

Rate constants for deactivation of $N_2(A)v' = 0, 1$ by O_2

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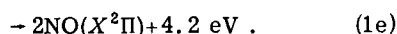
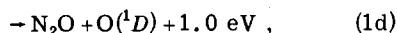
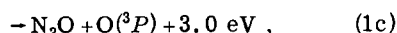
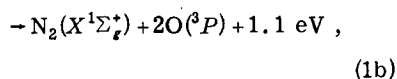
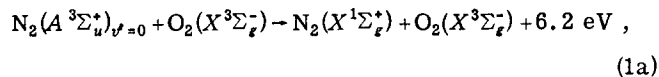
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The removal of $N_2(A^3\Sigma_u^+, v' = 0, 1)$ by O_2 has been studied in a room temperature discharge-flow apparatus by monitoring the temporal decay of the 0,6 and 1,10 bands of the Vegard-Kaplan system. Rate constants for the reaction with O_2 are (2.3 ± 0.4) and $(4.1 \pm 0.7) \times 10^{-12}$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for $v' = 0$ and 1, respectively. The rate constant measured for $v' = 0$ is about 35% lower than commonly accepted values for the rate constant for quenching $N_2(A)$ by O_2 . This discrepancy is shown to result from the fact that most other studies used a tracer to monitor the $N_2(A)$ number density. The rate of decay of the tracer reflects both the decay of the $v' = 0$ and $v' = 1$ levels of $N_2(A)$ and its value is midway between the decay rates of the individual vibrational levels.

I. INTRODUCTION

It has been suggested that the reactions of $N_2(A^3\Sigma_u^+)$ with atomic and molecular oxygen could be significant sources of odd nitrogen and vibrationally excited NO in the upper atmosphere.¹ For the interaction between $N_2(A)$ and molecular oxygen a number of possible exoergic reaction channels may be proposed:



Since O_2 is the main deactivator of $N_2(A^3\Sigma_u^+)$ in the atmosphere below 100 km,¹ significant amounts of atmospheric N_2O could be formed via Reactions (1c) and (1d), with possible vibrational excitation of the product. Further reactions of N_2O with $N(^2D)$ and $O(^1D)$ can lead to the formation of NO.¹ Direct formation of NO via Reaction (1e) is expected to be extremely slow due to the dynamic constraints which inhibit such four-center exchange reactions.

Previous measurements of the room-temperature rate constants for this reaction vary between 1.9 and 7.6×10^{-12} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (Table I). Because most previous measurements were made using a tracer, and were therefore not state specific, some of this scatter probably results in the variation in deactivation rate constant with vibrational level.

Meyer *et al.*² have observed that oxygen atoms are a major product from Reaction (1), but did not put their observations upon a quantitative basis. Very recent experiments by Zipf¹² have indicated that about 60% of Reaction (1) proceeds through channels (1c) and (1d) to make N_2O .

During the course of a program to study product formation in Reaction (1), we remeasured the rate con-

stant for this reaction for both vibrational levels 0 and 1. Our result for $k_1(v' = 0)$ of 2.3×10^{-12} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ is about 35% lower than the commonly accepted value of 3.5×10^{-12} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. We will show that most other measurements were non-state specific tracer measurements which measured an effective deactivation rate constant for a mixture of vibrational levels. Our results further show that vibrational level 1 is quenched by molecular oxygen almost twice as fast as vibrational level 0. Thus, the tracer measurements give a rate constant midway between those for $v' = 1$ and $v' = 0$, the magnitude being dependent upon the relative ratio $[N_2(A)_{v'=1}] / [N_2(A)_{v'=0}]$.

II. EXPERIMENTAL

A. Apparatus

The experiments were performed in a discharge-flow apparatus with the $N_2(A)$ number densities being monitored by spectroscopic observations of individual vibrational bands of the Vegard-Kaplan ($N_2A^3\Sigma_u^+ - X^1\Sigma_g^+$) system of nitrogen. The reactor (see Fig. 1) is a 2 in. diameter quartz tube which is pumped by a Roots blower that is capable of producing linear velocities up to 8×10^3 cm s^{-1} at pressures of 1 Torr. A 0.5 m monochromator (Minuteman) is mounted upon a set of rails parallel to the flow tube. Spectral observations of the luminous gases in the flow tube may therefore be made as a function of linear distance along the tube by sliding the monochromator up and down on its rails. Distances are converted to reaction times by dividing by the flow velocity. Light intensities are measured photoelectrically using a thermoelectrically cooled EMI 9558QA photomultiplier and an SSR 1105 photon-counting rate meter.

The metastable nitrogen molecules are produced in the reaction between metastable $Ar(^3P_{0,2})$ and molecular nitrogen.^{13,14} This transfer results in the production of nearly equal populations of the $C^3\Pi_u$ and $B^3\Pi_g$ states of N_2 ¹⁵ which quickly cascade radiatively to the metastable $A^3\Sigma_u^+$ state. A hollow-cathode discharge source was built to produce the argon metastables. While most experimenters have used tantalum for the electrodes,^{14,16} we found 0.005 in. thick aluminum shim

TABLE I. Rate constants for reactions of $N_2(A \ ^3\Sigma_u^+)$ $v=0, 1$ with O and O_2 .^a

k_{O_2}	k_O	Comments	Reference
6.0	22	Hg (6^3P_1) tracer k_O from $k_O/k_{O_2} = 3-4$ and listed number for k_{O_2} claim $k_{v=1}/k_{v=0} \approx 1.3$	2
2.9 ($v=0$)	15	Claimed $k_{v=1} = k_{v=0}$ Looked at VK 0, 6 and 1, 5 with interference filters Probably some interference from NO γ bands	4
3.8		NO γ -band tracer	6
3.3		NO γ -band tracer	7
3.7		Hg (6^3P_1) tracer Claim $k_{v=1} = k_{v=0}$	8
6.5		Hg (6^3P_1) tracer	9
7.6		Hg (6^3P_1) tracer—this value was measured relative to $k_{N_2(A)+N} = 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	10
1.9 ($v=0$)		Measured $N_2(A)$ with absorption on nitrogen	3
7.6 ($v=1$)		1^+ system	
3.5		Broad band filter—"mostly $v=0$ "—could have been contaminated with NO γ bands	11
4.5 ($v=0$)		$v=0$ and $v=1$ with monochromator—could have large uncertainty in reaction time	
5.1 ($v=1$)			
2.3 ± 0.4 ($v=0$)		Direct observation of Vegard-Kaplan emission in discharge-flow reactor	Present results
4.1 ± 0.7 ($v=1$)			

^aThe listed rate constants are for $T = 300 \text{ K}$. They are in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

made an excellent electrode material. The shim was rolled into a cylinder whose diameter was the same as the inside diameter of the glass tubing through which the gas flowed (13 mm). The cathode (the downstream electrode) is 40 mm long, the anode 15 mm long, and the two electrodes are separated by 45 mm. The discharge is operated in the dc mode with the anode biased at +210 V. A load resistor of 10 k Ω gives the discharge stability and limits the current; the current in the present experiments is about 3 mA. The argon was puri-

fied by flowing it through a trap filled with a 5 Å molecular sieve and cooled with dry ice. Since the experiments involved metastable nitrogen, it was not necessary to remove the nitrogen impurity from the argon carrier.

The metastables may be detected by the appearance of the characteristic reddish-violet flame which obtains upon the addition of nitrogen downstream from the discharge. At the concentrations of N_2 at the point of addition ($\approx 10^{15} \text{ molecules cm}^{-3}$) the flame length is about

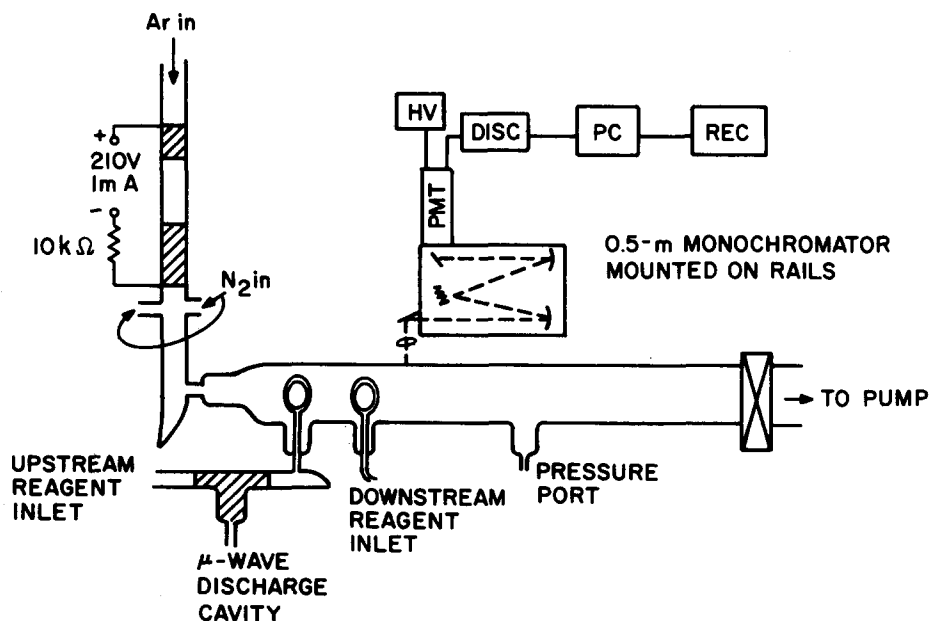


FIG. 1. Schematic of discharge-flow apparatus used in studies of $N_2(A)_{v=0,1}$ with O_2 .

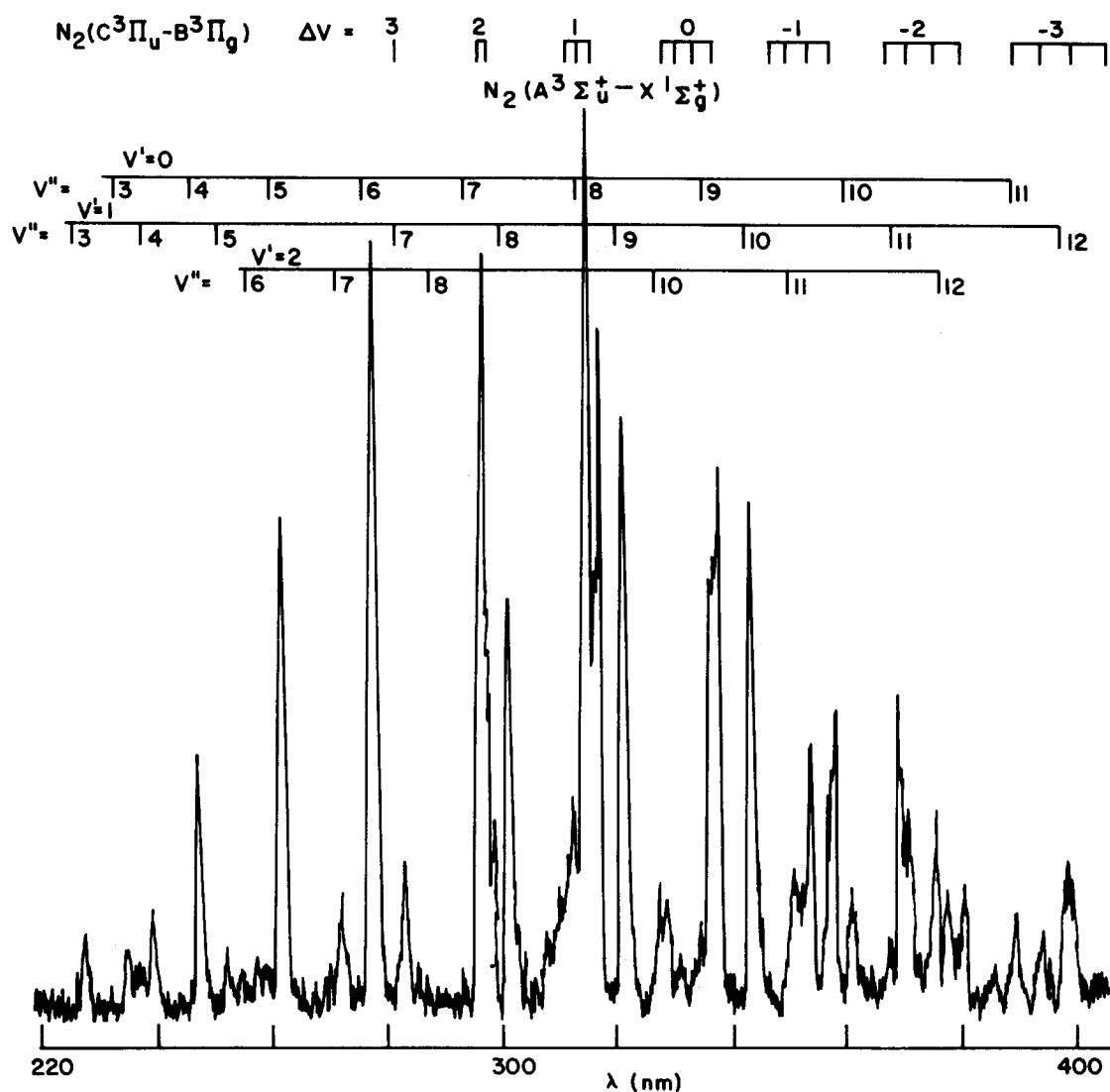


FIG. 2. Spectrum of Vegard-Kaplan bands emitted in discharge-flow reactor about 20 ms downstream from the discharge. $P = 2.08$ Torr, $\Delta\lambda = 0.66$ nm.

2 cm. This length is just governed by diffusional mixing of the two streams of gas, since at these nitrogen concentrations the collisional quenching times for nitrogen on argon are on the order of tens of microseconds.¹⁷ Typically, the argon flow rate is $\approx 1500 \mu\text{mol s}^{-1}$, the nitrogen flow rate $\approx 250 \mu\text{mol s}^{-1}$, and the flow-tube pressure about 1.5 Torr. Typical flow velocities ranged from 1100–1500 cm s^{-1} . These were obtained by throttling the Roots blower, or by shutting the blower off and using only the forepump on the flow tube.

A typical spectrum of the Vegard-Kaplan bands emanating from the flow tube is shown in Fig. 2. The spectrum shows that the first three vibrational levels of $N_2(A)$ are populated in our system with relative populations of approximately 100 : 50 : 10 for $v' = 0, 1,$ and 2, respectively. This is in contrast to the relative populations reported by Stedman and Setser of 100 : 95 : 10 for the same three levels, respectively.^{13,14} We performed some experiments which showed that the ratio $N_{v'=1}/N_{v'=0}$ increases under conditions of higher total pressure and higher mole fractions of nitrogen in the flow,

and when the nitrogen inlet is separated from the Ar metastable discharge by a Wood's horn light trap. These general conditions obtained in the work of Stedman and Setser, and for the most part did not in the present experiments. In particular, the intervention of a light trap between the hollow cathode discharge and the nitrogen addition point enhances the ratio $N_{v'=1}/N_{v'=0}$ by more than a factor of 2.

Molecular oxygen was introduced into the reactor through a 1 in. diameter loop injector fabricated from 2 mm o.d. polyethylene tubing. The flow of molecular oxygen ($1-5 \mu\text{mol s}^{-1}$) was mixed with a substantial flow of helium ($\approx 100 \mu\text{mol s}^{-1}$) prior to injection into the flow tube. The helium flow gave greater injection velocity and thus better mixing than was the case when the O_2 was injected with no helium carrier. This point was checked visually using the O/NO afterglow as a mixing diagnostic. Any effects to the kinetic measurements from small perturbations to the flow at the injection point were minimized by confining the measurement region to be 30–45 cm ($\approx 20-30$ ms) downstream

of the injector. The molecular oxygen was purified by pumping on liquid O_2 prior to expanding the middle portion of the liquid O_2 into a 5 l storage bulb.

Argon and nitrogen flow rates were measured using mass-flow meters (Teledyne Hastings-Raydist) whose calibrations were checked with a wet test meter. The flow rate of helium through the injector was measured with a rotameter which had also been calibrated against a wet test meter. Molecular oxygen flow rates were measured by timing the pressure increase into a calibrated volume. Flow tube pressures were measured using an MKS Baratron®.

B. Experimental technique

The two important processes leading to deactivation of the $N_2(A)$ in our reactor are Reaction (1) and diffusion to the reactor walls with subsequent deactivation at the walls. Quenching by Ar,¹⁸ N_2 ,¹⁸ and He¹⁹ in the reactor is entirely negligible. The differential equation describing the rate of change in metastable nitrogen number density with time is

$$d[N_2(A)]/dt = -(k_w + k_1[O_2])[N_2(A)] \quad (2)$$

Under pseudo-first-order conditions ($[N_2(A)] \ll [O_2]$) its solution is

$$\ln\{[N_2(A)]/[N_2(A)]_0\} = -(k_w + k_1[O_2])z/\bar{v} = K(z/\bar{v}), \quad (3)$$

where k_w is the first-order wall deactivation rate, z the distance down the flow tube, and \bar{v} is the bulk flow velocity. The wall deactivation rate constant k_w is inversely proportional to pressure, but is independent of molecular oxygen number density. Equation (3) provides us with two options for making the measurements: movable detector measurements or fixed-point determinations. In the movable detector measurements, $[O_2]$ and the total pressure are fixed and the pseudo-first-order decay rate K is measured by noting the change in $\ln[N_2(A)]$ as a function of z . Then the rate constant k_1 is given by a number of such pseudo-first-order decay rate measurements at fixed total pressure, but varying oxygen number density:

$$dK/d[O_2] = k_1 \quad (4)$$

In the fixed-point measurements, the mixing distance is fixed and the decay in $\ln[N_2(A)]$ is measured as a function of $[O_2]$. This gives a decay constant

$$\Gamma = d \ln[N_2(A)]/d[O_2] = k_1 z/\bar{v} \quad (5)$$

Because of problems with finite mixing time, it is best to make such measurements for several different mixing distances. Then on a plot of Γ vs z the rate constant is determined from the slope and the virtual point of mixing is obtained from the intercept on the abscissa.

The rate constants obtained from the above analysis assume a plug flow model. They must be increased by a factor of 1.6 to account for fluid dynamic effects in the reactor (see below).

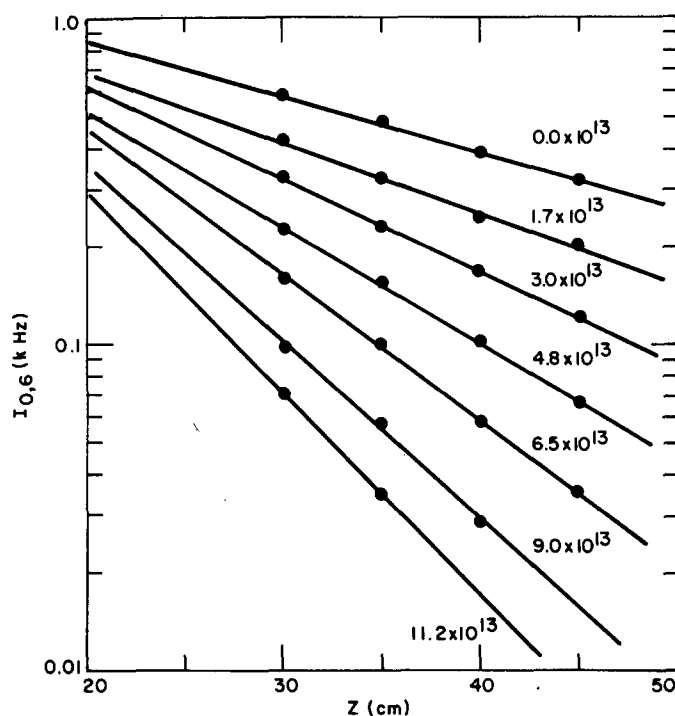


FIG. 3. The decay of $N_2(A)_{v=0}$ as a function of mixing distance and of $[O_2]$. The numbers by each line correspond to different $[O_2]$. $P=1.33$ Torr, $\bar{v}=1540$ cm s⁻¹, and $z_0 \approx 10$ cm.

C. Flow analysis

In our apparatus there is essentially unit probability of $N_2(A)$ deactivation in collisions with the reactor walls. Thus, a radial gradient in $N_2(A)$ number density is set up in the flow tube, and this radial gradient, when coupled with a parabolic velocity profile resulting from laminar flow within the flow tube, affects the analysis of the rate constant measurements. The proper fluid dynamic analysis of this situation has been considered exhaustively in the literature.²⁰⁻²⁷ In the ideal case, the parabolic velocity profile is fully developed, and the rate constants determined under the assumption of plug flow conditions must be multiplied by a factor of 1.6 to give the true rate constant. The time required for the development of a parabolic velocity profile in the reactor is usually translated into a traversal distance $z=0.227aR$, where z is the distance from the inlet of the tube, a is the tube radius, and R is the Reynolds number of the flow. In our experiments R ranges from 35-55 and typical entry lengths vary from 20-32 cm. All our measurements were done 30-45 cm downstream of the reagent inlet, thus ensuring that the flow was fully developed even if there was some perturbation to the flow from reagent addition. Thus, all our reported rate constants have been increased from the plug-flow values by a factor of 1.6. Possible corrections for the effects of axial diffusion, slip, and axial velocity gradients are entirely negligible under our conditions.¹⁹ Inlet effects are accounted for by our having made the measurements at a number of positions along the flow tube.

III. RESULTS

Figures 3 and 4 illustrate the movable detector method for the rate constant measurements, while Figs. 5 and

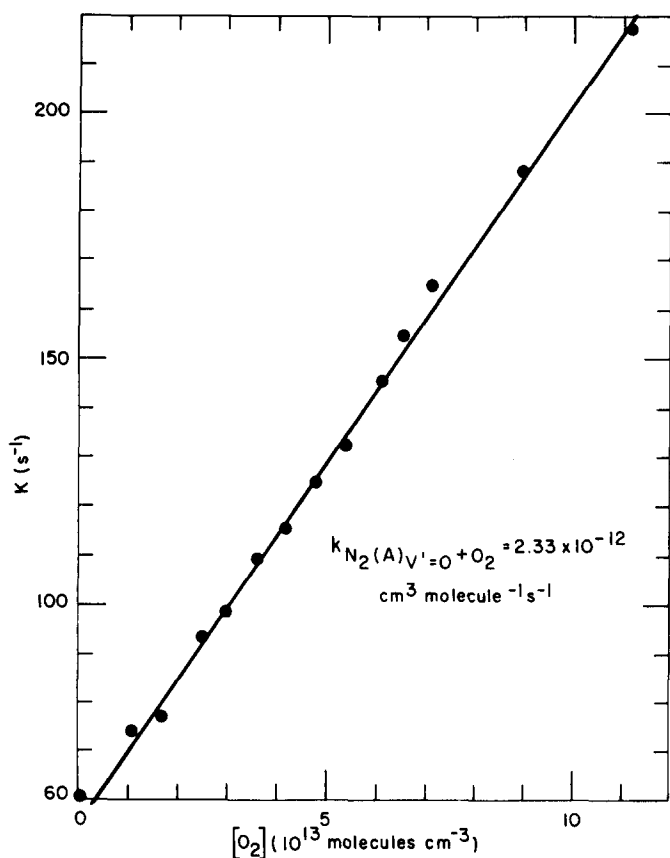


FIG. 4. $N_2(A)_{v'=0}$ decay rates as a function of $[O_2]$. $P=1.33$ Torr.

6 illustrate the fixed point technique. In both sets of measurements, the $v'=0$ level was monitored using the 0, 6 Vegard-Kaplan band. Five such measurements in all gave $k_1(v'=0) = (2.31 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

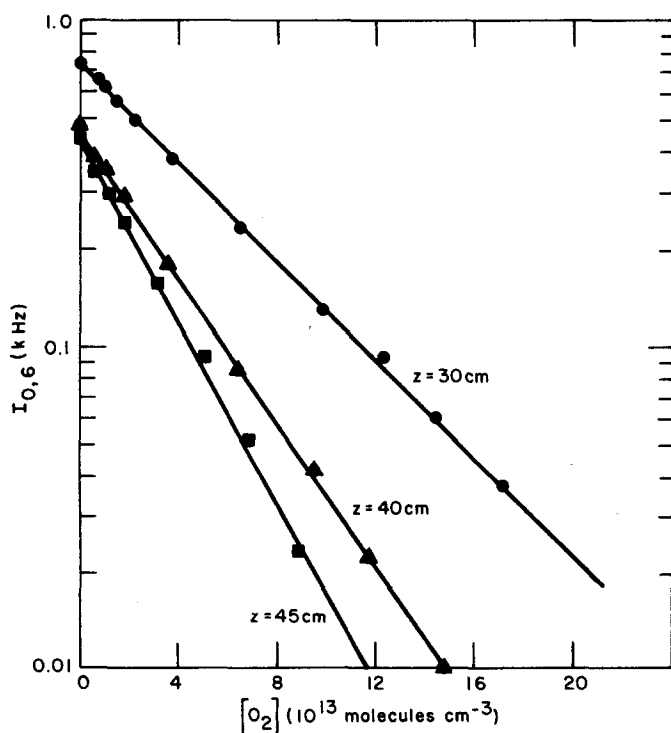


FIG. 5. Decay of $N_2(A)_{v'=0}$ as a function of $[O_2]$ for several different mixing distances. $P=1.44$ Torr, $\bar{v}=1330 \text{ cm s}^{-1}$.

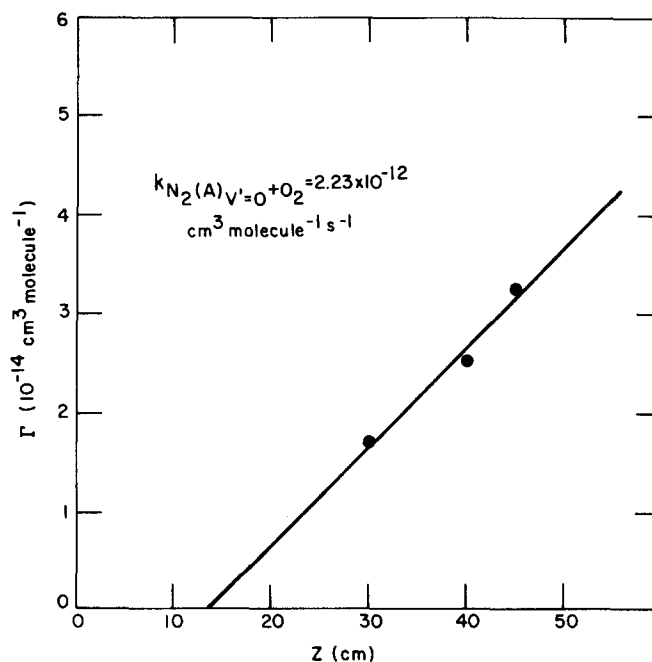


FIG. 6. Decay constants for $N_2(A)_{v'=0}$ removal by O_2 as a function of mixing distance. $P=1.44$ Torr, $\bar{v}=1330 \text{ cm s}^{-1}$.

where the uncertainty given is one standard deviation from the mean of the five sets of measurements.

Figure 7 shows the fixed-point decays of the $v'=0$ and $v'=1$ levels under the same conditions of mixing time and total pressure. Nine such measurements indicated that $k_1(v'=1)/k_1(v'=0) = 1.79 \pm 0.09$, where again the un-

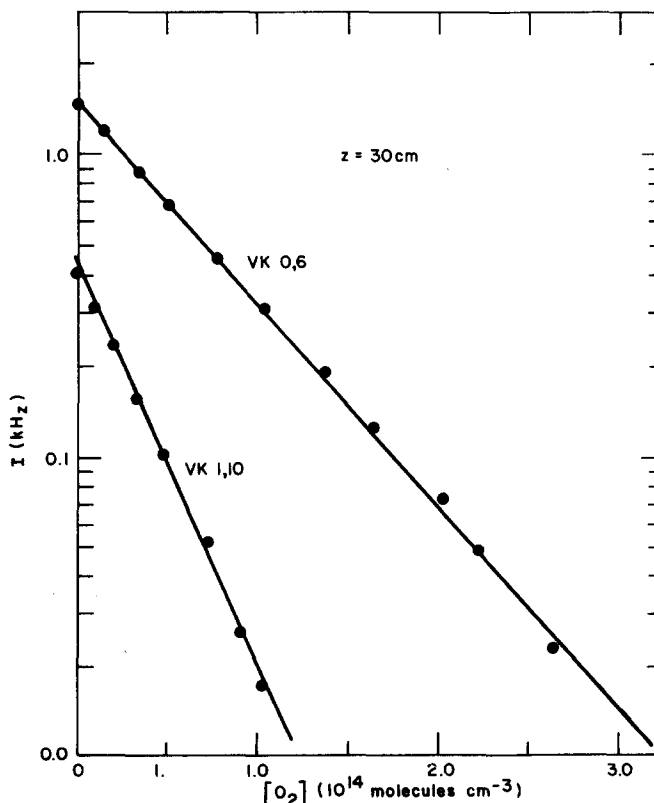


FIG. 7. The decay of $N_2(A)_{v'=0}$ and $v=1$ as a function of $[O_2]$ for a mixing distance of 30 cm. $P=1.52$ Torr, $\bar{v}=3271 \text{ cm s}^{-1}$.

certainty is one standard deviation from the mean. Given the result for $k_1(v'=0)$ above, we get that $k_1(v'=1)$ is $(4.14 \pm 0.32) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The total uncertainty (rms) including uncertainties in the experimental parameters, i.e., temperature, pressure, flow rate, etc., as well as the statistical variation in the measurements is 16% for the $v'=0$ measurements and 18% for the $v'=1$ measurements.

IV. DISCUSSION

Table I shows that our values are substantially in disagreement with most other measurements in the literature; although our values for the rate constants for $v'=0$ and $v'=1$ deactivation bracket the other values reported. Most of the other experimenters used either NO γ -band or Hg 6^3P_1 tracers and therefore made non-state-specific measurements, although Dunn and Young⁴ and Clark and Setser¹¹ used interference filters to isolate spectral lines or portions of the spectrum, and Dreyer, Perner, and Roy³ used an absorption diagnostic to monitor the $N_2(A)$ number density.

The use of interference filters can be misleading in the $N_2(A)$ system because the strong possibility of NO contamination in the system can lead to NO γ -band signals within the bandpass of the interference filter which can be much stronger than the signal from the $N_2(A)$ being monitored. The NO γ bands are very strongly excited in the energy-transfer reaction between $N_2(A)$ and NO.¹¹ In our system, even with a 1.7 nm bandpass, signals from the NO γ 0, 4 and 0, 5 bands at NO number densi-

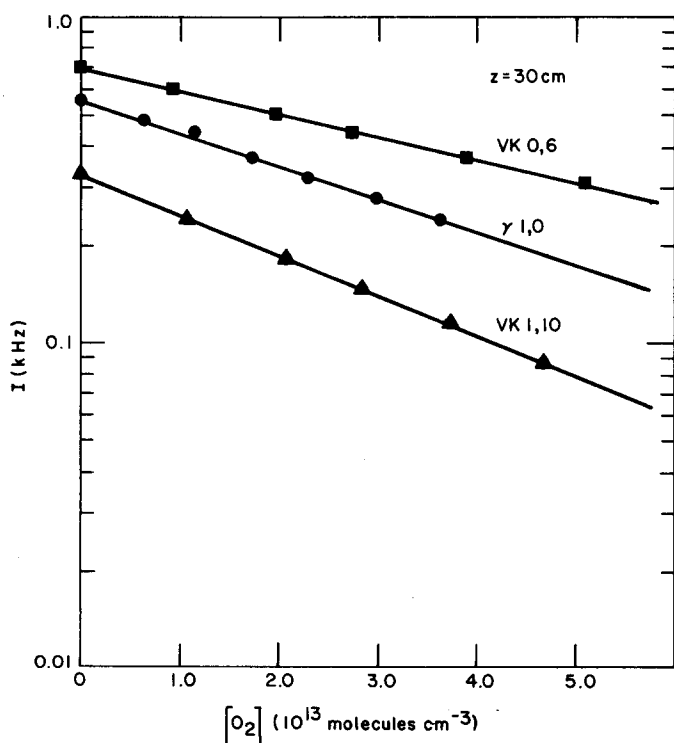


FIG. 8. Fixed-point decay of $N_2(A)$ as a function of $[O_2]$ for $v=0$, $v=1$ and a combination of vibrational levels using the NO γ 1, 0 band as a tracer. $P=1.30$ Torr, $\bar{v}=1714 \text{ cm s}^{-1}$, $[NO] \leq 5 \times 10^{10} \text{ molecules cm}^{-3}$.

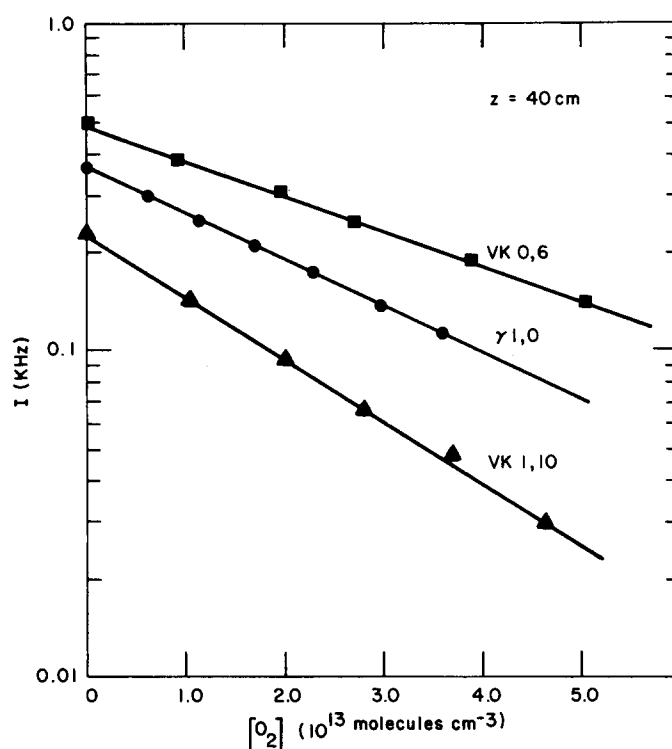


FIG. 9. Fixed-point decay of $N_2(A)$ as a function of $[O_2]$ for $v=0$, $v=1$ and a combination of both vibrational levels using the NO γ 1, 0 band as a tracer. $P=1.30$ Torr, $\bar{v}=1714 \text{ cm s}^{-1}$, $[NO] \leq 5 \times 10^{10} \text{ molecules cm}^{-3}$.

ties on the order of $10^{10} \text{ molecules cm}^{-3}$ significantly perturb the effective peak intensity of the Vegard-Kaplan 0, 6 band situated between them. The obliteration of the 1, 5 band of the Vegard-Kaplan system by the 0, 2 and 0, 3 γ bands is almost complete at such low number densities of NO. It is probably impossible in discharge-excited mixtures of N_2 and O_2 to avoid formation of significant amounts of NO. In our system, even very small leaks in the argon line, or sometimes slightly less pure gases, will give significant γ -band contamination of the Vegard-Kaplan spectrum even though the gas handling system appears to be tight. In this case small traces of air are converted to NO in the metastable argon discharge. We therefore feel that the experiments of Dunn and Young⁴ in which mixtures of N_2 and O_2 were discharged to make the $N_2(A)$ were almost certainly in fact tracer measurements.

A strong possibility also exists that the major experiments of Clark and Setser¹¹ were also tracer experiments because they could not spectrally scan the region they were monitoring to ensure that they had adequate gas purity. Clark and Setser do report two direct measurements in which the 0, 6 and 1, 9 Vegard-Kaplan bands were monitored directly as a function of molecular oxygen number density. These determinations, however, were done using the fixed observation point technique but only at one injector-to-observation region distance, so that the data could be seriously affected by a large mixing-length correction.

In balance we feel that all previous measurements of the rate constant for deactivation of $N_2(A)$ by O_2 could be

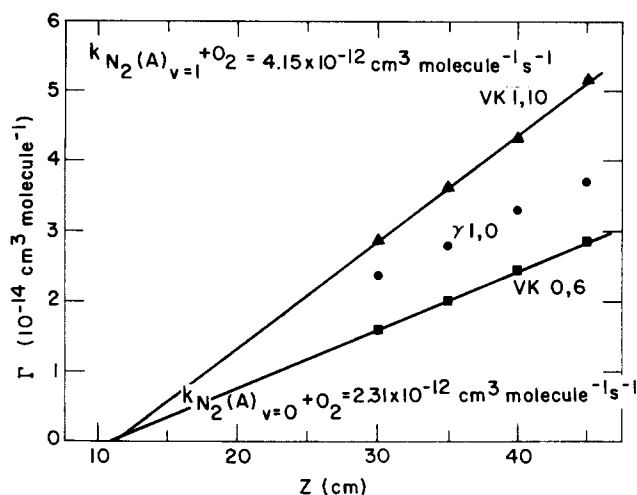


FIG. 10. Decay constants for $N_2(A)$ removal by O_2 as a function of reaction distance for $v=1$ and a mixture of vibrational levels using the NO γ 1, 0 band as a tracer. $P=1.30$ Torr, $\bar{v}=1714$ $cm\ s^{-1}$, $[NO] \leq 5 \times 10^{10}$ molecules cm^{-3} .

seriously affected by the use of a tracer or by NO impurities, which would act to make the measurements in effect tracer measurements. The one exception is the measurement of Dreyer *et al.*,³ who used an absorption diagnostic. Our results agree with Dreyer *et al.* for $v'=0$, but they obtained a value for $v'=1$ a factor of 2 larger than ours. In general, rather larger deviations from the Beer-Lambert law can occur in absorption systems which use discharge lamps as the source of radiation,²⁸ and such deviations can affect strongly the analysis used to extract rate constants. Dreyer *et al.* do not discuss corrections to their lamp diagnostic. Our measurements are direct and contain no such complications in the analysis.

We designed an experiment to test the effects of using a tracer to follow $N_2(A)$ decay. We measured the decay of the 0,6 and 1,10 Vegard-Kaplan bands as a function of molecular oxygen number density, and under identical conditions, the decay of the 1,0 γ band of NO when a small trace of NO was added to the reactor. The number density of NO added to the reactor was $\leq 5 \times 10^{10}$ molecules cm^{-3} , sufficient to give a strong tracer signal, but sufficiently small that NO quenching of $N_2(A)$ had little effect on the overall kinetics.

Two fixed-point decay plots are shown in Figs. 8 and 9. It is obvious from the plots that the $N_2(A)$ decay rate as monitored by the γ -band tracer is intermediate between the decays shown for the individual $N_2(A)$ vibrational levels. Figure 10 shows how the fixed-point decay constants vary with mixing distance. The γ -band-monitored decay constants are midway between the $v'=0$ and $v'=1$ decay constants, and at longer mixing times the tracer measurements approach more closely the decay of the $v'=0$ level.

Our system is not optimum for demonstrating the tracer effect because our kinetic observations are made far down stream of the point of mixing (our effective reaction times vary from 11 to 20 ms) and our initial $[N_2(A)]_{v=0}/[N_2(A)]_{v=1}$ was 1.74, which implies that only

about 35% of the total $N_2(A)$ number density was in the $v'=1$ state. In contrast to this, Callear and Wood⁸ and Young *et al.*,⁶ indicate that roughly two thirds of their initial $N_2(A)$ number density is in $v'=1$ while Setser's group^{2,5,9,11} has nearly equal number densities of the two states. Our tracer decay constants at the two shortest reaction times imply an $N_2(A)$ deactivation rate constant by O_2 of 3.3×10^{-12} cm^3 molecule $^{-1}$ s $^{-1}$ using the mixing correction determined from the VK 0,6 and 1,10 measurements.

V. SUMMARY

We have determined the rate constants for the deactivation of $N_2(A\ ^3\Sigma_u^+)$ $v'=0$ and 1 to be (2.3 ± 0.4) and $(4.1 \pm 0.7) \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$, respectively. Our rate constants for the two vibrational levels bracket the rate constants reported by most previous experimenters who used non-state-specific tracer techniques. The recent experimental observations of Zipf¹² of $k_{v'=0} = 1.9 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$ and $k_{v'=1} = 4.0 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$ are in excellent agreement with our own measurements.

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