PSU-IRL-SCI 380

THE PENNSYLVANIA
STATE UNIVERSITY

IONOSPHERIC RESEARCH

Scientific Report 380

THE REACTION OF OH WITH NO_2

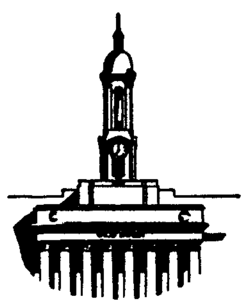
by

R. Simonaitis and Julian Heicklen

February 22, 1972

The research reported in this document has been sponsored by the National Aeronautics and Space Administration under Grant NGL 39-009-003 and in part by the National Science Foundation under Grant No. GA-12385.

IONOSPHERE RESEARCH LABORATORY



University Park, Pennsylvania

PSU-IRL-SCI 380

Scientific Report 380

"The Reaction of OH with NO_2"

by

R. Simonaitis and Julian Heicklen

February 22, 1972

"The research reported in this document has been sponsored by the National Aeronautics and Space Administration under Grant NGL 39-009-003 and in part by the National Science Foundation under Grant No. GA-12385."

Submitted by: Julian Heicklen

Julian Heicklen, Professor of Chemistry
Project Supervisor

Approved by: J S Nisbet

J. S. Nisbet, Director
Ionosphere Research Laboratory

Ionosphere Research Laboratory

The Pennsylvania State University

University Park, Pennsylvania 16802

ABSTRACT

NO_2 was photolyzed with 2288A radiation at 300 and 423°K in the presence of H_2O, CO, and in some cases excess He. The photolysis produces $O(^1D)$ atoms which react with H_2O to give HO radicals

$$O(^1D) + H_2O \rightarrow 2HO \qquad 3$$

or are deactivated by CO to $O(^3P)$ atoms

$$O(^1D) + CO \rightarrow O(^3P) + CO \qquad 5$$

The ratio k_5/k_3 is temperature dependent, being 0.33 at 300°K and 0.60 at 423°K. From these two points the Arrhenius expression is estimated to be $k_5/k_3 = 2.6 \exp(-1200/RT)$ where R is in calories/mole - °K.

The OH radical is either removed by NO_2

$$OH + NO_2(+M) \rightarrow HNO_3(+M) \qquad 1$$

or reacts with CO

$$OH + CO \rightarrow H + CO_2 \qquad 2$$

The ratio k_2/k^∞ is 0.019 at 300°K and 0.027 at 423°K, and the ratio k_2/k^o is 1.65×10^{-5} $\underline{M}$ at 300°K and 2.84×10^{-5} $\underline{M}$ at 423°K with H_2O as the chaperone gas, where $k^\infty = k_1$ in the high-pressure limit and $k^o[M] = k_1$ in the low-pressure limit. When combined with the value of $k_2 = 4.2 \times 10^8 \exp(-1100/RT)$ $\underline{M}^{-1}$ sec^{-1}, $k^\infty = 6.3 \times 10^9 \exp(-340/RT)$ $\underline{M}^{-1}$ sec^{-1} and $k^o = 4.0 \times 10^{12}$ $\underline{M}^{-2}$ sec^{-1} independent of temperature for H_2O as the chaperone gas; He is about 1/8 as efficient as H_2O.

TABLE OF CONTENTS

INTRODUCTION

The reaction of HO with NO_2

$$OH + NO_2 + (M) \rightarrow HNO_3 + (M) \qquad (1)$$

may play an important role in stratospheric ozone balance due to conversion of nitrogen oxides, present naturally and introduced as pollutants by SST aircraft, to nitric acid which eventually appears as nitrate in rain water.[1] Reaction (1) is probably also important in polluted air where it may be an important chain terminating step of NO to NO_2 conversion chains carried by the OH radical.[2]

Reaction (1) was first observed by Wilson and Donovan.[3] Mulcahy and Smith,[4] in a mass spectrometric study of the H + NO_2 system, have obtained an approximate rate coefficient at 300°K of 2×10^8 $\underline{M}^{-1}$ sec^{-1}. Berces et al., studying the photolysis of HNO_3 vapor, have obtained the relative rate coefficient between reaction (1) and the HO + HNO_3 reaction[5] as well as the relative rate coefficient between the HO + HNO_3 reaction and reaction (2)[6]

$$OH + CO \rightarrow CO_2 + H \qquad (2)$$

From their studies $k_1/k_2 = 1.2$ $\underline{M}^{-1}$ where reaction (1) was found to be third order and Kr was the chaperone gas. Because of the importance of reaction (1) to atmospheric chemistry and the lack of considerable kinetic data regarding this reaction, we have undertaken a detailed kinetic study.

The OH radials were generated by the photolysis of NO_2 with 2288 A radiation in the presence of CO and H_2O mixtures. The $O(^1D)$ atom produced by the NO_2 photolysis reacts with H_2O to give OH radicals.

The OH radicals react with either NO_2 in accordance with reaction (1) or with CO via reaction (2). From the measured quantum yield of CO_2 formation, $\Phi\{CO_2\}$, as a function of reactant pressures, inert gas pressure, and temperature, the rate coefficient ratio k_1/k_2 could be obtained as a function of total pressure and temperature. Reaction (2) has been extensively studied[7] and the rate coefficient k_2 is probably good to 30-50%. Thus an absolute value for k_1 could be computed.

In addition to obtaining values for k_1/k_2 it was possible with the same system to obtain relative quenching coefficients for the quenching of $O(^1D)$ by H_2O and CO. These rate constants are of great importance in the chemistry of planetary atmospheres. Confirmed reliable rate constants for these quenching reactions have not been available.

EXPERIMENTAL

A conventional high-vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. Pressures were measured with a dibutylphthalate manometer, a NRC alphatron gauge and a Veeco thermocouple gauge. The reaction vessel was a cylindrical quartz cell 10 cm long by 5 cm in diameter. The cell was enclosed in a wire wound aluminum block furnace, the temperature of which was controlled to $\pm 1^{o}C$ by a Cole-Parmer Proportio Null Regulator Series 1300.

The NO_2 was prepared in situ on the vacuum line from pure NO and O_2. It was purified periodically (when blue N_2O_3 could be seen in the solid NO_2) by the addition of excess O_2 and degassing at $-196^{o}C$. The NO was obtained from Matheson and was purified by distillation from liquid Argon. The CO, O_2 and He (Matheson) were purified by passage over traps maintained at $-196^{o}C$. The H_2O was taken from the tap and small amounts degassed at $-96^{o}C$ prior to use.

Irradiation was from a Phillips Cd resonance lamp TYP 93107 E. The radiation was passed through a 5 cm long cell filled with chlorine at 1 atm. The effective radiation was essentially at 2288 A with small contributions at 2265 and 2144 A.

Actinometry was done by irradiating NO_2 (at comparable pressures to those in an actual run) in the presence of excess N_2O. The reaction sequence is

$$NO_2 \rightarrow NO + O(^1D) \qquad I_a$$

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

$$O(^1D) + N_2O \rightarrow 2NO \qquad b$$

From a measurement of the nitrogen production rate, the absorbed intensity that leads to $O(^1D)$ production, I_a, could be determined, since k_a/k_b for translationally cold $O(^1D)$ atoms is accurately known to be 1.0 in this system.[8] The relative quenching coefficient for $O(^1D)$ by N_2O and NO_2 is known to be 1.6;[9] consequently the ratio $[N_2O]/[NO_2]$ was always maintained $\gtrsim 25$ to insure that $\leq 6\%$ of the $O(^1D)$ atoms react with the NO_2, and this correction was neglected. I_a was not determined for every pressure of NO_2, but was calculated by assuming that I_a was proportional to $[NO_2]$. This assumption is valid, because only a small fraction of the incident radiation was absorbed ($< 5\%$). Irradiation of N_2O in the absence of NO_2, but for otherwise identical conditions did not give N_2; thus direct photolysis of N_2O did not occur.

After irradiation, the condensable (at -196°C) gases were collected and analyzed for CO_2 by gas chromatography using a thermistor detector and a 24 ft. by 1/4" column packed with Porapak Q operating at 25°C. For the actinometry runs an aliquot of the N_2 was collected and analyzed by gas chromatography using a 10 ft. long by 1/4" in diameter column packed with 5 A molecular sieves.

At 25°C a background pressure of CO_2 of 1.5μ was always present independent of conditions and time. This quantity was always substracted from the CO_2 yield. At 150°C the CO_2 background was ~2.0μ and the appropriate correction was always made. At 25°C and 150°C this correction amounted to always $< 10\%$ and usually was of the order of 1-2%. At temperatures > 150°C a dark reaction to give CO_2 becomes important and experiments at temperatures $\gtrsim 150$°C were not possible.

RESULTS

The results of NO_2 photolysis in the presence of mixtures of CO and H_2O are presented in Table I. The CO pressure was varied from 1.32 to 235 torr at 300°K and from 3.56 torr to 348 torr at 423°K. The initial NO_2 pressure, $[NO_2]_o$, was changed from 0.39 torr to 2.78 torr at 300°K and from 0.54 to 1.55 torr at 423°K. Considerable NO_2 was consumed during the runs, and the average NO_2 pressure, $[NO_2]$, was lower than $[NO_2]_o$. The ratio of $[CO]/[NO_2]_o$ ranged from 0.61 to 224 at 300°K and from 3.23 to 295 at 423°K. The $[H_2O]/[NO_2]_o$ ratio ranged from 6.42 to 36 at 300°K and from 7.8 to 20 at 423°K. The $[CO]/[H_2O]$ ratio was varied from 0.065 to 17.4 at 300°K and from 0.193 to 22 at 423°K. The total pressure was altered by changing the H_2O pressure at lower CO pressures and by adding helium at higher CO pressures. At 300°K the H_2O pressure ranged from 5.40 to 20.2 torr and the helium pressure was varied from 59 to 1080 torr at about a constant H_2O pressure of 12-15 torr. At 423°K the H_2O pressure ranged from 4.26 to 18.5 torr and the He pressure ranged from 495 to 1040 torr with about 12-16 torr of H_2O also present. At higher CO pressures the CO also makes a small contribution to the total pressure. The contribution of NO_2 to the total pressure was neglected.

The data can be summarized as follows. The quantum yield of CO_2 formation, $\Phi\{CO_2\}$, is approximately proportional to $[CO]/[NO_2]$ under all conditions, is independent of $[H_2O]$ at low $[CO]/[H_2O]$ and constant total pressure, but decreases as $[CO]/[H_2O]$ becomes large. $\Phi\{CO_2\}$ also drops if He is added or the total pressure is raised, but this effect is less pronounced at higher pressures. At 423°K, $\Phi\{CO_2\}$ is generally higher than at 300°K for otherwise comparable conditions.

DISCUSSION

At low $[CO]/[H_2O]$ ratios the facts can be accounted for by the following scheme:

$$NO_2 \rightarrow NO + O(^1D) \qquad \text{Ia}$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (3)$$

$$OH + NO_2 \rightleftharpoons HONO_2^* \qquad (1a)$$

$$HONO_2^* + M \rightarrow HONO_2 + M \qquad (1b)$$

$$OH + CO \rightarrow CO_2 + H \qquad (2)$$

$$H + NO_2 \rightarrow OH + NO \qquad (4)$$

At higher $[CO]/[H_2O]$ ratios the quenching of $O(^1D)$ by CO becomes important

$$O(^1D) + CO \rightarrow CO + O(^3P) \qquad (5)$$

The photolysis of NO_2 at 2288 A is known to give $O(^1D)$ atoms with a quantum efficiency of 0.3 - 0.4.[8,9] Any $O(^3P)$ produced is removed by reaction with NO_2. Reaction (3) is the dominant (>90%), if not exclusive reaction for $O(^1D) + H_2O$.[10] Reaction (1) is presumed to give nitric acid, though this has never been demonstrated. Reaction (1) is written in detail to account for the pressure dependence of $\Phi\{CO_2\}$. $HONO_2^*$ is an initially formed energy rich intermediate which may revert to starting material or be stabilized by collision with a chaperone M, where $[M] \cong$ a $[He]$ + b $[H_2O]$ + c $[CO]$ and a, b, and c represent the relative collision efficiencies. Reactions (2) and (4) are well known.[7,11] Since reaction

(4) is very fast ($k_4 = 4.8 \times 10^{-11}$ cm^3/sec[11]) it is the only reaction consuming H atoms. Reaction (5) is the dominant reaction for the quenching of O(^{1}D) by CO.[12, 13]

<u>Determination of k_1/k_2:</u> Based on the above scheme the following rate law for CO_2 formation may be obtained:

$$\Phi\{CO_2\} = \frac{2k_2}{k_1} \frac{[CO]}{[NO_2]} \left(\frac{k_3[H_2O]}{k_3[H_2O] + k_5[CO]} \right) \qquad \text{I}$$

where

$$k_1 = \frac{k_{1a} k_{1b}[M]}{k_{-1a} + k_{1b}[M]}$$

The limiting high and low pressure rate constants are:

$$M \to \infty \quad k_1 \to k_{1a} \equiv k^{\infty}$$

$$M \to 0 \quad k_1 \to \frac{k_{1a}}{k_{-1a}} k_{1b}[M] \equiv k^{o}[M]$$

In order to test the above rate law and to obtain k^{∞} and k^{o} it is convenient to rearrange equation I to

$$\Phi'\{CO_2\}[NO_2]/[CO] = \frac{2k_2}{k^{\infty}} + \frac{2k_2}{k^{o}} \frac{1}{[M]} \qquad \text{II}$$

where

$$\Phi'\{CO_2\} \equiv \Phi\{CO_2\} \left(1 + \frac{k_5[CO]}{k_3[H_2O]} \right)$$

A plot $\Phi'\{CO_2\}$ $[NO_2]/[CO]$ vs. $1/[M]$ should be linear with the intercept = $2k_2/k^{\infty}$ and the slope = $2k_2/k^{o}$. In order to calculate $\Phi'\{CO_2\}$, k_5/k_3 must be known. k_5/k_3 was determined from experiments at high $[CO]/[H_2O]$ ratios, as shown below, to be 0.33 and 0.60, respectively at 300 and 423°K. The efficiency of M in step 1b will depend on the gas. In general $[M] = a\,[He] + b\,[H_2O] + c\,[CO]$ (the contribution due to NO_2 is neglected since its pressure is always very low). If M is taken simply as the total pressure, then a plot of equation II gives a smooth but nonlinear curve for He + H_2O mixtures and a straight line in the absence of He. A straight line plot is obtained over the whole range of He + H_2O mixtures and over the complete range of H_2O pressures in the absence of He if we take a:b:c = 1:8:1.5. This plot is shown in Figure 1. Appreciable deviation of the plot from a straight line is observed when $b < 6$ or > 10. The value of 1.5 for c is not determined from our data, (since $c\,[CO] < a\,[He] + b\,[H_2O]$ the plot is very insensitive to c), but taken as the relative quenching efficiency of a diatomic gas compared to a monatomic gas observed in other systems.

The plot in Figure 1 does not clearly demonstrate the dependence of $\Phi'\{CO_2\}$ on the $[CO]/[NO_2]$ ratio. This dependence is clearly shown by a log-log plot in Figure 2 of $\Phi'\{CO_2\}$ vs. $[CO]/[NO_2]$ at 500 - 1100 torr He and 300°K. In this pressure range of He, $\Phi'\{CO_2\}$ is virtually independent of [M] as is demonstrated in Figure 1. Figure 2 also shows a plot of the same quantities in the absence of He and an approximately constant H_2O pressure (13-20 torr) but varying CO pressure ($[CO] \leq 0.5\,[H_2O]$). Both plots in Figure 2 are linear with unit slopes, and thus conform to the prediction of equation I and show that $b\,[H_2O] \gg c\,[CO]$.

The plots of Figures 1 and 2 clearly establish the validity of the rate law for CO_2 formation. The intercepts in Figure 1 are 0.038 and 0.055 at 300°K and 423°K respectively; thus $k_2/k^\infty = 0.019$ at 300°K and $k_2/k^\infty = 0.027$ at 423°K. The slopes of the plots in Figure 1 are 4.9 and 11.9 torr at 300 and 423°K, respectively; consequently $k_2/k^o_{H_2O} = 1.65 \times 10^{-5}$ $\underline{M}$ at 300°K and $k_2/k^o_{H_2O} = 2.84 \times 10^{-5}$ $\underline{M}$ at 423°K for H_2O as a chaperone gas. With He as the chaperone, the values for k_2/k^o are 8 times larger, but still the value at 300°K is 6300 times smaller than that found by Berces et al.[5,6]

The Arrhenius expression may be obtained from the results at the two temperatures to be $k_2/k^\infty = 6.7 \times 10^{-2} \exp(-760/RT)$ and $k_2/k^o_{H_2O} = 10.5 \times 10^{-5} \exp(-1100/RT)$ $\underline{M}$. Absolute values for k^o and k^∞ may be calculated from the known value of k_2, which has been the subject of numerous determinations. Baulch et al.[7] give $k_2 = 4.2 \times 10^8 \exp(-1100/RT)$ $\underline{M}^{-1}$ sec^{-1} based on a critical evaluation of all the determinations. It is very unlikely that the values for k_2 given by Baulch et al. are off by more than a factor of 2 and are probably good to 20 - 30% in the temperature range of interest here. The results are $k^\infty = 6.3 \times 10^9 \exp(-340/RT)$ $\underline{M}^{-1}$ sec^{-1} and $k^o_{H_2O} = 4.0 \times 10^{12}$ $\underline{M}^{-2}$ sec^{-1} independent of temperature. For He as the third body $k^o_{He} = 5 \times 10^{11}$ $\underline{M}^{-2}$ sec^{-1}.

It is interesting to compare our results for k_1 to the semiquantitative value for k_1 obtained by Mulcahy and Smith[4] at 300°K and in the pressure range of 0.2 - 1 torr (principally Ar or He). These authors were unable to decide whether reaction 1 was heterogeneous or homogeneous under their experimental conditions, but assuming the reaction is homogeneous a second order rate constant of 2×10^8 $\underline{M}^{-1}$ sec^{-1} was obtained. This value is a factor of 14 less than ours. However, according to our results reaction (1) will be third order in the pressure range used by Mulcahy and Smith. If their value is recomputed on a third order basis $k^o_{Ar, He} = 6 \times 10^{12}$ $\underline{M}^{-2}$ sec^{-1}. This value for k^o is a factor of 12 larger than our value for He as the third body. The present results definitely exclude the possibility that under our conditions reaction (1) could be heterogeneous for 2 reasons: 1) Pressures as high as 1100 torr were employed; thus diffusion could not compete with reaction (5), which has a time constant of $\sim 10^{-4}$ sec, 2) The pressure dependence is in the wrong direction of that expected if reaction (1) was heterogeneous.

The values of $k^o_{H_2O} = 4.0 \times 10^{12}$ $\underline{M}^{-2}$ sec^{-1} is very large, but not unreasonable for the complexity of the $HONO_2$ molecule as demonstrated by the following crude computation. The lifetime of the $HONO_2^*$ complex may be computed from $\tau^{-1} = k_{-1a} = A\left(\frac{E - E^o}{E}\right)^{n-1}$ where A is a frequency factor, E is the total energy of the complex, E^o is the activation energy for decomposition of the complex and n is the effective number of oscillators. Taking $A \cong 10^{13}$ sec^{-1}, n = 5 and E^o = 49 kcal/mole (the bond dissociation energy D $\{HO - NO_2\}$), τ is calculated to be $\sim 1 \times 10^{-8}$ sec at 300°K. The lifetime computed from k^o and k^∞ is the same, assuming that $k_{1b} = 1 \times 10^{11}$ $\underline{M}^{-1}$ sec^{-1} for H_2O as the chaperone.

<u>Determination of k_5/k_3:</u> In order to determine k_5/k_3 expression I may be rearranged to

$$\Phi''\{CO_2\}^{-1} = 1 + \frac{k_5[CO]}{k_3[H_2O]} \qquad \text{III}$$

where

$$\Phi''\{CO_2\} = \Phi\{CO_2\} \frac{k_1}{2k_2} \frac{[NO_2]}{[CO]}$$

A plot of $\Phi''\{CO_2\}^{-1}$ vs. $[CO]/[H_2O]$ should be linear with a slope of k_5/k_3. This expression is useful only when $k_5[CO] \geq k_3[H_2O]$, or at relatively high $[CO]/[H_2O]$ ratios. In order to obtain k_5/k_3, k_1/k_2 must be known and vice versa. To get around this problem initially experiments were done at low $[CO]/[H_2O]$ ratios such that $\Phi'\{CO_2\} \approx \Phi\{CO_2\}$. A plot of $\Phi\{CO_2\}$ $[NO_2]/[CO]$ vs. $1/[M]$ (equation II) gave an initial value of k_2/k^{∞}. This initial value of k_2/k^{∞} was used to obtain an approximate value of k_5/k_3 via equation III. Using this approximate value for k_5/k_3, $\Phi'\{CO_2\}$ was caluclated and accurate values of k_2/k_1^{∞} and k_2/k^{o} obtained. Finally, using the accurate value of k_2/k^{∞} the final value of k_5/k_3 was obtained. Experiments at high $[CO]/[H_2O]$ ratios were done also at high He pressures so that reaction (1) was in the second order region. A plot of $\Phi''\{CO_2\}^{-1}$ vs. $[CO]/[H_2O]$ is shown in Figure 3. The fit at 300^{o}K is good, but at 423^{o}K some scatter is present. From the plots in Figure 3, k_5/k_3 is found to be 0.33 and 0.60 at 300^{o}K and 423^{o}K, respectively. From these two points the Arrhenius expression can be estimated to be $k_5/k_3 = 2.64 \exp(-1240/RT)$. This small though definitely real temperature effect implies that the deactivation of $O(^1D)$ by CO proceeds via an excited CO_2 state which probably is the $^1B_2$ state. The activation energy arises from a potential barrier for crossing to products. It is interesting to correlate the present results with our earlier study of $O(^3P)$ + CO recombination.[14] In that study it was concluded that recombination proceeds via the $^1B_2$ state with a potential barrier 1.2 kcal/mole above the $^1B_2$ state. Consequently the reverse process should have an activation energy of 1.2 kcal/mole in agreement with the activation energy observed here for $O(^1D)$ deactivation by CO.

Several determinations of k_5 and k_3 relative to k_6 have been made, where reaction 6 is

$$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2 \qquad (6)$$

These values may be combined to give k_5/k_3. Table II lists the relevant rate constant ratios. Combination of our room temperature value of 0.33 for k_5/k_3 with the value of 2.76 for k_3/k_6 gives $k_5/k_6 = 0.91$. This value is in reasonable agreement with that of Yamazaki,[18] but somewhat higher than that found by others (except the value of Clerc and Reiffsteck,[15] which appears to be erroneous).

ACKNOWLEDGEMENT

A conversation with Dr. M.F.R. Mulcahy was helpful. This work was supported by the National Aeronautics and Space Administration under Grant No. NGL 39-009-003 and the atmospheric Sciences Section of the National Science Foundation under Grant No. GA-12385, for which we are grateful.

REFERENCES

1. M. Nicolet, Aeronomie Acta, 79 (1970).
2. J. Heicklen, R. Westberg and N. Cohen, Center for Air Environment Studies Report No. 115-69, Penn State University (1969).
3. W. E. Wilson and J. T. O'Donovan, J. Chem. Phys., 47, 5455 (1967).
4. M. F. R. Mulcahy and R. H. Smith, J. Chem. Phys., 54, 5215 (1971).
5. T. Bérces and S. Förgeteg, Trans. Faraday Soc., 66, 640 (1970).
6. T. Bérces, S. Förgeteg, and F. Marta, Trans. Faraday Soc., 66, 648 (1970).
7. For a critical review see D. L. Baulch, D. D. Drysdale and A. C. Lloyd, "High Temperature Reaction Rate Data," Dept. of Phys. Chem., Leeds University No. 1 (1968).
8. P. M. Scott, K. F. Preston, R. J. Andersen, and L. M. Quick, Canad. J. Chem., 49, 1808 (1971).
9. K. F. Preston and R. J. Cvetanović, J. Chem. Phys., 45, 2888 (1966).
10. R. Simonaitis and J. Heicklen, unpublished work (1971).
11. L. F. Phillips and H. I. Schiff, J. Chem. Phys., 37, 1233 (1962).
12. O. F. Raper and W. B. DeMore, J. Chem. Phys., 40, 1053 (1964).
13. G. Paraskevopoulos and R. J. Cvetanović, J. Am. Chem. Soc., 91, 7572 (1969).
14. R. Simonaitis and J. Heicklen, J. Chem. Phys., in press.
15. M. Clerc and A. Reiffsteck, J. Chem. Phys., 48, 2799 (1968).
16. R. A. Young, G. Black and T. G. Slanger, J. Chem. Phys., 49, 4758 (1968).
17. W. B. DeMore, J. Chem. Phys., 52, 4309 (1970).
18. H. Yamazaki, Canad. J. Chem., 48, 3269 (1970).
19. P. M. Scott and R. J. Cvetanović, J. Chem. Phys., 54, 1440 (1971).
20. E. Lissi and J. Heicklen, J. Photochem., in press (1972).

Table I: Photolysis of NO_2 at 2288 A in the Presence of CO and H_2O

$[CO]/[NO_2]$ [a]	$[NO_2]_o$, Torr	[CO], Torr	$[H_2O]$, Torr	[He], Torr	Irradiation Time, min	I_a, μ/min [b]	$\Phi\{CO_2\}$
			Temp = 300°K				
0.67	2.78	1.70	18.7	0	35.0	1.86	0.0462
1.42	1.00	1.32	18.6	0	30.0	0.66	0.103
1.43	2.71	3.56	17.4	0	35.0	1.82	0.0850
1.72	0.96	1.32	20.2	0	90.0	0.60	0.124
2.23	1.01	2.10	19.0	0	31.0	0.66	0.153
3.50	1.20	3.92	15.6	620	30.0	0.79	0.200
3.76	1.20	4.06	15.7	620	45.0	0.79	0.188
3.79	1.01	3.56	14.3	0	30.0	0.67	0.284
5.72	0.388	1.98	3.84	0	45.0	0.23	0.875
6.05	0.735	3.96	7.05	0	45.0	0.46	0.563
6.90	0.580	3.48	5.40	0	40.0	0.39	0.715
6.93	1.01	6.82	12.4	0	10.0	0.67	0.483
6.95	1.08	6.95	15.4	1080	32.0	0.71	0.310
7.35	1.05	7.12	15.0	560	30.0	0.70	0.287
7.43	1.01	6.97	15.2	0	30.0	0.66	0.462
7.57	1.01	7.12	14.3	348	30.0	0.66	0.337
7.65	1.01	7.12	15.0	0	32.0	0.66	0.530
7.82	1.08	7.82	14.1	560	32.0	0.71	0.310
7.83	1.01	7.30	13.1	164	30.0	0.66	0.395
7.88	1.01	7.35	13.1	59	30.0	0.65	0.475
8.10	1.01	7.45	13.3	0	34.0	0.72	0.490
8.50	0.97	7.50	13.9	0	34.0	0.69	0.485
9.20	1.01	6.90	16.5	0	116.0	0.60	0.358
11.18	0.735	7.35	12.4	740	45.0	0.46	0.483
20.4	0.387	7.20	14.4	560	45.0	0.187	1.05
20.6	0.430	7.85	15.4	0	45.0	0.25	1.70
23.5	1.08	23.5	12.4	689	31.0	0.70	0.666
64.6	1.08	68	12.7	645	10.0	0.72	1.05
69.5	1.06	68	12.8	660	30.0	0.68	1.17
124	1.12	128	12.8	560	30.0	0.76	1.30
228	1.16	235	13.5	476	45.0	0.71	1.46

Table I Continued

$[CO]/[NO_2]^a$	$[NO_2]_o$, Torr	[CO], Torr	$[H_2O]$, Torr	[He], Torr	Irradiation Time, min	I_a, μ/min^b	$\Phi\{CO_2\}$
Temp = 423°K							
3.20	1.16	3.56	18.5	0	32.0	0.667	0.832
5.75	1.55	8.45	11.6	705	30.0	0.692	0.364
6.21	1.43	8.40	12.0	1040	25.0	0.845	0.331
7.72	0.543	3.80	10.7	0	40.0	0.308	1.36
7.95	0.543	3.87	4.80	0	40.0	0.304	2.05
8.75	0.543	4.30	4.26	0	36.0	0.303	2.20
56.0	1.24	65	14.0	780	30.0	0.720	1.24
118	1.20	132	13.5	870	30.0	0.692	1.30
125	1.16	135	12.6	890	30.0	0.668	1.05
300	1.24	348	15.8	495	30.0	0.720	1.10

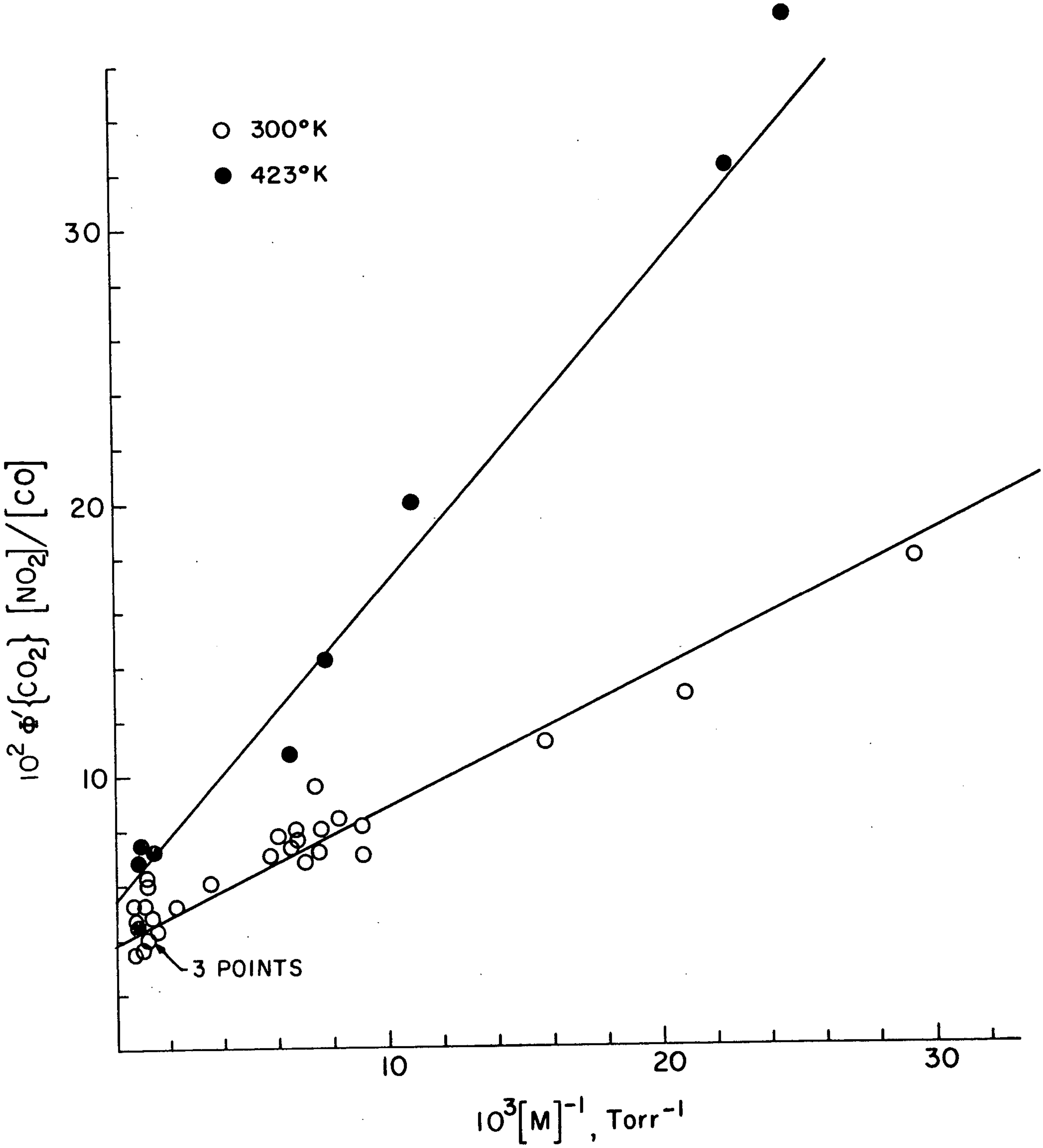
a) $[NO_2]$ assumed equal to $[NO_2]_o - (7 + \Phi\{CO_2\}) I_a t/2$

b) $I_a = 0.710\ \mu/min$ at $[NO_2] = 1.05$ torr and 300°K. $I_a = 0.790\ \mu/min$ at $[NO_2] = 1.30$ torr and 423°K. Values of I_a at other pressures of NO_2 are computed by assuming that I_a is proportional to $[NO_2]$. Pressures used in I_a and the reactant pressures are at the temperature of the experiment. I_a is not the true absorbed intensity, but only that fraction (~ 1/3) leading to $O(^1D)$ production.

Table II: Relative Rate Coefficients for $O(^1D)$ Deactivation

Ratio	Value	Reference
k_5/k_6	55	Clerc and Reiffsteck[15]
k_5/k_6	0.22	Young et al.[16]
k_5/k_6	0.59	Paraskevopoulos and Cvetanović[13]
k_5/k_6	0.41	DeMore[17]
k_5/k_6	0.79	Yamazaki[18]
k_3/k_6	2.76	Scott and Cvetanović[19]
k_3/k_6	3.00	Lissi and Heicklen[20]

LIST OF FIGURES



○ 300°K
● 423°K
30
20
10
$10^2\,\Phi'\{CO_2\}\ [NO_2]/[CO]$
3 POINTS
10
20
30
$10^3[M]^{-1}$, Torr^{-1}

Figure 1

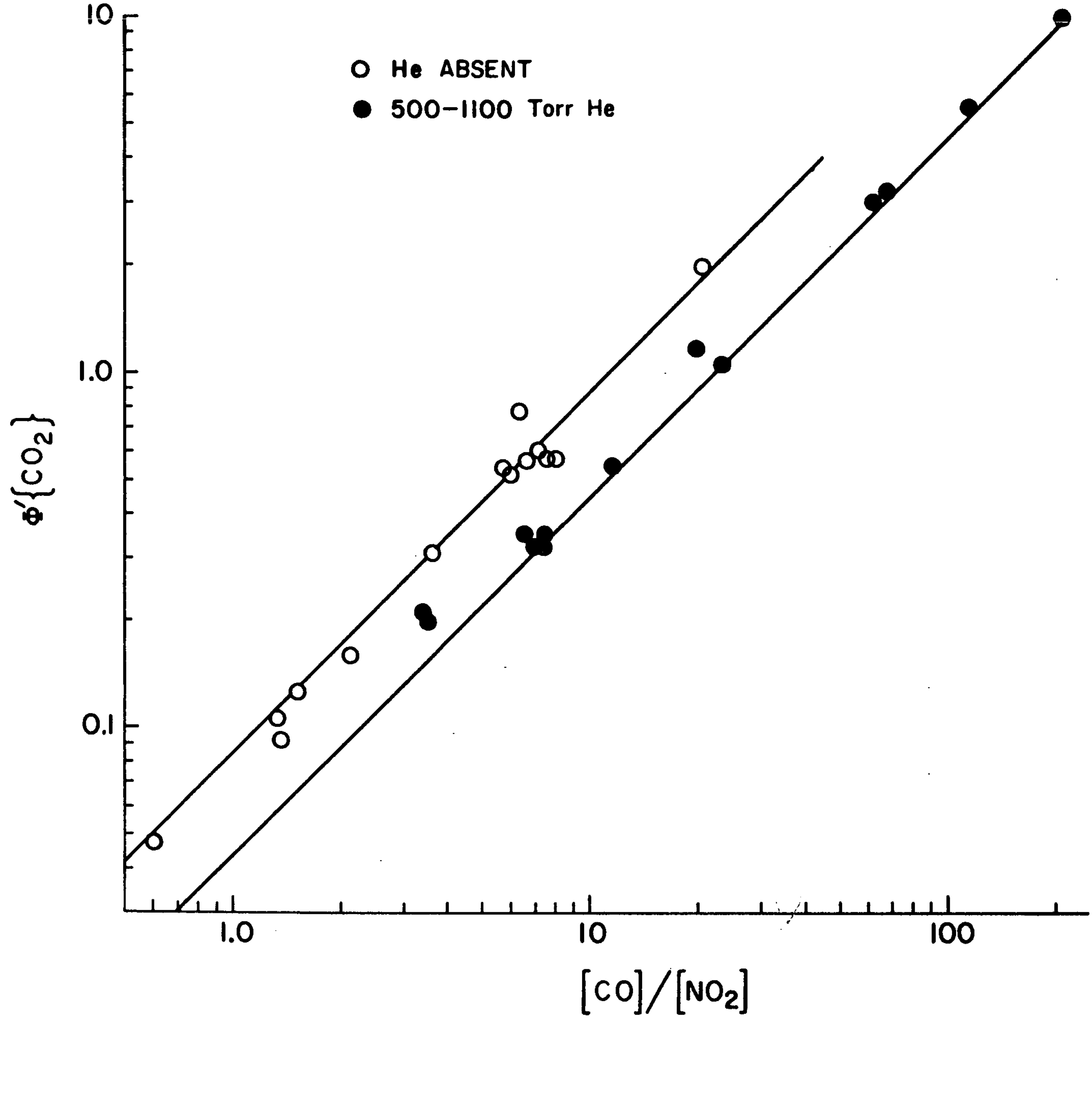


Figure 2

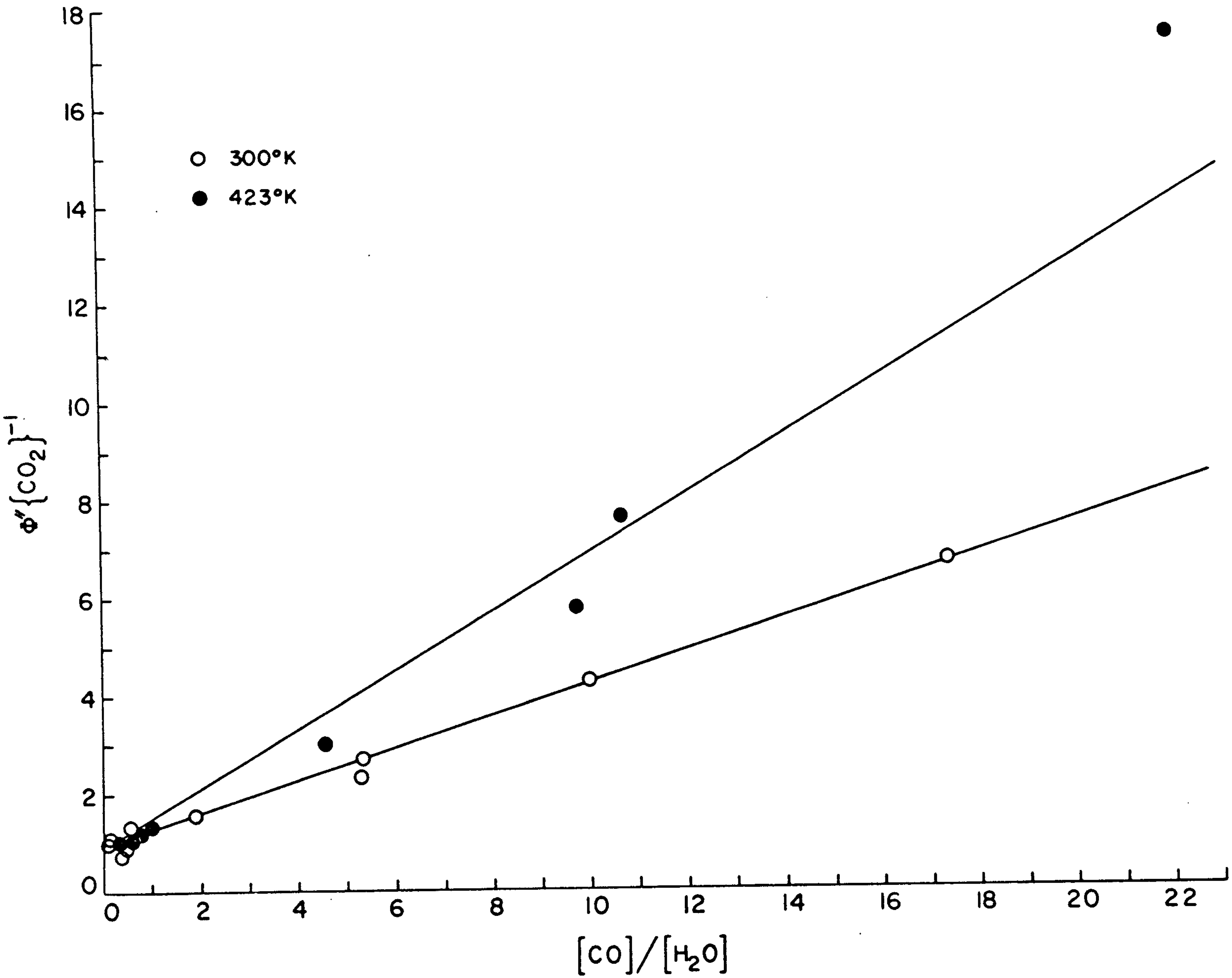


Figure 3