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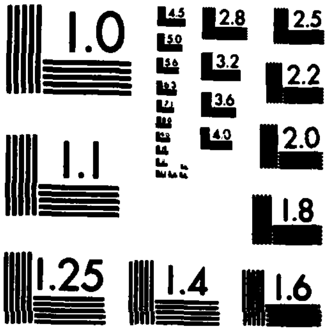

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CHEMICAL REACTIONS, RADIATIVE AND ENERGY TRANSFER PROCESSES OF IMPORTANT ATMOSPHERIC SPECIES

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NO_2 fluorescence and radiative lifetime; $N(^2D, ^2P)$ reaction with O_2; $N_2(A)$ detection and reaction with O_2; $N_2(A) + O_2$ product channels, N_2O- and O-yield; $N_2(A)$ vibrational relaxation by CH_4 and CF_4; Vibrational energy dependence of $N_2(A,v)$ relaxation and reaction with O_2.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Laser excited NO_2 fluorescence was measured as function of time, pressure, fluorescence wavelength, and temperature. Rate constants were measured for the decay of banded and continuous emission features due to quenching by 13 added gases. A general mechanism for the radiative and collisional processes was established. The rate constants of the $N(^2D$ and $^2P) + O_2$ reactions at 298 K were measured by vacuum u.v. resonance fluorescence and found to be 5.3×10^{-12} and 3.5×10^{-12} $cm^3\ s^{-1}$, respectively. The reaction rate constant of $N_2(A,v=0-2)$ with O_2 was measured by laser induced fluorescence of $N_2(A)$ in the first positive

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system and found to be 2.5, 3.9, and 4.1 x 10^{-12} cm^3 s^{-1}, respectively, at 298 K. The product channels of the reaction were found to be (2 ± 0.5)% N_2O, (65 ± 10)% O-atoms, and about 30% excited O_2. The stepwise, vibrational relaxation of $N_2(v=1-3)$ by CH_4 and CF_4 was measured and found to be 1.5, 3.1, and 5.0 x 10^{-12} cm^3 s^{-1} for CH_4 and 0.47, 1.8, and 5.5 x 10^{-12} cm^3 s^{-1} for CF_4. The $N_2(A,v=3)$ + O_2 rate constant was also measured and found to be 5.7 x 10^{-12} cm^3 s^{-1}.

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I. INTRODUCTION

The understanding and modeling of perturbed atmospheres requires a knowledge of production and removal processes of energetic species, both electrically charged and neutral, and including both "air" and extraneous molecules depending on the details of the perturbation. In the context of satellite surveillance problems and of the work under way in our laboratory, the emphasis is on neutral excited species whose importance arises in two contexts: (a) as precursors in ionization chemistry, and (b) as emitters or emitter-precursors of radiation in the infrared or visible, particularly in the short wavelength infrared from 2 to 6 μm. There, the important emitters are NO, CO, H_2O, CO_2, N_2O, and O_3, and the radiation involves vibrational excitation processes, either by collisional energy transfer or by chemical reactions that produce the emitter in non-thermal distributions such as the steps $N(^2D) + O_2 \rightarrow NO(v) + O$ or $N_2(A) + O \rightarrow NO(v) + N$. The characterization and modeling of the radiative processes then not only requires a knowledge of the rate parameters for the production steps but also for all major loss processes such as collisional energy transfer and chemical removal.

Furthermore, it is highly desirable to gain greater insight into the nature of these elementary processes and to link their experimental study with theoretical prediction at various levels of rigor and sophistication ranging from semi-empirical treatments based on thermochemical analogy to ab initio quantum theoretical calculations of potential energy surfaces and of the state-to-state dynamics. All too often large experimental efforts are expended to provide specific, needed parameters in narrowly defined contexts, without attention to broader issues. When needs or perceived conditions are then changed, it may turn out that little had been learned that allowed generalization or extrapolation. The research problem is thus two-fold: (1) to identify and measure important rate processes under controlled laboratory conditions; and (2) to add to our basic understanding in order to improve our predictive power, since it is often sufficient to be able to place approximate bounds on rate parameters to establish their importance in a particular process.

Our present, small research project (annual funding level of 40 to 43 k$) has contributed significantly to both aspects of this problem. It has been quite productive (16 publications since 1975, 8 since 1979), has provided rate parameters for some excited atomic, diatomic, and triatomic "air" species, and has shed light on the fundamental physical and chemical interactions. In the following sections, we will briefly review the scientific accomplishments under this contract, provide a list of its completed papers, and indicate what unfinished work remained at the time of its termination.

II. SCIENTIFIC ACCOMPLISHMENTS

At the beginning of this three-year contract in November 1980, we had just completed and written up the last part of our fluorescence lifetime studies of NO_2, i.e. Part IV. Temperature Dependence of Fluorescence Spectra and of Collisional Quenching of Fluorescence, J. Chem. Phys. 71, 569 (1979) and 73, 1514 (1980) in which we characterized and explained the origin of the banded and continuous spectral features of NO_2 fluorescence and measured its temperature dependence.

In a side issue, we reported flow tube measurements of the rate constants of the reactions of N(^{2}D, ^{2}P, and ^{4}S) with Cl_2 at 298 K, because the only available information had come from a crossed molecular beam experiment on arc-heated atomic nitrogen at 7000 to 15,000 K which could not distinguish between the three reaction channels. Our results, J. Am. Chem. Soc. 101, 4002 (1979), clearly showed the N(^{2}D) reaction to be fastest, $k = 3.6 \times 10^{-11}$ cm^3 s^{-1}, the N(^{2}P) reaction to be almost as fast, 2.2×10^{-11} cm^3 s^{-1}, and the ground-state N(^{4}S) reaction to be four orders of magnitude slower, $\sim 2 \times 10^{-15}$ cm^3 s^{-1}.

We also re-investigated the rates of the important reactions of N(^{2}D) and N(^{2}P) making use of resonance fluorescence near 149 and 174 nm to monitor the decay of the atomic metastables, J. Chem. Phys. 73, 4701 (1980). Rate constants of $(5.3 \pm 0.7) \times 10^{-12}$ cm^3 s^{-1} for N(^{2}D) + O_2 and $(3.5 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1} for N(^{2}P) + O_2 were measured at 300 K, more accurate than earlier published values. A rough estimate of about 1.8×10^{-12} cm^3 s^{-1} was also obtained for the N(^{2}D) + O(^{3}P) reaction rate constant, but that value may have been an upper limit.

The emphasis then changed from atomic to molecular nitrogen metastables, $N_2(A^3\Sigma_u^+)$ in its three lowest vibrational states, v = 0, 1, and 2. Laser-induced-fluorescence (LIF) detection of N_2(A) was added as a sensitive diagnostic technique using excitation at the P_1 bandheads of the $\Delta v = 4$ bands of the first positive system of N_2 at

618.7, 612.7, and 606.9 nm. The LIF emission was measured at longer wavelengths, mainly due to the Δv = 3 bands near 660 to 680 nm. $N_2(A)$ was generated as the ultimate product of the $Ar(^3P_{0,2})$ + N_2 reaction, mixed with variable amounts of O_2 and detected 6 to 7 ms downstream. Rate constants of $(2.5 \pm 0.4) \times 10^{-12}$, $(3.9 \pm 0.6) \times 10^{-12}$, and $(4.3 \pm 0.7) \times 10^{-12}$ $cm^3\ s^{-1}$ were measured for the reactions of $N_2(A)$, v = 0, 1, and 2, respectively, with O_2. The work was published in J. Phys. Chem. 85, 2163 (1981) and J. Photochem. 17, 397 (1981).

The important question of the product channels of this reaction was then considered, since Zipf had reported a large yield (60 ± 20)% of N_2O, a matter of great significance both for potential IR emission and for NO_x formation. The fast-flow apparatus was therefore modified to allow gas chromatographic (GC) analysis of N_2O in addition to vacuum u.v. resonance fluorescence (VUVRF) detection of $O(^3P)$ at the downstream end of the flow tube. The N_2O GC analysis consisted of filling a 12 liter glass bulb with product gas at flow tube pressure (2 Torr), cryopumping with liquid He into a stainless steel or quartz collection tube, and analyzing by electron capture GC using a carbosieve-S column. Following both static and dynamic calibration with known contributions of N_2O, the N_2O product yield was found to be (2 ± 0.5)% and the $O(^3P)$ yield (65 ± 10)%. The latter was based on the VUVRF signal from $Ar(^3P_{0,2})$ + O_2 which gives quantitative O_2 dissociation and on the assumption of quantitative formation of $N_2(A)$ in the $Ar(^3P_{0,2})$ + N_2 system. This work was published in Chem. Phys. Lett. 87, 570 (1982).

In the next phase of our studies, which has been completed, we examined the vibrational relaxation of $N_2(A)$ by collisions with quenchers such as CH_4 and CF_4 whose electronic quenching rates are known to be very slow. The experiments involve monitoring the $N_2(A)$ concentrations in v = 0, 1, 2, and 3 (the latter is observed by reducing the concentration of added N_2), while adding variable concentrations of CH_4 or CF_4. Stepwise vibrational relaxation is suggested by the curvature of $\ell n I_{LIF}$ vs. quencher concentration, [Q], plots for small [Q], because intermediate v-levels are fed by the faster relaxation from the next-higher v. For v = 0, there is an increase of concentration with increasing [Q], because electronic quenching is two to three orders of magnitude slower than vibrational relaxation. This system of successive pseudo-first-order relaxation steps is computer modeled to extract both the quenching rate constants and the initial relative populations in the different v-levels. The following results have been obtained: Quenching rate constants, $k^{Q}_{v,v-1}$ (10^{-12} cm^3 s^{-1}): $k^{CH_4}_{1,0}$ - 1.5; $k^{CH_4}_{2,1}$ - 3.1; $k^{CH_4}_{3,2}$ - 5.0; as well as $k^{CF_4}_{1,0}$ - 0.47; $k^{CF_4}_{2,1}$ - 1.8; and $k^{CF_4}_{3,2}$ - 5.5. The precision of these values is ±4 to 13%, and the accuracy about ±15 to 20%. This work was published in Chem. Phys. Letters <u>102</u>, 50 (1983).

III. LIST OF PUBLISHED PAPERS SINCE 1979

"Fluorescence Lifetime Studies of NO_2. III. Mechanism of Fluorescence Quenching," V. M. Donnelly, D. G. Keil, and F. Kaufman, J. Chem. Phys. 71, 569 (1979).

"Flow Tube Measurement of the Rate Constants of the $N(^2D, ^2P$, and $^4S) + Cl_2$ Reactions," M. P. Iannuzzi and F. Kaufman, J. Amer. Chem. Soc. 101, 4002 (1979).

"Fluorescence Lifetime Studies of NO_2. IV. Temperature Dependence of Fluorescence Spectra and of Collisional Quenching of Fluorescence," , D. G. Keil, V. M. Donnelly, and F. Kaufman, J. Chem. Phys. 73, 1514 (1980).

"Rates of Some Reactions of $N(^2D$ and $^2P)$ Near 300 K," M. P. Iannuzzi and F. Kaufman, J. Chem. Phys. 73, 4701 (1980).

"Rate Constants for the Reaction of $N_2(A^3\Sigma_u^+, v=0,1,2)$ with O_2," M. P. Iannuzzi and F. Kaufman, J. Phys. Chem. 85, 2163 (1981).

"Laser Studies of Atmospheric Reactions," F. Kaufman, J. Photochem. 17, 397 (1981).

"Product Channels of the $N_2(A^3\Sigma_u^+) + O_2$," M. P. Iannuzzi, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. 87, 570 (1982).

"Vibrational Relaxation of $N_2(A^3\Sigma_u^+)$ in v = 1, 2, and 3 by CH_4 and CF_4," J. M. Thomas, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. 102, 50 (1983).

IV. UNFINISHED WORK AT THE TIME OF TERMINATION OF THE CONTRACT

In connection with our work on vibrational relaxation of $N_2(A,v)$ by CH_4 and CF_4, we were able to produce measurable $N_2(A)$ concentrations in its v=3 state by reducing the N_2 fraction in the N_2 + Ar mixtures from 20% to 6%. With this extention to $N_2(A,v=3)$, we re-investigated the $N_2(A)$ + O_2 reaction rate in order to gather more information on its v-dependence. The experimental procedure was essentially unchanged, involved increasing O_2-additions at constant reaction times of 4.6 ms while monitoring the $N_2(A,v)$ concentration by LIF in the first positive system, A ← B, using excitation in the $\Delta v = 4$ band heads. For the sake of comparison, we also re-measured the v = 0, 1, and 2 rate constants of the $N_2(A)$ + O_2 interaction whose principal production channel had been *found to be O_2 dissociation.*

The following table shows the data and their comparison with earlier values. For v = 0, only a single experiment was run, whereas for v = 1, 2, and 3, five experiments were run for each v-level.

TABLE 1. QUENCHING/REACTION RATE CONSTANTS FOR $N_2(A, v \leq 3) + O_2$

	$k^v(10^{-12}\ cm^3\ s^{-1})$				
v =	0	1	2	3	Reference
	1.9	7.4	5.0	3.4	Dreyer et al.[1]
	1.9	4.0	---	---	Zipf[2]
	2.3	4.1	---	---	Piper et al.[3]
	2.5	3.9	4.2	---	Iannuzzi and Kaufman
	(3.0)	4.3	5.4	5.7	This work

The accuracy of k^v values is about 15-20%.

[1] J. Chem. Phys. 61, 3164 (1974); [2] Nature 287, 523 (1980); [3] J. Chem. Phys. 74, 2888 (1981); [4] J. Phys. Chem. 85, 2163 (1981).

The results indicate a slow, steady rise of k^v with increasing v and disagree with early findings of Dreyer et al. that there is a large peak at v = 1 and that $k^{v=3} < k^{v=2}$.

In another unfinished phase of our work, much preliminary work was done in preparation of a study of the $N_2(A,v) + O(^3P)$ reaction, e.g. producing large relative yields of $O(^3P)$ in O_2-Ar microwave discharges without concomitant production of NO, measuring O-atom concentrations by NO_2-titration and calibrating O + NO chemiluminescence intensity measurements, and characterizing interfering emission signals due to excited O_2 species.

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