Hz).³⁵ The ratio of the peak heights, N-Me/Xy-Me, is then compared with a calibration curve obtained for a series of standard solutions of varying $C_6H_5NHCH_3/C_6H_5NH_2$ concentrations containing constant amounts (6.0 μ L) of p-xylene and the concentration of anilide in the original PhNHK/PhNH₂ stock solution calculated.

Solubility of Deuterium in Aniline. This was determined by a gas chromatographic method^{36,37} and data are given in Table I, together with some values for H_2 for comparison.

Kinetics of Deuterium Exchange. The reaction vessel used in the kinetic studies has been described before.^{5,37} The side arms permitted connection of the flask to a vacuum pump and, by a septum and syringe needle, to a manometer and deuterium gas cylinder. The reaction vessel was evacuated and transferred to a drybox, and appropriate volumes of the PhNHK/PhNH₂ stock solution (1.0-4.0 mL) were introduced through the septum by a gas-tight syringe, followed by 25.0 mL of freshly distilled aniline.

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After mixing, 2.0 mL of the diluted PhNKH/PhNH₂ solution was withdrawn by syringe for determination of the anilide concentration. The reaction vessel was then cooled to 0 °C, degassed, and placed in the constant temperature bath. Following equilibration, D_2 was introduced to a pressure of 1 atm and stirring (500 rpm) started. Samples of gas (0.5 mL) were withdrawn periodically by the gas-tight syringe equipped with a 6-in. needle and two-way valve and analyzed as previously⁵ by using a Picker Nuclear MS10 mass spectrometer which was calibrated with a standard mixture of $D_2/HD/H_2$ before each run.

Rate constants for exchange were obtained by a computer curve-fitting method. A program was set up which gave a best fit between experimental values of mole % D2, HD, and H2 and theoretical values calculated by assuming two consecutive pseudo-first-order processes (eq 1).³⁷ The resulting vapor-phase rate constants were converted into in-solution first-order rate constants as previously⁵ by using the solubilities of D_2 in aniline.

Acknowledgment. Financial support of this research by the Atomic Energy of Canada Limited and the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. The authors also thank Drs. J. H. Rolston and E. A. Symons of AECL for their interest and for valuable discussions. Helpful comments by referees are also acknowledged.

Rate Coefficients for N(²D) Reactions

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We have measured rate coefficients for the reactions of $N(^2D)$ with O_2 , CO_2 , N_2O , CO, and H_2 in a discharge-flow reactor. The values are 4.6 \pm 0.5, 0.35 \pm 0.03, 2.2 \pm 0.3, 1.7 \pm 0.4, and 2.3 \pm 0.5 in units of 10⁻¹² cm³ molecule⁻¹ s⁻¹ for O₂, CO₂, N_2O , CO, and H_2 , respectively. A resonance-fluorescence diagnostic having an ultimate sensitivity of better than 1×10^8 atoms cm⁻³ monitors the number density of $N(^{2}D)$. The extreme sensitivity of the diagnostic allows kinetic measurements to be made in regions of the flow reactor far downstream from the source of the metastables. This feature removes fluid dynamic complications which plague most flow reactor studies of metastable kinetics. The diagnostic sensitivity also affords over two orders of magnitude in $N(^2D)$ number density decays, thereby ensuring the accurate determination of kinetic decay rates. A movable injector for the reactants allows measurements at a variety of reactions times, thereby eliminating uncertainties caused by imperfect mixing in the reactor.

Introduction

Metastable atomic nitrogen, $N(^{2}D, ^{2}P)$, plays an important role in the chemistry of the nonequilibrium upper atmosphere and of systems employing nitrogen or air discharge plasmas. $N(^{2}D)$, through its chemiluminescent reaction with molecular oxygen

$$N(^{2}D) + O_{2} \rightarrow NO(v) + O$$
(1)

controls the production of NO in the thermosphere and provides a key source of vibrationally excited NO (and perhaps electronically excited O) in electron-irradiated air.^{1,2} Similarly, quenching of $N(^{2}D)$ by other common atmosphere species such as CO_{2} , $N_{2}O_{3}$, CO, H_2 , or H_2O may proceed by chemical or energy-transfer reactions to form internally excited molecular products.

Several investigators³⁻⁸ have studied the quenching kinetics of $N(^{2}D)$ using either discharge-flow or flash photolysis techniques. Most of these studies employed relatively insensitive and errorprone techniques for detecting the commonly obtained, low concentrations of N(²D), viz. resonance absorption,^{4,5,8} electron-spin resonance (ESR) spectroscopy,⁶ and tracer fluorescence.⁷ Since

the maximum obtainable $N(^{2}D)$ number densities are typically only slightly above the detection limits of techniques such as resonance absorption or ESR, it is difficult to obtain the factor of 10 to 100 first-order $N(^{2}D)$ decays which are required not only for precise rate-coefficient determinations but also to rule out interference from secondary reactions. The limitation in dynamic range imposes additional uncertainties on the flow reactor studies,^{4,6,8} where the measurements must be made at fairly short flow distances under conditions of poorly characterized flow development. As a result, $N(^{2}D)$ quenching rate coefficients available in the literature still exhibit considerable disparity, often as much as a factor of 3.

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Figure 1. Apparatus for N^{*}(²D, ²P) studies.

The diagnostic technique of N(2D) atomic resonance fluorescence, first described briefly by Iannuzzi and Kaufman,3 provides the high sensitivity and correspondingly large dynamic range required to overcome the above difficulties. However, the use of this technique requires careful correction for spectroscopic interference from other species as well as considerable optimization of the light source and detection system. We describe here the use of N(²D) resonance fluorescence, coupled with proper delineation of fluid dynamic conditions in a discharge-flow reactor, to obtain unequivocal rate coefficients for quenching of $N(^{2}D)$ by several atmospherically important molecular species.

Experimental Section

Apparatus. The apparatus is a modification of one we have used previously in a number of other studies.⁹⁻¹³ It consists of a 2-in. flow tube pumped by a Leybold-Heraeus Roots blower/ forepump combination capable of producing linear velocities up to 5×10^3 cm s⁻¹ at pressures of 1 Torr. The flow-tube design is modular (see Figure 1), with separate source, reactions, and detection sections which clamp together with O-ring joints. The detection region is a reactangular stainless-steel block bored out internally to a 2-in. circular cross section and coated with Teflon (Dupont Poly TFE No. 852-201) to retard surface recombination of atoms.¹⁴ The surface was primed with black primer prior to the Teflon coating to reduce scattered light inside the block. Two sets of viewing positions consisting of circular ports on each of the four faces of the block are separated by a distance of 7.5 cm. The circular ports, all of which contain MgF2 windows, accommodate vacuum ultraviolet resonance lamps, vacuum-UV and visible monochromator interfaces, laser delivery side arms, and a spatially filtered photomultiplier/interference filter combination.

The upstream observation position is fitted with two microwave-discharge resonance lamps placed normal to each other, and a 0.2-m vacuum ultraviolet monochromator (Minuteman 302 VM) diametrically opposite one of the resonance lamps. The lamp which is viewed by the monochromator is used in absorption studies while the lamp normal to the monochromator's optical axis is used to excite resonance fluorescence of atomic species formed in the flow reactor. The lamps and the monochromator are separated from the flow tube by 25-mm-diameter MgF₂ windows which have a short-wavelength cutoff of 115 nm.

A schematic showing the resonance lamps and detection cell is given in Figure 2. The lamps are constructed from 13-mm (o.d.), medium-wall Pyrex tubing. He or Ar flow through each lamp at rates of ~150 μ mol s⁻¹ and total pressures of ~1.5 Torr. The discharge plasmas are excited by Evenson¹⁵ cavities powered

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Figure 2. Cross-section view of the absorption/fluorescence cell showing the placement of the lamps. The direction of the flow in the reactor is perpendicular to the figure.

by 2.45-GHz supplies (Raytheon PGM-10) operating at a power of about 20 W for the absorption lamp and 50 W for the resonance-fluorescence lamp. The gas flow enters the lamp near the window and passes from front to back. This procedure inhibits the buildup of pockets of absorbing atoms between the emitting region and the exit window. Controlled amounts of air can be added to the lamp to enhance nitrogen emissions, but usually the impurity level of N2 (i.e., a few ppm) in the He or Ar bath gases is sufficient to give intense but optically thin multiplets at 149 and 174 nm. Instability in the emission intensity, due to long-term variations in the lamp cooling rate and thereby in the steady-state operating temperature of the lamp (typically 500-600 K), is minimized by regulating the flow of cooling air to the cavity. In practice, He bath gas was commonly used in the lamps. We have observed previously¹⁰ that excitation by metastable argon gives excessive nonthermal line broadening of the NI emission.

Atomic nitrogen metastables are made in the flow tube by discharging mixtures of nitrogen and either argon or helium in a McCarroll¹⁶ cavity powered by another Raytheon 2.45-GHz supply. Molecular nitrogen is moderately efficient at quenching the atomic metastables $(k_{N(^{2}D)+N_{2}} = 1.6 \times 10^{-14} \text{ cm}^{3} \text{ molecule}^{-1}$ s⁻¹),^{4,5} so that the best metastable yields come from fairly dilute mixtures of N₂ in the Ar or He, typically $\leq 1\%$ N₂.

Quenching reagents enter the flow reactor through a movable injector which consists of a 0.25-in.-diameter length of stainless steel tubing with a loop constructed from 3-mm-o.d. polyethylene epoxied onto its downstream end. The loop is slightly more than 1 in. in diameter and is set on the stainless steel tube so that it is concentric with the flow reactor. A total of 20 small holes (~0.5 mm diameter) have been drilled around both the inside and outside of the loop to allow reagent gas to escape into the gas stream. The quality of mixing was checked by observing the air afterglow when NO was added through the loop injector to a flow containing O atoms. The 0.25-in. stainless tube slides along the bottom of the flow reactor and exits it through a Swagelok fitting in the end flange of the flow reactor. The Swagelok fitting has been slightly modified for this purpose by boring it out completely to accept the tube, using a double O-ring seal in place of the front ferrule, and by reversing the rear ferrule. The zero of the scale relating the distance between the injector and the detection region was calibrated by measuring the point at which the scattered light from the resonance fluorescence lamp suddenly increased as the injector was moved into the detection region.

Mass-flow meters monitor the flow rates of all gases. All flow meters were calibrated by measuring rates of increase of pressure with time into 6.5- or 12-L flasks, using appropriate differential pressure transducers (Validyne DP-15) which had themselves been calibrated with silicon oil or mercury manometers. Typically the flow rates for argon or helium, nitrogen, and quencher were 2000-5000, 50, and 0-120 μ mol s⁻¹, respectively. The total pressure was generally 1-3 Torr, and the flow velocity was 1000-3500 cm s⁻¹.

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Figure 3. Resonance fluorescence spectrum from N(²D) 18 ms downstream from an Ar/N₂ discharge, $X_{N_2} = 0.01$.

The argon or helium and the nitrogen flow through molecular-sieve traps to remove water and carbon dioxide prior to entry into the flow reactor. In most experiments the quenchers flowed straight from their cylinders into the reactor without further purification.

A MgF₂ lens collected vacuum ultraviolet fluorescence from the flow tube and focused the light on the entrance slit of a 0.2-m monochromator which employed a concave grating. A turbomolecular pump maintained a pressure $\leq 1 \times 10^{-6}$ Torr in the monochromator. A solar blind photomultiplier with KI photocathode detected photons exiting the monochromator, with the aid of a photon-counting rate meter. In some cases, a scaler counted individual photons. Since the dark count of the vacuum-UV solar blind PMT was about 0.4 Hz, count rates on the order of 1 Hz could be determined with reasonable precision. When pulse counting, the procedure generally was to average 4-10 sets of 10-s counts. A laboratory personal computer and dataacquisition system (IBM PC, Data Translation DT2801 A D/A board, and Laboratory Technologies, Labtech Notebook software) read photon-counter and mass-flow-meter outputs and stored them on floppy disks for subsequent analysis. The data were reduced and analyzed with LOTUS 123 spread sheets which we designed to average the raw signals, convert them to appropriate engineering units, and to perform the requisite least-squares fitting and plotting of the data.

Resonance-Fluorescence Diagnostic. A resonance fluorescence diagnostic monitored the number density of the $N(^{2}D)$. While this technique is straightforward for most systems, 17-19 several interferences make it more difficult to apply to $N(^{2}D)$ studies. The observed signal consisted of four components: the resonance-fluorescence signal of interest ($0 \le I_f \le 2000 \text{ Hz}$); Lyman-Birge-Hopfield (LBH, $N_2(a^1\Pi_g - X^1\Sigma_g^+)$) and a small amount of Ogawa-Tanka-Wilkinson-Mulliken (OTWM, N2- $(a'^{1}\Sigma_{u} - X^{1}\Sigma_{g}^{+}))$ emission from the gas stream $(0 \le I_{LBH} \le 100)$ Hz); scattered light from the excitation source ($I_{sc} \sim 3-6$ Hz); and dark counts from the photomultiplier ($I_{dk} \approx 0.4 \text{ Hz}$). Separating these phenomena required four sets of measurments: (1) metastables and lamp on, $I_1 = I_f + I_{LBH} + I_{sc} + I_{dk}$; (2) metastables on, lamp off, $I_2 = I_{LBH} + I_{dk}$; (3) metastables off, lamp on $I_3 =$ $I_{sc} + I_{dk}$; and (4) metastables and lamp off, $I_4 = I_{dk}$. The desired signal then was $I_f = I_1 - I_2 - I_3 + I_4$. The LBH emission is excited primarily in collisions between buffer gas and $N_2(a'^1\Sigma_u^{-})^{.20,21}$

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WAVELENGTH (nm)

Figure 4. Background spectrum of Ar/N_2 discharge effluent 18 ms downstream from the discharge with the N(²D) resonance-fluorescence lamp off.



Figure 5. Variation of N(²D) resonance fluorescence intensity at 174 nm as a function of relative N(²D) number density. A_{149} is the fractional absorption of 149-nm resonance radiation by N(²D), i.e., $(I_{initial} - I_{transmitted})/I_{initial}$. Ar buffer: 250- μ m slits.

Because most gases rapidly quench $N_2(a'^1\Sigma_u^-)$,²¹ I_{LBH} varies with number density of added reagents. This variation must be determined. Generally, the scattered light and dark counts remained constant with quencher flow but did vary from day to day. In the case of the reaction with carbon monoxide, both I_{LBH} and I_{sc} increased with added quencher. This was because of CO fourth-positive $(A^1\Pi - X^1\Sigma^+)$ excitation by $N_2(a'^1\Sigma_u^-)^{21}$ in the gas stream and some CO fourth-positive resonance fluorescence excited by impurity emissions in the lamp. Fugures 3 and 4 illustrate the emissions observed in the reactor with the resonance-fluorescence lamp on and off, respectively.

At sufficiently high number densities, the observed resonance-fluorescence intensity varies nonlinearly with the number density of the species being monitored because the resonance

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reactant	group				
	PSI ^b	Cambridge Univ ⁵	Univ of Pittsburgh ^{3,4}	Boston College ⁶	SRI ^{7,8}
O ₂	4.6 ± 0.5	5.2 ± 0.4	6 ± 2 5.3 ± 0.5	6.1 ± 1.8	7.0 ± 1.8
N ₂ O	2.2 ± 0.3	1.6 ± 0.1	3.5 ± 1.2	3 ± 1	3.0 ± 0.8
CÔ,	0.35 ± 0.03	0.18 ± 0.02	0.5 ± 0.2	0.7 ± 0.2	0.60 ± 0.15
co	1.7 ± 0.4	2.1 ± 0.2			6.0 ± 1.5
H ₂	2.3 ± 0.5	2.1 ± 0.3		3.5 ± 1	5.0 ± 1.2

^a Units are 10^{-12} cm³ molecule⁻¹ s⁻¹, T = 300 K. ^b Present results.

fluorescence is absorbed by metastables between the excitation region and the monochromator. This nonlinearity complicates the interpretation of kinetic measurements.²² In order to determine the safe region for operation, we measured the resonance-fluorescence intensity and, under identical conditions, determined the N(²D) number density via resonance absorption at 149 nm. Figure 5 shows a plot of the data. Above about 1.5 kHz the resonance-fluorescence signal falls off from linearity under the observation conditions employed. When the abscissa of the plot is placed on an absolute basis,²³ we find a signal of 1 Hz corresponds to a number density of $<10^8$ atoms cm⁻³. Enhancements in sensitivity over the conditions of Figure 5 result from using larger slits and monitoring the 149-nm fluorescence rather than that at 174 nm.

The final and most nagging problem in applying resonancefluorescence to the detection of $N(^2D)$ lies in separating its resonance-fluorescence signal from that of accompanying $N(^{2}P)$ metastables. The two metastable nitrogen atoms, $N(^{2}D)$ and $N(^{2}P)$, have a common upper state for their resonance lines so that one of the lines must be filtered from the lamp to discriminate between the two levels. A laser reflector centered at about 175 nm on a MgF₂ substrate discriminates moderately well against the 174-nm line which is absorbed by $N(^{2}P)$ while passing the 149-nm multiplet which is absorbed by $N(^{2}D)$. We found that commercially available reflectors were imperfect, however, giving a transmission ratio, T_{149}/T_{174} , of about 8:1. Some further discrimination which enhances resonance fluorescence from N(²D) pumping over that from N(²P) pumping results from a greater intensity in the 149-nm multiplet, a slightly larger oscillator strength for 149-nm absorption,²⁴ and the fact that $N(^{2}D)$ outnumbers $N(^{2}P)$ in the flow reactor. Absorption measurements on the ratio of $[N(^{2}D)]$ to $[N(^{2}P)]$ showed a variation of greater than 7:1 in argon to as little as 2.5:1 in the helium. The lower N(²P) number density in an argon carrier results from an enhanced quenching of $N(^{2}P)$ relative to $N(^{2}D)$ by argon. The fraction of the initial resonance fluorescence observed in argon which could be attributed to $N(^{2}P)$ pumped by leakage through the lamp filter was only about 1%, but it was as much as 3-5% in helium buffer. This leakage causes severe problems in getting reliable kinetic data because the $N(^{2}P)$ is much less readily quenched by most gases than is N(²D)-generally by one to two orders of magnitude-so that after only one e-fold in measured resonance-fluorescence decay, as much as 15% of the residual resonance-fluorescence signal comes from unquenched N(²P). Thus, semilong decay plots in helium can become severely nonlinear over less than an order of magnitude decay. Such nonlinearity is unacceptable for obtaining reliable quenching measurements. One would like two orders of magnitude of linear decay if possible, and given the low background counts in our system, several orders of magnitude in resonance fluorescence decay as a function of added quencher is certainly attainable.

We overcame the problems of residual $N(^{2}P)$ resonance fluorescence interference by using two filters back-to-back to discriminate against the 174-nm line from the lamp, and by



Figure 6. Decay of the natural log of $[N(^2D)]$ as a function of $[O_2]$ at five different reaction times.

making most measurements at moderately high pressures of argon buffer. With this procedure we could obtain linear semilogarithmic decays over more than two orders of magnitude.

A final complication to using a resonance-fluorescence diagnostic is the possible absorption of the resonance radiation by the quencher. This problem will be most evident in studies with relatively inefficient quenchers for which larger number densities of reactant must be added to the reactor. For the species studied here, only CO_2 is a potential problem. We were careful to keep CO₂ number densities low enough to avoid significiant absorption, and worked at longer decay times to obtain adequate decays. Finally, the CO₂ results were carefully cross checked by using a resonance-absorption diagnostic, which gave results similar to the resonance-fluorescence runs.

Results

Rate coefficients are determined from measurements of the change in the natural log of the metastable nitrogen number density as a function of number density of added quenching reagent with fixed reaction distance z:

$$-\frac{d \ln [N(^{2}D)]}{d[Q]} = 0.62k_{Q}z/\bar{v} = \Gamma(z)$$
(2)

where k_0 is the reaction rate coefficient, z the distance between the injector and observation region, \bar{v} the bulk flow velocity, and the factor of 0.62 corrects for the coupling of a radial density gradient in $N(^{2}D)$ with a parabolic velocity profile of the gas stream.²⁵⁻²⁸ This anlysis requires corrections to the reaction distance, z, to account for imperfect mixing at the injector. Thus, one must measure decays at several different distances with all other conditions fixed and then determine the reaction-rate coefficient from a plot of Γ vs. z.

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Figure 7. Variation in decay coefficient with reaction time for $N(^{2}D)$ + O₂ reaction. The ordinates of the data points are determined from the slopes of the lines in Figure 6.

The slopes of lines in Figure 6 are the decay coefficients, $\Gamma(z)$, as defined by eq 2. The slope of a plot of Γ vs. effective reaction time, \bar{z}/v , determines the reaction rate coefficient. Figure 7 illustrates this for the data of Figure 6. Note the nonzero intercept indicating a finite mixing time for the experimental conditions employed. The first column of Table I lists our results. The error bars on our measurements are a root-mean-square weighting of the statistical uncertainties as reflected in reproducibility of results from one experiment to another, and the systematic uncertainties involved in measuring temperature, pressure, flow rates, reaction distances, etc. As a cross check on our results, we also measured $N(^{2}D)$ decays via resonance absorption for quenching by O₂, CO, N_2O_1 , and CO_2 . Although an inherently much less sensitive diagnostic technique (see below), the absorption measurements agreed excellently with the more comprehensive set of resonance-fluorescence kinetic runs.

Table I also compares our results with other measurements in the literature. The flash photolysis measurements of Husain et al.5 agree well with our determinations except for the rate coefficient for quenching by CO₂. Iannuzzi and Kaufman's³ measurement on the total rate coefficient for reaction with O2 also agrees well. Most of the other measurements are substantially larger than our results. The flow reactor measurements of Lin and Kaufman⁴ and Fell et al.⁶ suffer greatly from overall lack of sensitivity as well as from uncertainties in the development of their flow profile. We discuss these problems in some detail below. The photolysis studies of Black et al.^{7,8} monitored temporal decays of emission between 300 and 400 nm in mixtures of N₂O and reactant. Their analysis is based on the assumption that $N(^{2}D)$ is produced in the photolysis and that it reacts with N_2O to give NO(B²II-X²II) emission. The NO emission is then a tracer of their $N(^{2}D)$ number density. Kinetic measurements employing tracers is often somewhat dangerous unless one can be absolutely certain of the identity of the precursor to the tracer.⁹ Black et al.'s measurements also lacked sensitivity, having a dynamic range of less than a factor of ten.

Davenport et al.²⁹ studied the removal of $N(^{2}D)$ by O_{2} , $N_{2}O_{3}$, CO₂, and O in a discharge flow apparatus, using atomic resonance absorption as the N(²D) diagnostic. Uncertainties in their mixing length led them to consider their values to be reliable only relative to one another. They reported $k_{CO_2}/k_{O_2} = 0.142 \pm 0.055$, $k_{N_2O}/k_{O_2} = 0.65 \pm 0.10$, and $k_{CO_2}/k_{N_2O} = 0.22 \pm 0.09$. Only this last value agrees with our measurement of 0.196 ± 0.020 . Our rate coefficients for CO₂ and N₂O relative to that for O₂ are 0.076 \pm 0.005 and 0.47 ± 0.06 , respectively. Because the flow time between the discharge and the observation was so short in Davenport et al.'s experiment, their reaction-zone temperature was somewhat above ambient. Their larger rate coefficients for CO2 and N2O relative to O₂ compared to ours could occur if the rate coefficient temperature dependence were somewhat larger for CO2 and N2O than for O_2 . The experiments of Black et al.⁸ indicate such an effect for N₂O relative to O₂. Davenport et al. also observed roughly equal rate coefficients for $N(^{2}D)$ removal by $N_{2}O$ and H_{2} , in accord with our observations.

The experimental approach described above, together with the extreme sensitivity of the resonance fluorescence diagnostic, eliminates most large systematic errors inherent in flow-reactor studies of metastable kinetics. A major potential source of error lies in correcting for the coupling between the radial density gradient of the metastable and the parabolic velocity profile of the bulk gas. Under conditions such that laminar flow is fully developed, the rate coefficient as determined under the assumption of plug flow must be multiplied by a factor of 1.6 to correct for these fluid dynamic effects.²⁵⁻²⁸ The formula commonly given for the entry length, i.e., the distance the gas must flow down the tube before laminar flow is fully developed, is generally written in terms of the product of the flow reactor radius and the Reynolds number.³⁰ Because, at constant gas flow rate, the Reynolds number varies inversely with flow tube radius, the entry length in reality has no dependence on the reactor diameter. Only the molar flow rate of the gas, its molecular weight, and its viscosity affect the entry length. Thus, we find the entry length, l_e , is best expressed as

$$l_{\rm e} = 7.23 \times 10^{-8} \frac{fM}{\eta} \tag{3}$$

where f is the flow rate in μ mol s⁻¹, M is the gram molecular weight of the gas, and η is the viscosity in Poise. Under typical conditions in our studies, $f \sim 2500 \ \mu \text{mol s}^{-1}$, M = 40, $\eta \sim 2.22$ \times 10⁻⁴, we find the entry length is 32 cm. In order to ensure fully developed flow in our system, therefore, our detection region is generally ≥ 60 cm downstream from the entrance of the flow reactor, and our measurements cover reaction distances no closer than 25 cm from the upstream end of the reactor.

Adding very large amounts of gas through the injector, especially at high velocities, could disturb the fluid flow in the reactor, and thereby alter the validity of the fluid mechanical correction required to obtain meaningful kinetic rates. This was not a problem in these experiments for which the maximum flow rate through the injector was always less than 4% of the total gas flow rate. The maximum Reynold's number of each jet exiting the injector loop was approximately five. This is well below the range of critical Reynold's numbers of 40 to 100 which separates stable, laminar jets from turbulent ones.³¹⁻³³ The injection of reagent gas, therefore, is stable and has no significant effect on the laminar flow conditions in the reactor.

Another potentially large source of error lies in correcting for imperfect mixing at the injector. Figure 7 shows that under our conditions the effective mixing correction for O_2 is 2 ms. This value is a function of pressure, flow velocity, bath gas species, reactant species, and injector design. The mixing correction must be determined, therefore, for each set of conditions. Clearly, under the conditions of Figure 7, a fixed point determination at a reaction time of 24 ms would produce a reasonably accurate result even if the mixing correction were ignored. If sensitivity constraints confine one to short reaction times (<10 ms), however, then neglect of the mixing correction will produce results substantially in error.

Allowing adequate flow time to eliminate uncertainties in the fluid dynamic or mixing corrections requires an extremely sensitiver diagnostic. In most systems absorption measurements become impractical for fractional absorptions below 0.01 to 0.02. Under the conditions employed in producing Figure 2, the resonance fluorescence intensity is several hundred Hertz for a fractional absorption of 0.01. Thus, the resonance-fluorescence

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system still has more than two orders of magnitude of dynamic range left after an absorption diagnostic has become useless. This dynamic range is important in kinetic measurements because one cannot ensure linear semilog decay plots, indicative of freedom from competing processes, with less than one order of magnitude decay.

Summary and Discussion

We have developed a flow reactor technique for measuring metastable reaction kinetics accurate to 15%. The current studies involve monitoring $N(^{2}D)$ number densities with a resonancefluorescence diagnostic which has an ultimate sensitivity $\lesssim 10^8$ atoms cm⁻³. This sensitivity allows long enough flow times in the reactor to eliminate uncertainties in fluid dynamic and mixing corrections and further gives large enough dynamic range in decay measurements to allow accurate determination of decay rates.

The quenching rate coefficients obtained here are consistent with those of previous investigators, especially in view of the uncertainties inherent in the earlier work, but offer significantly improved absolute accuracy and relative precision. For most of the quenchants tested, the observed rate coefficients correspond to cross sections on the order of 1/100 of the gas kinetic value, with the value for CO_2 being another order of magnitude smaller. Thus, the rate coefficients may have a significant temperature dependence (e.g., see ref 8). Furthermore, the quenching may occur through formation of reactive complexes, with energy

barriers in the exit channels such that vibrationally excited molecular products are formed. The work of Lin and Kaufman⁴ seemed to indicate that quenching of $N(^{2}D)$ by O₂, N₂O, and CO₂ proceeds primarily by chemical reaction. More recent observations of NO vibraluminescence from the O_2 reaction^{2,34} appear to be quantitatively consistent with this view. Similarly, efficient vibraluminescence has been observed from NH(v) formed from $N(^{2}D) + H_{2}^{35}$ and from CO(v) excited by energy transfer from $N(^{2}D)$.³⁶ In continuing investigations, we hope to determine product branching ratios for reactions of $N(^{2}D)$ and $N(^{2}P)$.

Acknowledgment. This work was performed under Contract F19628-85-C-0032 with the Air Force Geophysics Laboratory and sponsored by the Defense Nuclear Agency under Project SA. Task SA, Work Unit 00115 and by The Air Force Office of Scientific Research under Task 2310G4. The comments and advice of Dave Green, George Caledonia, Hart Legner, and Peter Wu, and the experimental expertise of Henry Murphy greatly benefited our efforts.

Registry No. N, 17778-88-0; O₂, 7782-44-7; CO₂, 124-38-9; N₂O, 10024-97-2; CO, 630-08-0; H₂, 1333-74-0.

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Kinetics of One-Electron Oxidation by the Cyanate Radical

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The reaction of cyanate ions with hydroxyl radicals was studied by pulse radiolysis and found to lead to formation of a transient absorbing at 330 nm ($\epsilon = 970 \text{ M}^{-1} \text{ cm}^{-1}$). The rate of formation of this transient is slower than the rate of reaction of NCO⁻ with OH, in agreement with previous results. This indicates that the initial OH adduct, NC(OH)O⁻, which is known from ESR experiments to rearrange to NHCO₂⁻, reacts with another NCO⁻ to form the observed transient. Rate constants for oxidation by this cyanate radical were determined for several compounds, including ascorbate, urate, and several phenols and anilines. They were found to vary from $<10^6$ to 3×10^8 M⁻¹ s⁻¹. Comparing these rate constants with those for other oxidizing radicals, and taking into consideration the redox potentials of the radicals and the substrates, we conclude that the cyanate radical has a one-electron oxidation potential of about 0.6-0.7 V vs. NHE. Such a weak oxidant cannot be assigned the structure $(NCO)_2^{\bullet-}$ and we suggest, therefore, the alternate structure $(^{-}O_2CNHNCO^{-})^{\bullet-}$.

Introduction

One-electron oxidized forms of many inorganic anions have been produced and studied by pulse radiolysis. These species often are produced by the reaction of the anion with hydroxyl radicals, the primary radicals formed in the radiolysis of N_2O -saturated aqueous solutions. For example, the reactions of OH with sulfite, nitrite, and chlorite ions yield the radicals SO_3^- , NO_2 , and ClO_2 , respectively.¹⁻⁴ In certain cases, complex radicals are produced by reaction of the oxidized species with another nonoxidized anion.

$$\mathbf{X} + \mathbf{X}^{-} \rightleftharpoons \mathbf{X}_{2}^{-} \tag{1}$$

Such complexes have very high stability when X^{-} is a halide or thiocyanate⁵⁻⁷ but only low stability when X^- is azide.⁸ The above-mentioned radicals behave as one-electron oxidants. Kinetics of oxidation of a variety of organic and inorganic compounds by these radicals have been determined by pulse radiolysis.^{1-4,9-11}

In contrast with the case of thiocyanate, the reactions of OH with cyanide and cyanate ions take place by addition of OH to the carbon and the adducts rearrange by proton shifts, e.g.¹²

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