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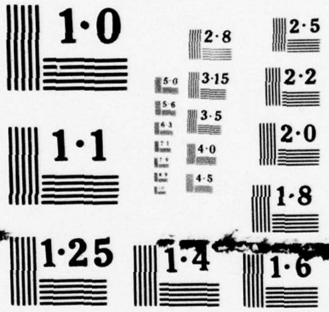

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MEASUREMENTS ON $O(^1D)/N_2O$ AND HNO_2/O_3 KINETICS

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June 1977

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16. Abstract

The branching ratio, R, for $N_2 + O_2$ and NO production in the $O(^1D)/N_2O$ reaction at 290 K has been measured to be 0.73 ± 0.11 and 0.92 ± 0.10 for "hot" and thermal $O(^1D)$, respectively. $O(^1D)$ was produced from N_2O photolysis at 184.9 nm. The product N_2 was determined by gas chromatography; NO and its oxidation product NO_2 were each determined with a chemiluminescence analyzer. Arguments are given that the $O(^1D)/N_2O$ reaction in the stratosphere is dominated by thermal $O(^1D)$ and a value of R = 0.9 ± 0.1 (+ or -) is recommended for stratospheric modeling.

An unsuccessful attempt at measuring HNO_2/O_3 kinetics is described.

17. Key Words

Odd Nitrogen	Branching Ratio
Stratosphere	HNO_2
N_2O	O_3
$O(^1D)$	

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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in ≡ 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

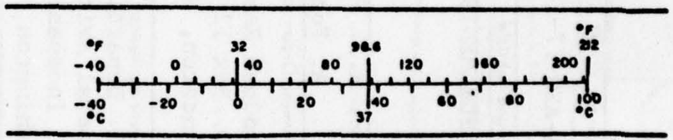

TABLE OF CONTENTS

PART I

$O(^1D)/N_2O$ BRANCHING RATIO

by

H.N. Volltrauer, W. Felder, R.J. Pirkle, and A. Fontijn

I. INTRODUCTION

The reaction of $O(^1D)$ with N_2O

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (1a)$$

$$\rightarrow 2NO \qquad (1b)$$

may be the most important source of odd nitrogen in the natural stratosphere[1] and hence an accurate value of the ratio $R = k_{1a}/k_{1b}$ is required for modeling and predicting stratospheric composition. Other $O(^1D)/N_2O$ reaction paths possible, such as deactivation[2] to $O(^3P)$ and formation[3] of $N + NO_2$, have been shown to account for $\leq 3\%$ of the reaction events. The overall Reaction (1) proceeds at a nearly gas kinetic rate (k_{1a} and k_{1b} are each about 1×10^{-10} ml molecule^{-1} sec^{-1} at ≈ 300 K).[4,5] The ΔH of reaction paths (1a) and (1b) are -124 and -81 kcal mole^{-1}, respectively.[6] On this basis it is concluded that

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[1] Department of Transportation, "The Natural Stratosphere of 1974," CIAP Monograph 1, DOT-TST-75-51, A.J. Grobecker Ed.-in-Chief, September 1975, pp. 5-107 - 5-109.

[2] Paraskevopoulos, G., Symonds, V.B., and Cvetanovic, R.J., "Relative Rate of Reaction of $O(^1D_2)$ with N_2O, "Can. J. Chem. 50, 1808 (1972).

[3] Scott, P.M., Preston, K.F., Andersen, R.J., and Quick, L.M., "The Reaction of the Electronically Excited Oxygen Atom $O(^1D_2)$ with Nitrous Oxide," Can. J. Chem. 49, 1808 (1971).

[4] Ref. 1, p. 5-210.

[5] Ghormley, J.A., Ellsworth, R.L., and Hochanadel, C.J., "Reaction of Excited Oxygen Atoms with Nitrous Oxide. Rate Constants for Reaction of Ozone with Nitric Oxide and Nitrogen Dioxide," J. Phys. Chem. 77, 1341 (1973).

[6] JANAF Tables, Dow Chemical Company, Midland, MI (continuously updated).

the N_2 and NO must be produced in their ground electronic states. However, Reaction (1a) is sufficiently exoergic to produce O_2 in the singlet states, $a^1\Delta$ and $b^1\Sigma$; singlet O_2 production by this reaction conserves spin, but triplet O_2 production does not. Since it is unlikely that a spin-forbidden reaction of these light elements has such a high rate coefficient, singlet O_2 is the most likely product of Reaction (1a). Wiesenfeld et al[7] have obtained indirect evidence that singlet O_2 is indeed produced.

R has been determined in a number of experiments using $O(^1D)$ derived from uv photolysis of suitable parent molecules (N_2O, NO_2, O_3, O_2). These experiments have led to conflicting results. Several investigators[3,8] have found that $R \approx 1$, but others[5,9] suggest $R \approx 0.7$. It has been suggested[9] that this difference in R is related to thermalization of the originally hot $O(^1D)$ formed in the photolysis; indeed Heicklen's group showed[9] that the addition of He to thermalize the $O(^1D)$ led to an increase in R from 0.65 ± 0.07 to 0.83 ± 0.06. The latter value is in reasonable agreement with that from Preston's group,[3] 1.00 ± 0.07, and Wiebe and Paraskevopoulos' (WP)[8] measurement of 1.0 ± 0.17. Thus for thermalized $O(^1D)$, $R = 0.9 \pm 0.1$ appears to be a reasonable value. However, this picture is not as satisfactory as it may seem. WP measured the same value of R both from translationally hot $O(^1D)$, and from $O(^1D)$ thermalized by He and Ne. Furthermore, stratospheric $O(^1D)$, which is primarily formed by Hartley band photolysis of O_3, is initially produced

---

7. Foo, P.D., Lohman, T., Popolske, J., and Wiesenfeld, J.R., "Deactivation of Electronically Excited Thallium Tl(6p $^2P_{3/2}$) in Collision with Small Molecules," J. Phys. Chem. 79, 414 (1975).

8. Wiebe, H.A. and Paraskevopoulos, G., "The Effect of the Excess Kinetic Energy of the $O(^1D)$ Atoms from the Flash Photolysis of N_2O on Their Reaction with N_2O," Can. J. Chem. 52, 2165 (1974).

9. Simonaitis, R., Greenberg, R.I., and Heicklen, J., "The Photolysis of N_2O at 2139 Å and 1849 Å," Int. J. Chem. Kin. 4, 497 (1972).

with excess translational energy.[10-13] Hence the question of the influence of translational energy on R is important.

Some experimental problems are associated with these earlier R determinations. The majority were made[2,3,9] using gas chromatographic (g.c.) diagnostics in which reaction products are sampled and analyzed externally. In such methods introduction of the NO, O_2, N_2 mixture into the g.c. allows reaction of NO with O_2, giving rise to possible systematic errors in the NO yield determinations. Indeed NO is actually measured as a higher oxide and several investigators[2,3] have assumed the stoichiometry $2NO + O_2 = 2NO_2$, whereas Heicklen and coworkers[9] obtained indications for $4NO + O_2 = 2N_2O_3$. Thus systematic errors, e.g., if the actual stoichiometry is some combination of these, could easily go undetected and self-consistent but erroneous results be obtained. WP[8] measured NO directly and in situ, but only before and after the actual experiments; thus some oxidation to NO_2 could have occurred. Other determinations of R[3,5] were indirect, i.e., the product NO_2 of the reaction of NO with O_2[3] or O_3[5] was measured. Such determinations, because interpretation of the measurements requires an accurate knowledge of the rates and mechanisms of a number of reactions, are more readily subject to error than direct determinations.

In this work we have re-examined this problem by measuring the N_2 and NO produced by Reaction (1) with $O(^1D)$ from N_2O photolysis at 184.9 nm

$$N_2O + h\nu \rightarrow N_2 + O(^1D) ; \qquad (2)$$

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10. Cvetanovic, R.J., "Excited State Chemistry in the Stratosphere," Can. J. Chem. 52, 1452 (1974).

11. Nicolet, M., "Aeronomic Chemistry of the Stratosphere," Planet. Space Sci. 20, 1671 (1972).

12. Calvert, J.G. and Pitts, J.N., Photochemistry (Wiley, New York, 1967), p. 208.

13. Ref. 1, p. 1-13 and 3-90 ff.

the method of analysis allows measurement of both [NO] and [NO_2] after the photolysis (their sum corresponds to the total [NO] formed in Reaction (1b)) and is independent of subsequent reactions after photolysis. A chemiluminescence NO, NO_2 analyzer[14],[15] based on the NO/O_3 chemiluminescent reaction was used for this analysis. Our findings, like those of the earlier work, pertain to room temperature.

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[14] Fontijn, A., "Chemiluminescence Techniques in Air Pollutant Monitoring," in Modern Fluorescence Spectroscopy: Newer Techniques and Applications, Vol. 1, E.L. Wehry, Ed. (Plenum Press, New York, 1976), p. 159.

[15] Fontijn, A., Sabadell, A.J., and Ronco, R.J., "Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Implications for Continuous Selective Monitoring of Gaseous Air Pollutants," Anal. Chem. 42, 575 (1970).

II. EXPERIMENTAL

A. APPARATUS

A simplified diagram of the apparatus is shown in Fig. 1. The reactor, a 360 ml Pyrex sphere containing a Teflon stirring bar, was provided with a 2.1 cm i.d., 4.5 cm long sidearm which was sealed with a 0.3 cm thick suprasil quartz window. The flask was attached to an Hg-free vacuum line for filling and evacuation. Sample pressures were measured using either of two absolute dial gauges, 0-20 and 0-400 Torr, respectively, which were calibrated against a Zimmerli-type Hg manometer. During calibration, a liquid N_2 trap was placed between the Zimmerli gauge and the dial gauges to prevent contamination of these dial gauges with Hg. Actinic radiation at 184.9 nm was provided by a low pressure glow of Hg in argon sustained by a 120 Watt microwave (2450 mHz) discharge source operated at 70-100% of maximum output. The discharge tube (0.8 cm i.d.) was attached directly to the quartz window of the reaction flask for maximum intensity.

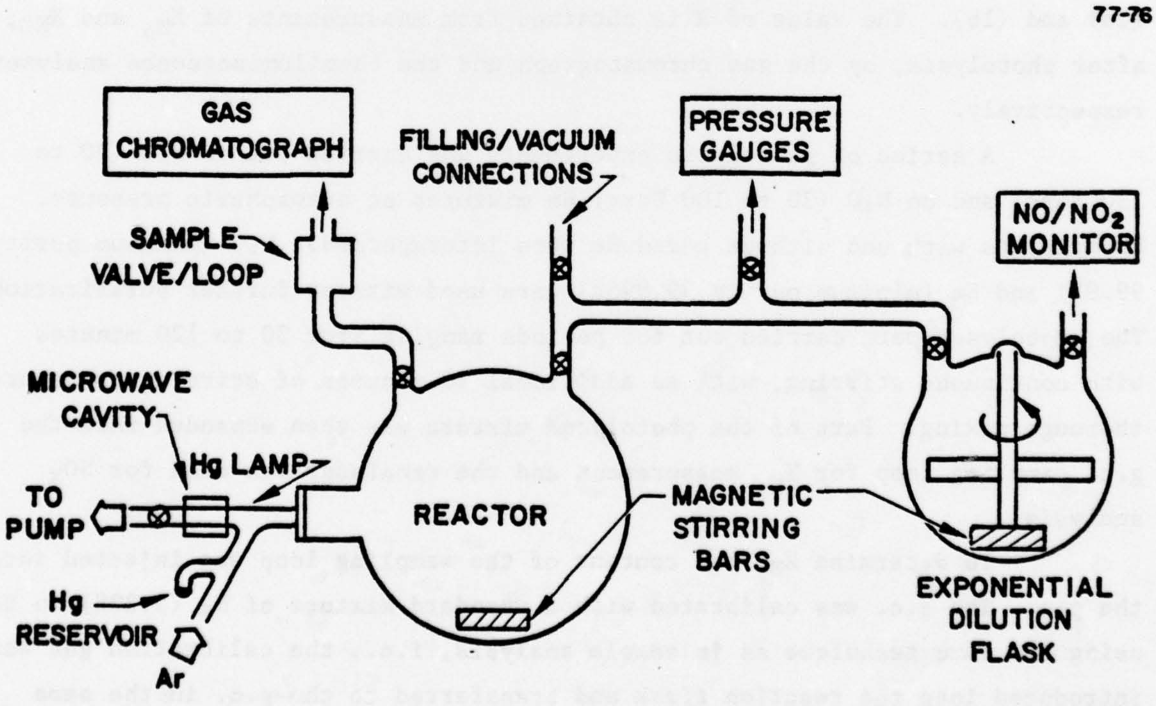

FIGURE 1 SCHEMATIC OF APPARATUS FOR $O(^1D)/N_2O$ MEASUREMENTS

N_2 product analyses were performed using a gas chromatograph equipped with a molecular sieve 5A column operated at ≈ 380 K. To facilitate sampling without accidental contamination with air, a He-purged (surrounded) gas chromatographic sampling valve with a ≈ 10 ml stainless steel sample loop was attached directly between the gas chromatograph and the reaction flask. [NO] and [NO_2] were measured with a NO/NO_x(= NO + NO_2) chemiluminescence analyzer. The instrument used has a sample flow rate of 3 ml(STP)sec^{-1} and operates at a reactor pressure of ≈ 4 Torr. A number of different NO_2 to NO converters were used with the instrument (see Section II.B). This low flow rate instrument was chosen because of the limited sample available.

B. METHOD

From the steady-state assumption for $O(^1D)$ for Reactions (1) and (2) it follows, cf. e.g. Ref. 8, that

$$R = k_{1a}/k_{1b} = [N_2]/[NO] - 1/2 = X_{N_2}/X_{NO} - 1/2 \qquad (A)$$

where X_{N_2} and X_{NO} are the mole fractions of N_2 and NO produced from Reactions (1a) and (1b). The value of R is obtained from measurements of X_{N_2} and X_{NO}, after photolysis, by the gas chromatograph and the chemiluminescence analyzer, respectively.

A series of photolysis experiments was carried out on N_2O (30 to 130 Torr) and on N_2O (30 to 100 Torr)/He mixtures at atmospheric pressure. Experiments with and without added He were interspersed. N_2O (minimum purity 99.9%) and He (minimum purity 99.995%) were used without further purification. The photolyses were carried out for periods ranging from 30 to 120 minutes with continuous stirring, with an additional 10 minutes of stirring to ensure thorough mixing. Part of the photolyzed mixture was then expanded into the g.c. sampling loop for X_{N_2} measurement and the remainder was used for NO_x analysis.

To determine X_{N_2} the content of the sampling loop was injected into the g.c. The g.c. was calibrated with a standard mixture of N_2 (5.22%) in He using the same technique as in sample analysis, i.e., the calibration gas was introduced into the reaction flask and transferred to the g.c. in the same manner as the photolyzed mixture. The g.c. response at a number of reactor pressures, P_r, was measured vs. $P_rX_{N_2}$. Using this calibration plot the g.c.

response from the photolyzed mixtures was determined. To ascertain that no systematic errors resulted in the analysis due to the presence of He, in one undiluted N_2O experiment the reaction flask was brought to acmospheric pressure with He before N_2 and NO analysis.

For determination of X_{NO} a portion of the photolyzed mixture, (containing about 5 to 10 Torr N_2O) remaining in the reactor following N_2 analysis was admitted to the 2ℓ exponential dilution flask, Fig. 1, where it was brought to atmospheric pressure with N_2. After stirring for an additional 10 minutes the flask was connected to the NO/NO_x monitor. NO/NO_x measurements were made over about 16 minute long dilution periods. N_2 was used as dilution gas and stirring was continuous. NO and NO_x were monitored alternately for periods of ≈ 4 minutes each. Plots of these measurements, NO(NO_x) versus time, were then extrapolated to $t = 0$ to determine the [NO] and [NO_x] (and hence by subtraction, also [NO_2]) originally present in the dilution flask. Via knowledge of the original pressure of the undiluted sample in the dilution flask, the mole fractions, X'_{NO} AND X'_{NO_2}, in the photolyzed mixture were obtained. Since the NO_2 is due to oxidation of NO (via

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

with O_2 formed during the photolysis), the sum of these quantities is the X_{NO} of Eq. (A). In some experiments a second sample was admitted from the reactor into the dilution flask for analysis; the resulting X_{NO} was found to agree within experimental error with those of the first determination. The calibration of the monitor was checked before and after each photolysis experiment with a standard mixture of 96 ± 2 ppm NO in N_2. Calibration of the standard mixture was checked against a pure NO sample using a syringe infusion pump.

A complicating factor in these NO_x measurements was the presence of N_2O. The low flow Pt/Rh catalytic NO_2-to-NO converter[14]* used in most of this work is normally heated resistively to ≈ 1300 K at which temperature 99% of the NO_2 is converted to NO. At this temperature up to 1% of the N_2O is also converted to NO. Because of the large excess of N_2O in the photolyzed mixture, such high N_2O conversion was unacceptable in the present work. However, by reducing the temperature of the converter to ≈ 1100 K, the N_2O conversion was reduced to an acceptable level (0.01 to 0.08%), for which level reasonable corrections could be made. Under

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* This converter uses eight 0.1 cm bore 5 cm long alumina tubes containing 0.025 cm Pt/Rh wire.

these conditions the NO_2 to NO conversion efficiency was 75 ± 15%. In attempts to use a stainless steel converter[14] at ≈ 1100 K, it was found that while N_2O conversion was again minimal, the response of this converter is highly erratic under these conditions and therefore it was not used. Chemical converters[14] operate at lower temperatures and do not convert N_2O. In some experiments we used a Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) converter at room temperature[16,17]; no measurable N_2O conversion occurred and the NO_2 to NO conversion efficiency was found to be 90 ± 10%. Results obtained with the Pt/Rh and the Mohr's salt converters are in good agreement (see below).

C. CORRECTION FACTORS AND ERROR ANALYSIS

The data were analyzed in two groups (photolyses of "pure" N_2O and N_2O diluted in He) using a propagation of errors treatment for random errors.[18] Each experimental value of R_i was subjected to this treatment, and an uncertainty, σ_i, due to random errors obtained. The values of σ_i were used to obtain a weighted average of R according to[19]:

$$\overline{R} = \Sigma_i (R_i/\sigma_i^2) / \Sigma_i (1/\sigma_i^2)$$

The standard deviation in the mean, σ, was obtained from

$$\sigma = \left[1/\sum_i (1/\sigma_i^2) \right]^{1/2}$$

Systematic errors were summed for each experiment and the average of these was added to σ to obtain an estimate of the absolute accuracy.

---

16. Winfield, T.W., "A Method for Converting NO_2 to NO by Ferrous Sulfate Prior to Chemiluminescent Measurements," Preprints of Papers presented before the Division of Environmental Chemistry, Am. Chem. Soc. 17, 372 (1977).

17. McClenny, W.A. and Stevens, R.K., EPA, NERC, private communication to A. Fontijn, April 1977.

18. Cvetanovic, R.J. Overend, R.P., and Paraskevopoulos, G., "Accuracy and Precision of Gas Phase Kinetics Techniques," Int. J. Chem. Kin. Symp. 1, 249 (1975).

19. Bevington, P.R., Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill, New York, 1969), Chap. 5.

A number of correction factors to the raw data had to be applied. These are discussed below with the associated random and systematic errors.

1. Random Errors

(i) A small difference in response was observed between measurements of the same "NO_2-free" NO samples in the NO and NO_x modes of the chemiluminescence analyzer. The "NO_x" mode yielded consistently lower readings than the "NO" mode, by 2 ± 1% with the Pt/Rh converter and by 3.5 ± 1% with the Mohr's salt converter. These differences are apparently related to a small decrease in sample flow in the NO_x mode and the NO_x measurements obtained were corrected downward for this effect.

(ii) The random error in extrapolating the NO/NO_x exponential dilution plots back to $t = 0$ is estimated not to exceed ± 1%.

(iii) For experiments with the Pt/Rh converter a correction had to be applied for N_2O conversion to NO. Because of variations in the efficiency of this process, which is strongly temperature dependent, the magnitude of the correction needed was frequently checked in the course of the program. In most of the work this correction was 0.08% resulting, in the worst case, in having to subtract 7.8% from the NO_x read. We estimate the error in this procedure to be $\leq$ 50% of the correction factor; this thus introduces a maximum random uncertainty of ± 3.9% in X_{NO}. When the Mohr's salt converter was used, of course, no such error was involved.

(iv) $[NO_2]$ in the photolyzed mixtures was in the range 0-15% of total $[NO_x]$. As discussed in Section II.B the Pt/Rh converter operated at an NO_2 to NO conversion efficiency of 75 ± 15% and the Mohr's salt converter at 90 ± 10%. The maximum random error in X_{NO} due to uncertainties in the NO_2 conversion efficiency is ± 2.25% for the Pt/Rh converter and ± 1.5% using the Mohr's salt converter.

(v) Errors resulting from reading the dial pressure gauges are estimated to be a maximum of ± 2% over the pressure range measured in these experiments for both the N_2 and NO determinations.

(vi) The error in individual gas chromatographic determinations of N_2 from the photolysis mixture was obtained from the scatter in the calibration data as ± 7.2% in the undiluted N_2O samples and ± 2.5% in the N_2O diluted with He samples.

2. Systematic Errors

Systematic errors arise due to uncertainties in concentrations of N_2 and NO in the two calibration mixtures, uncertainties in the calibration of pressure gauges, and uncertainties in the determination of the various correction factors.

(i) The uncertainty in the concentration of NO in the calibration sample is estimated to be $\leq \pm 2\%$. This estimate is based on comparisons with measurements of NO in successively diluted mixtures of "pure" NO.

(ii) The calibration gas obtained from the Matheson Co. was analyzed by the manufacturer to be 5.22% N_2 in He with an accuracy of ± 2% of the N_2 content. A second analysis on this gas cylinder performed at M.G. Scientific yielded 5.23% with an accuracy of ± 1%; because of the good agreement the latter was used as the accuracy figure.

(iii) From the dial pressure gauge calibration against the Zimmerli gauge, the absolute pressure is ± 0.3% in the range of the present measurements.

(iv) The systematic error in the g.c. calibration was taken to be the standard deviation of the calibration measurements, i.e., ± 1.8% for undiluted N_2O measurements and ± 1.2% for the N_2O/He mixtures.

(v) The N_2O interference resulting from the use of the Pt/Rh converter was taken to add 25% of its value as a systematic error. This is one half the uncertainty of a given measurement (four such interference determinations were made). No such error contribution is present for the Mohr's salt converter measurements.

(vi) A ± 4% systematic error was taken for the NO_x converter efficiency. This reflects the 15% uncertainty of an individual measurement weighted against the relatively large number (≈ 15) of such efficiency measurements which were made. For the Mohr's salt converter the same uncertainty was taken since fewer efficiency measurements were made and this converter has not been as well investigated as the Pt/Rh converter. In either case the error contribution is $\leq \pm 0.1\%$.

The total error estimate obtained below by addition of these systematic error estimates is conservative since it is unlikely that all these errors will be in the same direction.

III. RESULTS

The results obtained are summarized in Table 1. Within each group (He absent and He present) the R values may be seen to be independent of $[N_2O]$ and irradiation time. Since all the systematic errors, except for the g.c. calibration, are the same for the experiments with and without He, the difference between these two groups should be judged by the random errors in the respective ratios plus the ± 1.2% and ± 1.8% uncertainty in the g.c. calibrations for these two sets of experiments, respectively, Calculated this way the R's are $0.73_2 \pm 0.05_8$ and $0.91_9 \pm 0.03_9$. This difference therefore appears indicative of a definite influence of the thermalization of $O(^1D)$ on R. The results may moreover be seen to be independent of whether a Mohr's salt or Pt/Rh converter was used in the X_{NO} determination and, for the undiluted N_2O experiments, whether the photolyzed sample was brought to atmospheric pressure with He in the reactor or was transferred to the g.c. and the dilution flask at reaction pressure.

Summing the estimated systematic errors with σ yields

(i) for R in the absence of He, $0.73_2 \pm 0.11_3$

(ii) for R in the presence of He, $0.91_9 \pm 0.10_0$.

TABLE 1

SUMMARY OF $R = k_{1a}/k_{1b}$ MEASUREMENTS AT 290 K

[He] Torr	$[N_2O]$ Torr	Δt_{irr} min	X_{N_2}	X_{NO}	R_i	σ_i	Systematic error in R_i
0	28.8	129	0.0670	0.0527	0.77	0.10_2	0.08_2
0	54.2	60	0.0299	0.0243	0.73[a]	0.09_3	0.08_4
0	100.0	57	0.0240	0.0193	0.74	0.07_3	0.09_0
0	116.5	50	0.0185	0.0151	0.72[b]	0.09_3	0.06_6
0	128.5	30	0.0072	0.0059	0.72	0.09_8	0.07_2
0	128.5	60	0.0130	0.0107	0.71	0.09_3	0.07_1
Weighted mean, standard deviation and average systematic error					0.73_2	0.03_7 (5.0%)	0.07_8 (10.6%)
$\overline{R}$ and its estimated accuracy					$0.73_2 \pm 0.11_3$		
648.0	29.1	50	0.0268	0.0184	0.95[b]	0.09_6	0.06_9
730.4	29.5	110	0.0658	0.0497	0.82	0.07_4	0.07_0
724.0	34.0	81	0.0420	0.0294	0.93	0.08_5	0.07_5
725.0	35.5	86	0.0377	0.0287	0.81	0.07_7	0.07_0
719.5	40.5	93	0.0368	0.0285	0.79	0.07_2	0.06_9
628.0	51.5	60	0.0279	0.0187	0.99[b]	0.06_7	0.07_1
622.1	66.0	90	0.0256	0.0169	1.00[b]	0.06_0	0.07_2
669.8	73.5	45	0.0156	0.0103	1.04	0.07_2	0.10_7
688.0	75.5	45	0.0193	0.0141	0.87	0.04_5	0.08_9
668.0	97.0	49	0.0221	0.0143	1.04	0.08_0	0.10_6
Weighted mean, standard deviation and average systematic error					0.91_9	0.02_1 (2.4%)	0.08_0 (8.7%)
$\overline{R}$ and its estimated accuracy					$0.91_9 \pm 0.10_0$		

[a] Photolysis mixture brought to atmospheric pressure with He before analysis; in all other experiments with undiluted N_2O the samples were transferred directly at low pressure.

[b] $[NO_x]$ analysis used Mohr's salt converter; in all other experiments the Pt/Rh converter was used.

IV. DISCUSSION AND CONCLUSIONS

The value determined here for R in the absence of He, 0.73 ± 0.11 is in good agreement with those of Heicklen et al,[9] 0.65 ± 0.07, and Ghormley et al,[5] 0.70 ± 0.02,* but lies barely within the combined error limits of WP;[8] 1.0 ± 0.1, and the present work. The most reliable[9] measurement of the three made by Preston et al[3] pertains to $O(^1D)$ with little excess energy, which is to be considered below. We cannot find any obvious error source in the WP experiment, apart from the likelihood that some NO was oxidized in their experiment (which on the time scale of their experiments cannot have been a major fraction) which would lead to a slight underestimate of the NO yield and hence to an R value somewhat too high. Another difference is that WP used continuum radiation from a flashlamp and photolyzed N_2O over the 185-230 nm region. However, the radiation intensity from such lamps increases by about a factor of three over this range toward the long wavelength end,[20] while the photodissociation cross section decreases by a factor of 10^3 in the same direction,[21] which suggests that most $O(^1D)$ was produced with energies close to those of the present work. Moreover, since Heicklen et al[9] did not see any influence on R in either undiluted N_2O photolysis or N_2O/He photolysis between 184.9 and 213.9 nm radiation this is an unlikely explanation for the difference in results. A value of 0.8 ± 0.1 would be within the error limits of all these determinations. It should be remembered that "hot" $O(^1D)$ will have somewhat different energies under various experimental and stratospheric

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* It is, however, unclear whether or not the $O(^1D)$ was thermalized in the work of Ref. 5, since reaction conditions are not clearly defined. WP[8] conclude that it pertains to hot $O(^1D)$. However, at least one of these O_3 flash photolysis experiments was done in 760 Torr O_2, in which case, by the same arguments as given below for the stratosphere, the $O(^1D)$ would have been thermalized.

[20] McNesby, J.R., Braun, W., and Ball, J., "Vacuum Ultraviolet Techniques in Photochemistry," in Creation and Detection of the Excited State, A.A. Lamola, Ed., Vol. 1, Part B (Marcel Dekker, New York, 1971), p. 503.

[21] Bates, D.R. and Hays, P.B., "Atmospheric Nitrous Oxide," Planet. Space Sci. 15, 189 (1967).

conditions and it will be argued below that such O(^{1}D) is not directly of interest to stratospheric chemistry.

For thermalized O(^{1}D) WP[8] report 1.0 ± 0.1$_7$. Preston's[9] third set of experiments (with O(^{1}D) from NO_2 photolysis under conditions leading to little excess energy) yielded 1.01 ± 0.06. Heicklen[9] reports a value of 0.83 ± 0.06 for thermalized O(^{1}D), while the present work yielded 0.92 ± 0.11. Heicklen recommended a value of 0.90 ± 0.10 on the basis of the data then obtained[9]; this value is in perfect agreement with our value and we therefore recommend that the value of 0.9 ± 0.1 be adopted for R for thermal O(^{1}D).

While there thus is fair agreement in the value for thermalized O(^{1}D), this should not obscure the fact that both the present work and that from Heicklen's laboratory observe a definite influence of addition of excess He on R, and WP do not observe such an influence. The cause of this discrepancy is not clear.

An important question in the present context is whether the O(^{1}D) in the stratosphere is thermal or hot, i.e., which of the above values of R is most pertinent to the stratosphere. O(^{1}D) in the stratosphere is primarily due to Hartley band photo-dissociation of O_3.[13] At the short wavelength cutoff (≈ 200 nm) this process leading to O(^{1}D) and $O_2(^1\Delta)$ is about 50 kcal exoergic and at the absorption maximum in the 250-260 nm range, it is 20 kcal mole^{-1} exoergic.[12] These energies are only somewhat smaller than the exoergicity of N_2O photolysis in the present work, 70 kcal mole^{-1}. However, the O(^{1}D) formed in the stratosphere will collide with N_2 and O_2 in the overwhelming number of collision events and it is the relative probability of translational energy loss vs. deactivation that determines the energy of the O(^{1}D) which reacts with the trace constituent N_2O. If O(^{1}D) were deactivated on every collision with N_2 and O_2 then those collisions would have no influence on the thermal energy of the remaining O(^{1}D); however, Streit et al[22] have shown that at stratospheric temperatures only one in ten collisions of O(^{1}D) with N_2 or O_2 is effective in quenching O(^{1}D), i.e., in nine of ten

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[22] Streit, G.E., Howard, C.J., Schmeltekopf, A.L., Davidson, J.A., and Schiff, H.I., "Temperature Dependence of O(^{1}D) Rate Constants for Reactions with O_2, N_2, CO_2, O_3 and H_2O," J. Chem. Phys. 65, 4761 (1976).

collisions the $O(^1D)$ only loses translational energy. The amount of excess translational energy lost in each collision can be estimated from the hard-sphere collision model: $E_T'/E_T = (M_1^2 + M_2^2)/(M_1 + M_2)^2$ where E_T' is excess translational energy after collision and E_T before collision. For $O(^1D)$ and N_2, $E_T'/E_T = 0.54$. Hence the excess translational energy after nine collisions is $(0.54)^9 = 3.9 \times 10^{-3}$, and the excess translational energy of $O(^1D)$ is thus $\leq 3.9 \times 10^{-3} \times 50 = 0.2$ kcal mole^{-1}, i.e., the $O(^1D)$ in the stratosphere is effectively thermalized. This argument assumes that hot $O(^1D)$ is not removed much more rapidly by N_2 and O_2 than thermal $O(^1D)$. However, since Streit et al[22] show a slight negative activation energy for the $O(^1D)/N_2$ and $O(^1D)/O_2$ reactions this assumption appears reasonable. Thus R for thermal $O(^1D)$ should be used in stratospheric models.

Since R for thermal $O(^1D)$ may be temperature sensitive it remains important to extend the measurements of its reaction with N_2O down to 200 K, to cover the temperature range of interest in the stratosphere. While the present technique could be adapted to such measurements, insufficient time was left on the present contract to obtain these data. It should be noted that if such an extension to measurements at lower temperatures were to be undertaken, it would be desirable to first improve the accuracy of the methods for converting NO_2 to NO in the presence of N_2O. The latter is indicated since k_3 has a negative activation energy[23,24] which would result in a larger fraction of the NO being converted to NO_2 prior to X_{NO} determination and hence a larger uncertainty in that figure and in R. For such experiments the use of a larger dilution flask in combination with a regular fast-flow (25 ml(STP)sec^{-1}) NO/NO_x chemiluminescence monitor appears useful. We have found the Pt/Rh converters in such instruments to be much more stable and reproducible than in the slow flow monitor used in the present work, at the ≈1100 K required to reduce the N_2O conversion to an acceptable level.

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23. Heicklen, J. and Cohen, N., "The Role of Nitric Oxide in Photochemistry," Adv. in Photochemistry 5, 157 (1968).

24. Ref. 1, p. 5-213.

PART II

HNO_2/O_3 KINETICS

by

R.J. Pirkle and A. Fontijn

V. INTRODUCTION

HNO_2 is an important stratospheric sink for OH radicals and acts as a temporary reservoir of odd nitrogen.[1] The reaction

$$HNO_2 + O_3 \rightarrow \text{Products} \qquad (4)$$

could be of major importance to stratospheric chemistry depending upon its rate coefficient.[25,26] In this work an attempt was made to measure k_4 directly. The method to be used was to measure HNO_2 disappearance by uv absorption measurements, where the absorption measurements were corrected for NO_2, which is present[27] due to

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \qquad (5)$$

and absorbs in the same wavelength range. As a check, separate measurements of initial HNO_2 as well as of NO_2 and O_3 were to be made with a $NO/NO_x/O_3$ chemiluminescence analyzer. A static reactor was built for this work, since k_4 was thought to be too small to allow its measurement in a flow reactor.

While the method to be used appears feasible in principle, unforeseen difficulties were encountered in the uv absorption measurements, which in the time available for this work, prevented obtaining k_4 measurements.

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25. Hastie, D.R., Freeman, C.G., McEwan, M.J., and Schiff, H.I., "The Reactions of Ozone with Methyl and Ethyl Nitrites," Int. J. Chem. Kin. 8, 307 (1976).

26. Schiff, H.I., Proceedings of the Fourth Conference on the Climatic Assessment Program, T.M. Hard and A.J. Broderick, Eds., DOT-TSC-OST-75-38, February, 1975, p. 397; see also statement by the same author quoted as Ref. 12 in Ref. 25.

27. Chan, W.H., Nordstrom, R.J., Calvert, J.G., and Shaw, J.H., "Kinetic Study of HONO Formation and Decay Reactions in Gaseous Mixtures of HONO, NO, NO_2, H_2O and N_2," Env. Sci. Techn. 10, 674 (1976).

VI. EXPERIMENTAL

A. APPARATUS

A schematic of the apparatus used is shown in Fig. 2. It consists, clockwise from bottom left, of four parts which will be discussed in sequence, (i) the reactant feed system, (ii) the external optical system, (iii) the reactor and in-situ optics, and (iv) the external (chemiluminescence) analyzer system.

1. Reactant Feed System

Before entering the reactor, reactants O_3 and HNO_2, and bath gas N_2 were mixed in the 2ℓ Teflon lined mixing chamber, Fig. 2. The O_3 generating system consisted of four corona discharge ozonators operated in parallel from individual high voltage transformers. This system could deliver ≈ 2.4% O_3 in O_2 at flow rates of 25 ml(STP)sec^{-1} corresponding to $[O_3] \approx 3 \times 10^{16}$ ml^{-1} in the reactor. HNO_2 was to be generated by passing a 1% mixture of HCl in N_2 over hot (≈ 400 K) $NaNO_2$ contained in a 1.6 cm i.d., 65 cm long stainless steel U-tube.* The resulting mixture of N_2 and HNO_2, NO and NO_2 entered the mixing chamber via 0.6 cm o.d. Teflon tubing. The desired initial $[HNO_2]$ could be selected by adjusting the flow of the HCl/N_2 mixture. While initial concentrations were being established, the total flow was to be vented without passing into the reactor. When the desired conditions were obtained, a valve in the vent line was to be slowly closed while simultaneously a valve to the evacuated reaction vessel was opened. From the feed system the reactor gases could be passed either into the reactor or to the chemiluminescence analyzer.

2. External Optics

The external optics consisted of a 150 W Xe arc lamp white light source and a 0.5 m monochromator for measurement of intensity of the radiation after passage through the reactor. The monochromator was equipped with

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* This method of producing HNO_2 was suggested to us by Dr. G.E. Streit (NOAA) and Prof. D.H. Stedman (Univ. of Michigan). Since the envisioned experiments were not carried out as a result of problems with the White cell (see Section VI.C), the HNO_2 production method was not verified in the course of the present work.

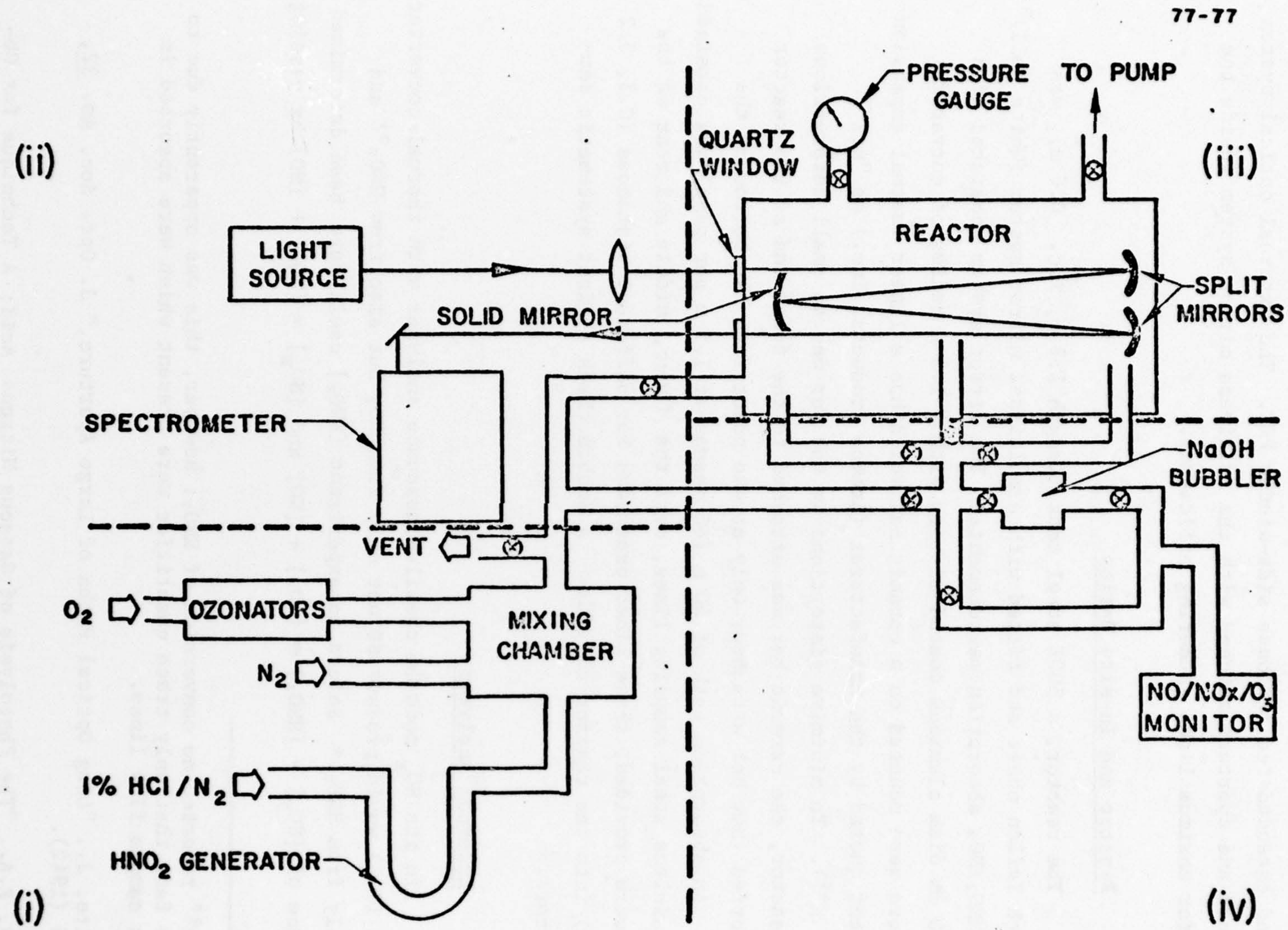

FIGURE 2 SCHEMATIC OF APPARATUS FOR HNO_2/O_3 MEASUREMENTS
(i) reactant feed system, (ii) external optics, (iii) reactor and (iv) external analysis system.

a flat and extended red response side-window PMT. The external optical system was aligned and aperture matched with the multipass mirror system inside the reactor for maximum light gathering efficiency.

3. Reactor and In-situ Optics

The reactor, a 500ℓ steel tank (length 1.8 m, i.d. 0.6 m), was lined with Teflon sheet and fitted with a multipass mirror system (White cell)[28] for the HNO_2/NO_2 absorption measurements. The mirror system consisted of a set of 10 cm diam aluminum coated mirrors with a 1.5 m radius of curvature. The mirrors were mounted on a ceramic bar which has a linear thermal expansion coefficient quoted by the manufacturer (Aremco Products, Inc.) as "nil" ($< 10^{-6}$ K^{-1}). To minimize distortions in the bar due to small deformations of the reactor, the ceramic bar was attached to the front end of the reactor and supported (but not attached) only at one point from the bottom of the reactor. An absorption path of 60 m (40 passes at 1.5 m per pass) was obtained. Three stainless steel sampling lines, near the front, middle and rear of the reactor were provided; these lines protruded for different distances (0.3, 0.2 and 0.1 m) into the reactor to allow a double check against systematic sampling errors.

4. External Analyzer

In its NO_x mode the chemiluminescence analyzer with thermal converter (Section II.B) would produce NO not only from NO_2 but also from HNO_2[29] and presumably from HNO_3.* Before an experiment $[HNO_2]$ could have been determined by difference of $[NO_y] = [HNO_2] + [NO_2] + [NO]$ and $[NO_x] = [NO_2] + [NO]$ by passing

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* Cox[29] reported no conversion of HNO_3; however, this was apparently due to the fact that only trace quantities were present which were absorbed in his sample flow lines.

28. White, J., "Long Optical Paths of Large Aperture," J. Opt. Soc. Am. 32, 285 (1942).

29. Cox, R.A., "The Photolysis of Gaseous Nitrous Acid; A Technique for Obtaining Kinetic Data on Atmospheric Photo-oxidation Reactions," Int. J. Chem. Kin. Symp. 1, 379 (1975).

the mixture through a bubbler containing a 0.1 N NaOH solution which quantitatively removes HNO_2.[29]* Since HNO_3 is most likely also absorbed and is almost certainly a product of Reaction (4), this type of $[HNO_2]$ measurement is not by itself suited to provide a measurement of k_4.

The absolute concentration of the reactant in excess, O_3, is readily determined by the chemiluminescent analyzer in its O_3 mode.

B. METHOD

The following data treatment procedures were envisioned. Reaction (4) is most likely a slow process, while self-decomposition of HNO_2 via Reaction (5) is, on the time scale of the present experiment, relatively rapid.[27] Since the rate of Reaction (5) is proportional to $[HNO_2]$ this necessitates the use of relatively low $[HNO_2]$. Using k_5 from Calvert et al[27] we calculate at room temperature an e-folding time of ≈ 3 hrs for $[HNO_2] = 1 \times 10^{14}\ ml^{-1}$, which appears a minimum useful reaction time. To achieve pseudo first-order kinetics $[O_3] >> [HNO_2]$ would be used. The rate of HNO_2 disappearance is then given by

$$-\frac{d}{dt}[HNO_2] = k_4[HNO_2][O_3] + 2k_5[HNO_2]^2 \qquad (B)$$

By measuring HNO_2 disappearance over a range of $[O_3]$, both k_4 and k_5 can be determined by numerically fitting Eq. (B). Since k_5 was published in the course of this work[27] this procedure could be simplified by substituting k_5. Simplification would, of course, also be possible when either reaction dominates.

During the course of a reaction, $[HNO_2]$ could be measured from its uv absorption at two wavelengths, e.g. 355 and 365 nm. Measurements at two wavelengths are necessary since NO_2, formed in Reaction (5) absorbs in the same wavelength range as HNO_2. The absorption cross sections of HNO_2 at these two wavelengths are taken to be[30] $2.9 \times 10^{-19}\ cm^2$ and $2.3 \times 10^{-19}\ cm^2$,

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* Since HNO_2 was not synthesized in the present work, we have not obtained information on the efficiency of the NaOH solution for trapping HNO_2 and HNO_3 and passing NO and NO_2.

30. Cox, R.A. and Derwent, R.G., "The Ultr-Violet Absorption Spectrum of Gaseous Nitrous Acid," J. Photochem. <u>6</u>, 23 (1976/77).

respectively; the cross sections for NO_2 are[31] 5.53×10^{-19} cm^2 and 5.89×10^{-19} cm^2, respectively. Based on these cross sections 12-15% HNO_2 absorption was anticipated for $[HNO_2] = 1 \times 10^{14}$ ml^{-1}. In order to correct these measurements for fluctuations in intensity due to spurious causes, such as drift in the light source intensity, it was planned to monitor intensity at a third wavelength, e.g. 800 nm, where HNO_2, NO_2 and O_3 do not absorb. Changes in intensity at this wavelength could then be used to normalize the intensities at 355 and 365 nm. As an independent check on the accuracy of the $[HNO_2]$ obtained by uv absorption, a separate $[NO_2]$ measurement was planned using the chemiluminescence monitor, after removal of the acids (HNO_2 + HNO_3) by the NaOH bubbler, cf. Section VI.A.4. Losses of NO_2 in the NaOH solution could then be checked by introducing NO_2 samples into the monitor with and without the bubbler in the sample line.

C. OBSERVATIONS

The first experiments made revealed large intensity excursions due to two causes (i) defocussing of the images on the solid mirror, Fig. 2, related to room temperature variations and (ii) translation of the focussed image on the monochromator slit when the reactor was filled or evacuated. The excursions exceeded in magnitude those which would be caused by $\gtrsim$50% HNO_2 absorption, too large to be meaningfully corrected. The time scale of these phenomena and their recovery was on the order of several hours making measurements effectively impossible. Their cause is distortion of the reactor magnified strongly by the 40-pass mirror system. The cure would have been to design and build another reactor not subject to such distortions. The effort involved would have been well beyond the scope of the present contract. Under these circumstances no further experiments were made.

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31. Johnston, H.S. and Graham, R., "Photochemistry of NO_x and HNO_x Compounds," Can. J. Chem. 52, 1415 (1974).

VII. DISCUSSION AND CONCLUSIONS

On the basis of the present work no information on k_4 is obtained. Considerable further effort, well beyond the funding and time limitations of the present contract, would have been required to obtain a direct measurement of k_4 by the uv absorption method discussed here.

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4. Ref. 1, p 5-210.

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REPORT OF INVENTIONS APPENDIX

No inventions have been achieved during the performance of work under this contract.