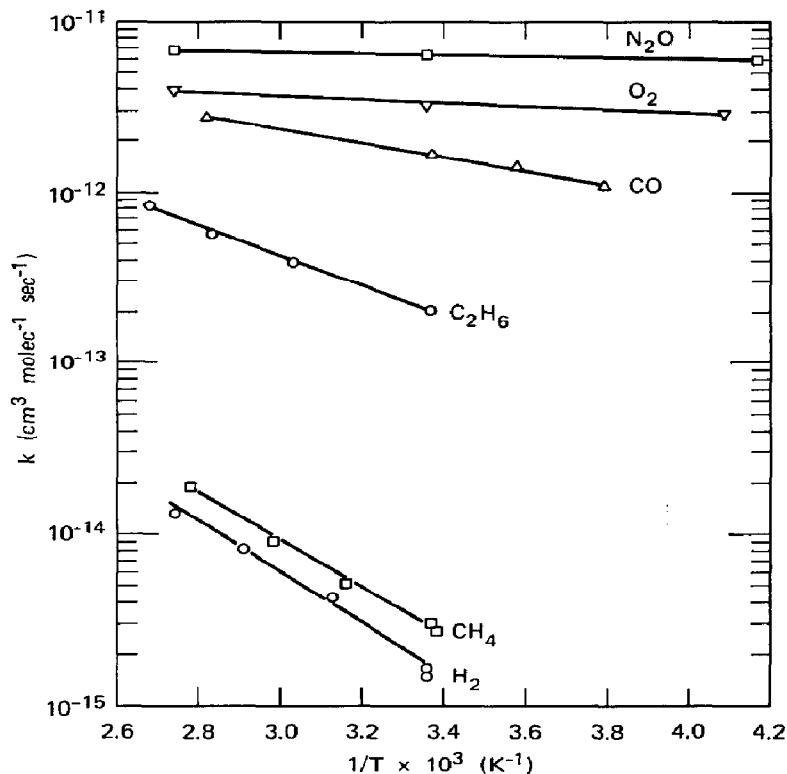
Fig. 2. $\log_{10} k$ vs. T^{-1}.

TABLE 1

ARRHENIUS PARAMETERS

Quencher	E_A (kcal/mol)	$\log A$ (cm^3 molecule^{-1} s^{-1})	k_{300} (cm^3 molecule^{-1} s^{-1})
H$_2$	6.97 ± 0.58	$- 9.66 \pm 0.40$	1.9×10^{-15}
CH$_4$	6.30 ± 0.60	$- 9.90 \pm 0.41$	3.2×10^{-15}
C$_2$H$_6$	3.94 ± 0.57	$- 9.79 \pm 0.39$	2.2×10^{-13}
CO	1.87 ± 0.40	$- 10.41 \pm 0.30$	1.7×10^{-12}
O$_2$	0.47 ± 0.32	$- 11.14 \pm 0.23$	3.3×10^{-12}
N$_2$O	0.24 ± 0.29	$- 11.03 \pm 0.21$	6.4×10^{-12}

The 300 K values given in Table 1 agree well with the data of Callear and Wood[7], the largest discrepancy being a factor of two for CH$_4$. It should be noted that the large activation energies for the ineffective quenchers indicate that it is the molecule in question, and not an impurity that is responsible for the quenching. Since reagent grade gases were used, an impurity would have to be present at levels less than 0.1%, and thus for the H$_2$ case, would need to have a 300 K rate coeffi-

TABLE 2

300 K QUENCHING RATE COEFFICIENTS FOR NH_3 (cm^3 molecule^{-1}s^{-1})

Investigators	Rate coefficient
Young, Black and Slanger[2]	1.8×10^{-10}
Callear and Wood[7]	$<2 \times 10^{-11}$
Meyer, Klosterboer and Setser[8]	1.6×10^{-10}
This work	1.3×10^{-10}

cient greater than 10^{-12} cm^3 molecule^{-1} s^{-1}. This would be incompatible with a 7 kcal/mol activation energy.

From the current data on N_2 (A) reaction rates, there is one distinct discrepancy, the values for NH_3. The rate coefficient given by Callear and Wood is a factor of ten or more lower than those of Young et al. [2] and Meyer et al. [8]. We thus repeated the NH_3 measurement, and it confirmed our previous values. Table 2 summarizes the data for N_2 (A) quenching by NH_3.

It should also be mentioned that the results of Setser and coworkers[8,9] for the three faster quenchers discussed in this note, O_2, N_2O, and CO are all higher by a factor of two to three than our results or those of Callear and Wood. Agreement is good for those species that have quenching coefficients faster than 5×10^{-11} cm^3 molecule^{-1} s^{-1}, and the slow ones could not be measured in the experiments of Meyer et al. [8]. The possibility thus exists that there is a systematic effect causing these deviations for quenching molecules that are "inefficient" in their apparatus ($k = 10^{-12} - 10^{-11}$ cm^3 molecule^{-1} s^{-1}).

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