

## PHOTOLYSIS OF NO AT 2139 AND 2265 Å IN THE PRESENCE OF CO<sub>2</sub>

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### SUMMARY

The room-temperature photolysis of NO in the absence and presence of CO<sub>2</sub> was studied at 2139 Å, and in the presence of CO<sub>2</sub> at 2265 Å. Both wavelengths produce the A<sup>2</sup>Σ<sup>+</sup> state of NO, but the former gives  $\nu = 1$ , whereas the latter gives  $\nu = 0$ . At both wavelengths the results are the same. The products measured were N<sub>2</sub> and N<sub>2</sub>O in the absence of CO<sub>2</sub>, and N<sub>2</sub> and CO in the presence of CO<sub>2</sub>. The ratio [CO<sub>2</sub>]/[NO] was varied by a factor of 2600. All of the CO production can be explained by interaction of NO(A<sup>2</sup>Σ<sup>+</sup>) with CO<sub>2</sub>. However, two reactive states are required to explain the production of N<sub>2</sub>. The second reactive state must be either NO(a<sup>4</sup>Π) or high vibrational levels of the ground electronic state of NO, and it is produced by collisional deactivation of NO(A<sup>2</sup>Σ<sup>+</sup>). The formation of N<sub>2</sub> and N<sub>2</sub>O may proceed via an energy rich N<sub>2</sub>O<sub>2</sub> dimer. Relative rate constants for the various quenching reactions are listed in Table IV.

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### INTRODUCTION

The reactions of NO(A<sup>2</sup>Σ<sup>+</sup>) with NO and CO<sub>2</sub> have been previously studied by Kleinberg and Terenin<sup>1</sup> and by Heicklen and co-workers<sup>2-4</sup>. Fluorescence quenching of NO(A<sup>2</sup>Σ<sup>+</sup>) by NO and CO<sub>2</sub> has been studied in a number of laboratories and the quenching constants are fairly well known<sup>1,5-8</sup>. The product formation studies were with a mixture of 2144 and 2265 Å radiation<sup>4</sup>. These wavelengths excite the  $\nu = 1$  and  $\nu = 0$  vibrational states of NO(A<sup>2</sup>Σ<sup>+</sup>) respectively. Basco *et al.*<sup>5</sup> reported that the  $\nu = 0$  level of the NO(A<sup>2</sup>Σ<sup>+</sup>) state does not chemically react with NO. In the present paper we present results for studies carried out with monochromatic radiation at 2139 Å and 2265 Å in order to determine if the  $\nu = 0$  and  $\nu = 1$  levels of the A<sup>2</sup>Σ<sup>+</sup> state have different reactivity. Furthermore,

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in the studies by Heicklen and co-workers<sup>2-4</sup> absolute product quantum yields were not determined. Thus, an evaluation of chemical *versus* physical quenching of  $\text{NO}(\text{A}^2\Sigma^+)$  by  $\text{NO}$  and  $\text{CO}_2$  was not possible. We have measured absolute quantum yields and were able to separate physical *versus* chemical quenching.

#### EXPERIMENTAL

The experiments were carried out in a quartz cell 10 cm long and 5 cm in diameter. The optical sources were quartz jacketed, cadmium and zinc resonance lamps from the Phillips Co., TYP 93107E and TYP 93106E, respectively. A quartz cell, 5 cm long and 5 cm in diameter, filled with  $\text{NH}_3$  at a pressure of 600 Torr was used as a filter for the cadmium lamp. This effectively removed the 2144 Å radiation and transmitted the 2265 Å radiation. A sodium chloride filter was used with the zinc lamp to remove radiation below 2050 Å.

The gases used were from the Matheson Co. The  $\text{N}_2\text{O}$  used for actinometry was degassed at  $-196^\circ\text{C}$  before use. The  $\text{CO}_2$  and  $\text{NO}$  were purified by distillation at  $-130^\circ\text{C}$  and  $-186^\circ\text{C}$ , respectively, and degassed at  $-196^\circ\text{C}$  immediately before use.

After irradiation of  $\text{NO}$  and  $\text{CO}_2$  mixtures, the contents were expanded into the vacuum line through a trap cooled by liquid nitrogen to retain the condensable gases. An aliquot of the non-condensable gases,  $\text{CO}$  and  $\text{N}_2$ , was analyzed on a gas chromatograph using a 12-ft. long by 1/4 in. diameter copper tube containing 5 Å molecular sieves connected to the vacuum line.

After irradiation of pure  $\text{NO}$  the cell contents were allowed to expand into the vacuum through a trap cooled by liquid nitrogen and an aliquot was analyzed by gas chromatography. The remaining non-condensable gases were pumped away and the gases condensable at  $-196^\circ\text{C}$  were distilled at  $-186^\circ\text{C}$  to remove the excess  $\text{NO}$ . The products remaining after this distillation were allowed to warm and expand into the vacuum line and an aliquot was analyzed by gas chromatography for  $\text{N}_2\text{O}$  using a 20-ft. long by 1/4 in. diameter copper tube containing Porapak Q resin.

$\text{N}_2\text{O}$  was used as an actinometer at 2139 Å by matching the absorbance with  $\text{NO}$  at the experimental conditions of each run. This was necessary because of the rather large pressure broadening of the  $\text{NO}$  spectrum by  $\text{CO}_2$ . To obtain an accurate matching of the absorbances and to cancel other lines emitted by the Zn lamp, but which are not absorbed by either  $\text{N}_2\text{O}$  or  $\text{NO}$ , a sensitive balance was established between two photo-tubes (RCA 935) incorporated into the arms of a Wheatstone bridge. The bridge was balanced for the empty cell and a base line was established on the recorder. The  $\text{NO}$  and  $\text{CO}_2$  were admitted into the cell, and the difference between the base line for the empty cell and the base line for the  $\text{NO}$  and  $\text{CO}_2$  was measured. After the run was completed actinometry was done by allowing enough  $\text{N}_2\text{O}$  in the cell to attain the same difference between the empty cell and cell with

N<sub>2</sub>O as observed between the empty cell and the cell with NO plus CO<sub>2</sub>. Actinometry could not be done at 2265 Å because of the strong line at 2288 Å of the cadmium lamp. In the actinometry experiments, the rate of N<sub>2</sub> production was measured. Since the quantum yield of N<sub>2</sub> production is 1.41,<sup>9</sup> the absorbed intensity, *I*<sub>a</sub> is the rate of N<sub>2</sub> production divided by 1.41. The units used here correspond to actual measurement, *i.e.*, mTorr/min. They can be changed to Einstein/l min by dividing by 1.86 × 10<sup>7</sup>.

## RESULTS

At 2139 Å, when mixtures of CO<sub>2</sub> and NO are irradiated, the only products observed and measured are CO and N<sub>2</sub>. Presumably N<sub>2</sub>O and NO<sub>2</sub> are also formed but N<sub>2</sub>O was not determined because of the difficulty of analysis of small amounts of N<sub>2</sub>O in the presence of a large excess of CO<sub>2</sub>. The results of the photolysis of NO in the presence of CO<sub>2</sub> are presented in Table I. The ratio [CO<sub>2</sub>]/[NO] was varied from 0.013 to 33.7. The CO<sub>2</sub> and NO pressures were varied from 1.25 to 695 Torr and 20–102 Torr, respectively. The quantum yield of CO,  $\Phi\{\text{CO}\}$ , in-

TABLE I

PHOTOLYSIS OF NO IN THE PRESENCE OF CO<sub>2</sub> AT 2139 Å AND 25°C

[CO <sub>2</sub> ] [NO]	[NO] (Torr)	[CO <sub>2</sub> ] (Torr)	Irradiation time (min)	<i>I</i> <sub>a</sub> (mTorr/min)	[CO] [N <sub>2</sub> ]	$\Phi\{\text{CO}\}$	$\Phi\{\text{N}_2\}$ <sup>a</sup>
0.013	96.7	1.25	1257	—	0.227	—	0.019 <sup>b</sup>
0.016	101.0	1.67	120	9.00	0.221	0.0055	0.025
0.021	96.0	2.00	1287	5.28	0.360	0.0053	0.018
0.028	100.0	2.80	120	10.00	0.416	0.0083	0.020
0.034	99.7	3.34	120	8.95	0.405	0.011	0.027
0.059	102.0	6.0	120	9.16	0.588	0.018	0.031
0.19	43.2	8.4	120	4.95	2.67	0.050	0.018
1.31	20.6	26.9	120	3.40	8.67	0.14	0.016
1.75	20.0	35.0	1164	1.55	15.1	0.15	0.011
2.59	20.6	51.8	1181	1.89	23.0	0.15	0.0064
2.88	20.6	65.0	1050	2.64	26.2	0.15	0.0056
3.80	20.6	79.4	1307	—	25.0	—	0.0061 <sup>b</sup>
7.67	20.6	158	1307	—	37.4	—	0.0042 <sup>b</sup>
8.88	20.6	183	1262	—	35.0	—	0.0045 <sup>b</sup>
9.00	20.0	180	120	5.73	—	0.16	—
12.4	21.2	263	120	6.60	—	0.17	—
12.8	20.6	263	1262	—	34.7	—	0.0046 <sup>b</sup>
16.5	20.0	330	240	—	48.0	—	0.0029
18.3	20.6	377	120	8.35	41.0	0.17	0.0041
19.0	20.6	392	1115	—	47.0	—	0.0035 <sup>b</sup>
24.4	20.0	488	1136	—	46.4	—	0.0035 <sup>b</sup>
26.9	20.0	538	1165	—	49.5	—	0.0033 <sup>b</sup>
33.7	20.6	695	1115	—	48.0	—	0.0036 <sup>b</sup>

<sup>a</sup> All N<sub>2</sub> yields corrected for 1.5 mTorr background value.

<sup>b</sup> Calculated from  $\Phi\{\text{CO}\}^{-1}$  vs. [NO]/[CO<sub>2</sub>] plot Fig. 5 and [CO]/[N<sub>2</sub>] ratio.

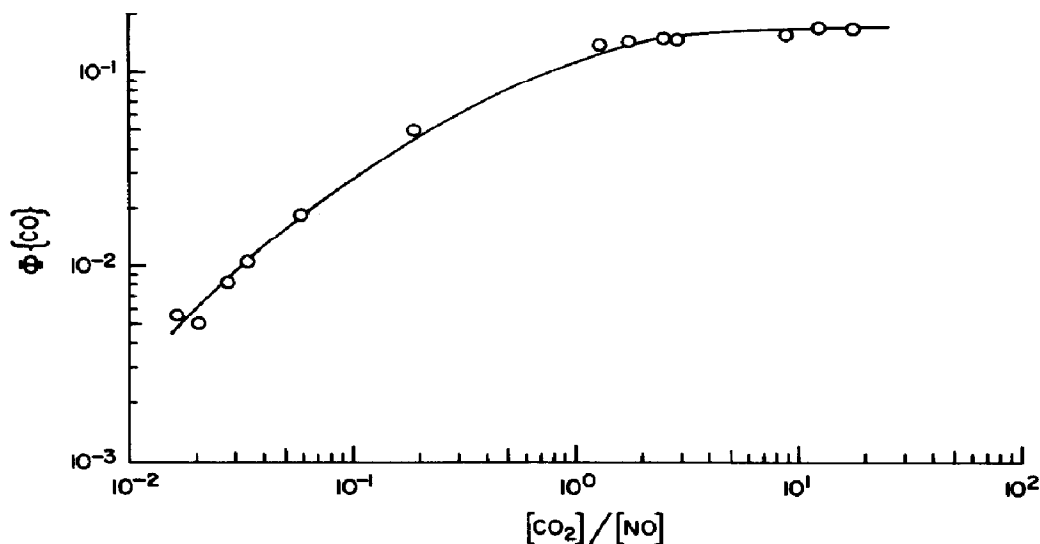


Fig. 1. Log-log plot of  $\Phi\{\text{CO}\}$  vs.  $[\text{CO}_2]/[\text{NO}]$  in the photolysis of NO in the presence of  $\text{CO}_2$  at 2139 Å and 25°C.

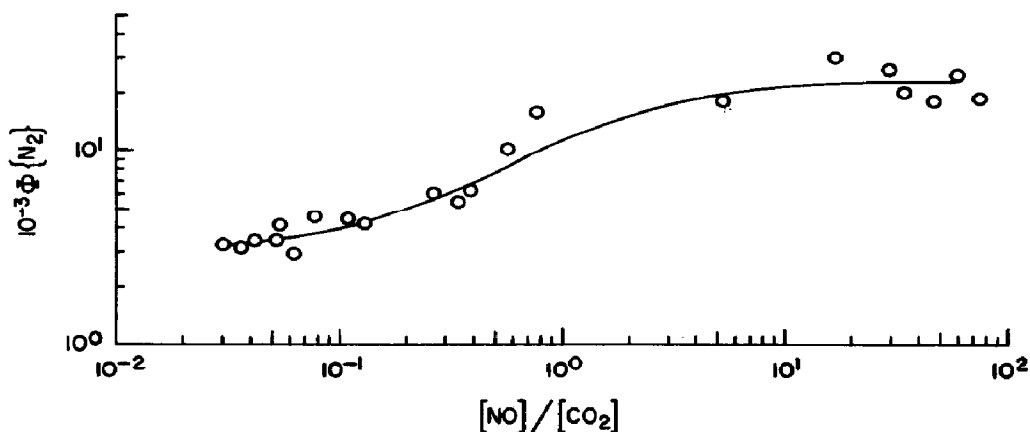


Fig. 2. Log-log plot of  $\Phi\{\text{N}_2\}$  vs.  $[\text{NO}]/[\text{CO}_2]$  in the photolysis of NO in the presence of  $\text{CO}_2$  at 2139 Å and 25°C.

TABLE II

PHOTOLYSIS OF NO AT 2139 Å AND 25°C

[NO], Torr	Irradiation time (min)	$I_a$ (mTorr/min)	$\Phi\{\text{N}_2\}$	$\Phi\{\text{N}_2\text{O}\}$
10.3	1312	0.74	0.025	0.014
51.5	1190	5.38	0.012	0.0070
72	1440	3.62	0.028	0.022
155	1190	17.4	0.016	0.0059
216	1440	17.5	0.022	0.0096
325	1120	11.4	0.026	0.0085

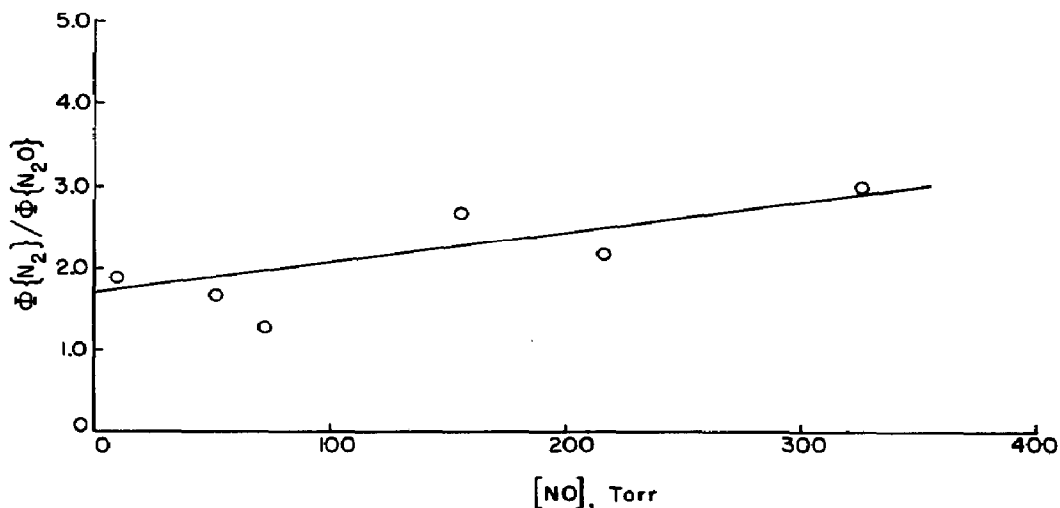


Fig. 3. Plot of  $\Phi\{N_2\}/\Phi\{N_2O\}$  vs.  $[NO]$  in the photolysis of NO at 2139 Å and 25°C.

TABLE III

PHOTOLYSIS OF NO IN THE PRESENCE OF CO<sub>2</sub> AT 2265 Å AND 25°C

$\frac{[CO_2]}{[NO]}$	[CO <sub>2</sub> ] (Torr)	[NO] (Torr)	Irradiation time (min)	[CO] (mTorr)	[N <sub>2</sub> ] <sup>a</sup> (mTorr)	$\frac{[CO]}{[N_2]}$
0.038	10.0	263	1310	24.6	35.9	0.69
0.156	10.0	64.0	1310	28.2	13.5	2.09
0.330	100	300	1050	244	75.5	3.23
0.525	43.0	82.0	1230	113	20.5	5.5
0.616	12.7	20.6	1327	23.6	6.0	3.94
0.618	21.0	34.0	1327	36.0	9.5	3.8
1.28	103	80.4	1305	246	43.0	5.72
2.32	52.4	22.6	1470	72.6	5.0	14.5
2.54	204	80.3	1180	760	55.6	13.7
2.75	55.0	20.0	1355	336	19.5	17.2
3.86	139	36.0	1470	147	7.1	20.8
4.15	333	80.3	1180	676	61.0	11.1
6.69	536	80.3	1335	1040	45.5	22.9
6.86	240	35.0	1270	1450	39.5	36.7
7.34	242	33.0	1260	1350	31.8	42.5
8.15	163	20.0	1355	565	15.5	36.5
12.1	423	35.0	1270	1300	32.5	40.0
12.6	417	33.0	1260	1220	25.5	48.0
25.9	534	20.6	1343	266	6.5	41.0
31.6	651	20.6	1285	222	6.3	33.7

<sup>a</sup> N<sub>2</sub> corrected by 1.5 mTorr for background.

creases as the  $[CO_2]/[NO]$  ratio increases and levels off at high  $[CO_2]/[NO]$ . The data is presented graphically in Fig. 1. The nitrogen quantum yield,  $\Phi\{N_2\}$ , as a function of the  $[NO]/[CO_2]$  ratio is shown in Fig. 2. At low  $[NO]/[CO_2]$ ,  $\Phi\{N_2\}$  is relatively constant and then rises as the  $[NO]/[CO_2]$  ratio increases, finally leveling off at a constant value at very high  $[NO]/[CO_2]$  ratios.

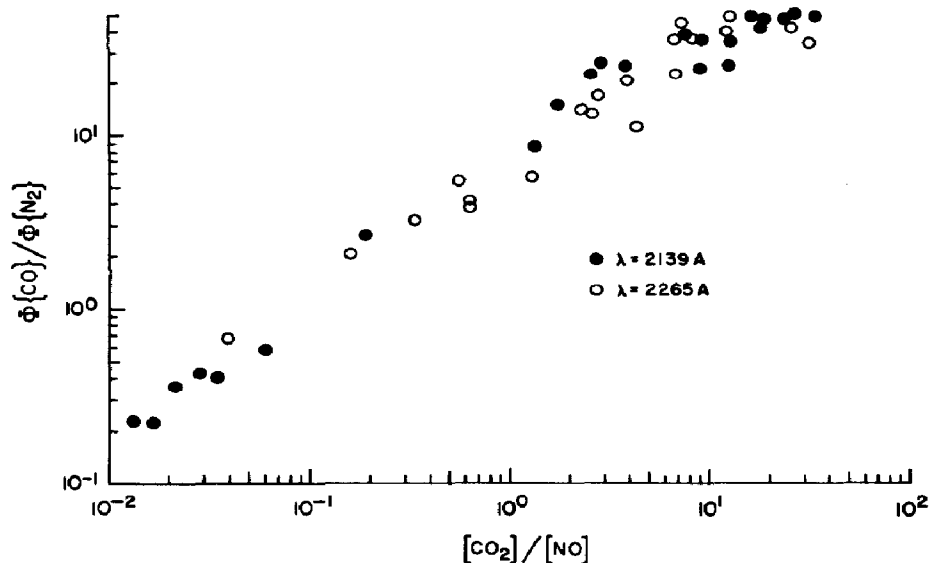


Fig. 4. Log-log plot of  $\Phi\{\text{CO}\}/\Phi\{\text{N}_2\}$  vs.  $[\text{CO}_2]/[\text{NO}]$  in the photolysis of NO in the presence of  $\text{CO}_2$  at  $25^\circ\text{C}$ .

Table II presents the results for the photolysis of NO in the absence of  $\text{CO}_2$  at 2139 Å. In this case the  $\text{N}_2$  and  $\text{N}_2\text{O}$  quantum yields were determined as a function of the NO pressure which varied from 10.3–325 Torr. There is considerable scatter in  $\Phi\{\text{N}_2\}$  and  $\Phi\{\text{N}_2\text{O}\}$  with no discernable trend, but the ratio  $\Phi\{\text{N}_2\}/\Phi\{\text{N}_2\text{O}\}$  appears to increase slightly with increasing NO pressure. This is shown in Fig. 3. The ratio can be determined considerably more accurately than the absolute quantum yields, thus this trend may be meaningful.

At 2265 Å the absolute quantum yields were not determined, because it is difficult to separate the strong 2288 Å line from the 2265 Å line. The  $[\text{CO}]/[\text{N}_2]$  ratio as a function of the  $[\text{CO}_2]/[\text{NO}]$  ratio is presented in Table III and graphically in Fig. 4. Figure 4 also presents this ratio at 2139 Å. The ratio is the same within experimental error at both wavelengths. The slope of the log-log plot is less than one, and therefore  $[\text{CO}]/[\text{N}_2]$  increases less than proportionately with  $[\text{CO}_2]/[\text{NO}]$ .

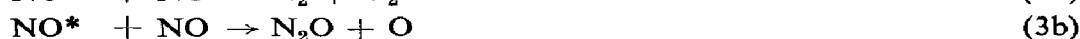
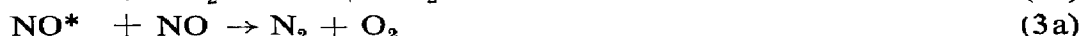
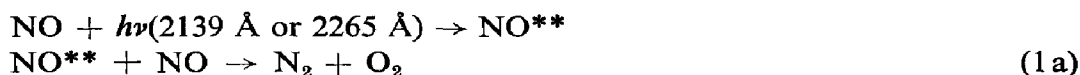
#### DISCUSSION

If all the CO and  $\text{N}_2$  were produced from one excited state by a competitive reaction with  $\text{CO}_2$  and NO, then the ratio  $\Phi\{\text{CO}\}/\Phi\{\text{N}_2\}$  should be proportional to  $[\text{CO}_2]/[\text{NO}]$ . The data in Fig. 4 show that this is not the case. Therefore at least two reactive states must be involved. At first thought it might seem that these could be the  $\nu = 1$  and  $\nu = 0$  levels of the  $\text{A}^2\Sigma^+$  state of NO. However, the data in Fig. 4 show that excitation to either vibrational level leads to the same results. While the  $\nu = 1$  level can be deactivated to  $\nu = 0$ , the reverse is not true. Thus we conclude that the relative reactivity from the vibrational levels is the same and that

NO(A<sup>2</sup>Σ<sup>+</sup>, *v* = 0.1) is one of the reactive states. For simplicity we shall call this NO<sup>\*\*</sup>. The other reactive state must lie lower in energy than the A<sup>2</sup>Σ<sup>+</sup> state.

The *v* = 0 level of the NO(B<sup>2</sup>Π) state is at 5.64 eV, therefore energetically it is possible to populate this state with 2139 Å (5.80 eV) radiation, but not with 2265 Å (5.47 eV). Since the results at 2265 Å and 2139 Å are the same, the second reactive state cannot be the B<sup>2</sup>Π state of NO. The only remaining possibilities for this state are the a<sup>4</sup>Π state which lies at 4.70 eV or the highly vibrationally excited ground state. With the present data it is not possible to distinguish between these possibilities. For simplicity we designate this state NO\*.

In order to analyze the data we begin with a completely general two state mechanism involving only bimolecular processes. The mechanism is the following:



Reactions (1a), (1b) and (3a), (3b) may be somewhat more complicated than indicated here. They may proceed via the N<sub>2</sub>O<sub>2</sub> complex; this problem is discussed later. The fate of the O atom produced in reactions (1b) and (3b) is to give NO<sub>2</sub>



From the two-state mechanism the expression for  $\Phi\{\text{CO}\}$  is obtained:

$$\Phi\{\text{CO}\} = \frac{k_{2a}[\text{CO}_2]}{k_1[\text{NO}] + k_2[\text{CO}_2]} + \left( \frac{k_{4a}[\text{CO}_2]}{k_3[\text{NO}] + k_4[\text{CO}_2]} \right) \times \left( \frac{k_{1c}[\text{NO}] + k_{2b}[\text{CO}_2]}{k_1[\text{NO}] + k_2[\text{CO}_2]} \right) \quad (i)$$

and for  $\Phi\{\text{N}_2\}$  the expression is

$$\Phi\{\text{N}_2\} = \frac{k_{1a}[\text{NO}]}{k_1[\text{NO}] + k_2[\text{CO}_2]} + \left( \frac{k_{3a}[\text{NO}]}{k_3[\text{NO}] + k_4[\text{CO}_2]} \right) \times \left( \frac{k_{1c}[\text{NO}] + k_{2b}[\text{CO}_2]}{k_1[\text{NO}] + k_2[\text{CO}_2]} \right) \quad (ii)$$

where  $k_1 \equiv k_{1a} + k_{1b} + k_{1c} + k_{1d}$ ,  $k_2 \equiv k_{2a} + k_{2b} + k_{2c}$ , etc.  $\Phi\{\text{CO}\}$  at first increases linearly with increasing  $[\text{CO}_2]/[\text{NO}]$  and then levels off. This suggests that a one-state mechanism may account for CO formation. For a one-state mechanism consisting of reactions (1) and (2), eqn. (i) reduces to

$$\Phi\{\text{CO}\}^{-1} = k_2/k_{2a} + k_1[\text{NO}]/k_{2a}[\text{CO}_2] \quad (\text{iii})$$

Figure 5 is a plot of  $\Phi\{\text{CO}\}^{-1}$  vs.  $[\text{NO}]/[\text{CO}_2]$ . The plot is linear over a wide range with a slope of 3.0 and an intercept of 6.0. Consequently, a one-state mechanism suffices to explain the CO data.

If the reactive state were  $\text{NO}^*$  rather than  $\text{NO}^{**}$ , then a straight line plot would not have resulted in Fig. 5 unless the last term in parentheses in eqn. (i) was independent of  $[\text{NO}]/[\text{CO}_2]$ . However, since this term is common to both eqn. (i) and eqn. (ii), it is necessary that it not be independent of  $[\text{NO}]/[\text{CO}_2]$  in order to fit the  $\text{N}_2$  data. Thus the state principally responsible for CO production must be  $\text{NO}^{**}$ . The slope of the plot in Fig. 5 gives  $k_{2a}/k_1 = 0.33$  and the intercept gives  $k_{2a}/k_2 = 0.17$ . Thus  $k_1/k_2 = 0.50$ .  $k_1/k_2$  has been measured previously by a number of investigators using fluorescence quenching methods<sup>1, 4-8</sup>. A comparison of our value with other determinations is shown in Table IV. Our value lies in the midst of the other determinations and the agreement between our value and that of Kleinberg and Terenin<sup>1</sup> is excellent.

$\Phi\{\text{N}_2\}$  is a more complicated function of the  $[\text{NO}]/[\text{CO}_2]$  ratio and can only be explained by considering that  $\text{N}_2$  may arise from two different states. The expression for the quantum yield of  $\text{N}_2$  based on reactions (1)–(4) is given by eqn. (ii).

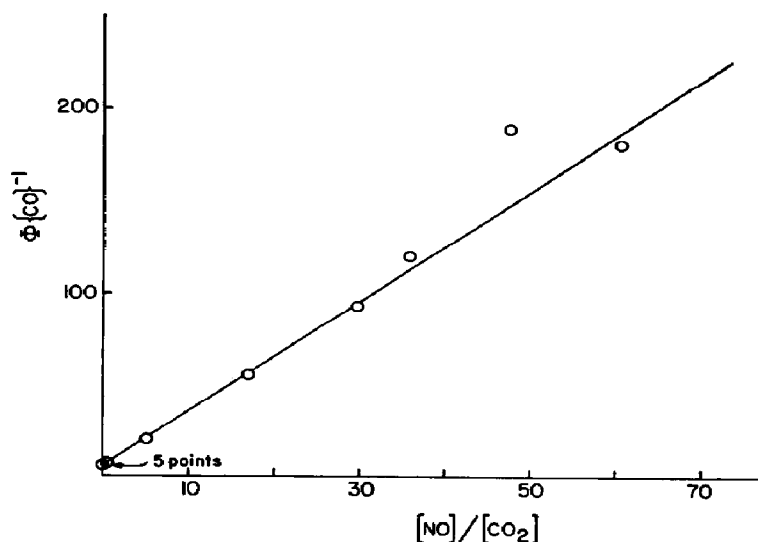


Fig. 5. Plot of  $\Phi\{\text{CO}\}^{-1}$  vs.  $[\text{NO}]/[\text{CO}_2]$  in the photolysis of NO in the presence of  $\text{CO}_2$  at 2139 Å and 25°C.



TABLE IV

SUMMARY OF RATE-CONSTANT DATA

Ratio	Value	Source
$k_{2a}/k_2$	0.17	Fig. 5, eqn. (i)
$k_{2a}/k_1$	0.33	Fig. 5, eqn. (i)
$k_1/k_2$	0.50	Fig. 5, eqn. (i)
$k_1/k_2$	0.50	Ref. 1
$k_1/k_2$	0.29	Ref. 4
$k_1/k_2$	0.93	Ref. 7
$k_1/k_2$	0.34	Ref. 8
$k_{2a}k_{2b}/k_1k_3$	$6.4 \times 10^{-3}$	Fig. 6, eqn. (iv)
$k_{1a}/k_1 + k_{1c}k_{3a}/k_1k_3$	0.022	Fig. 6, eqn. (iv)
$k_{1a}/k_1 + k_{1c}k_{3a}/k_1k_3$	0.17	Ref. 4
$k_{1a}/k_1 + k_{1c}k_{3a}/k_1k_3$	0.033	Ref. 4 <sup>a</sup>

<sup>a</sup> Recalculated assuming  $k_{2a}/k_2 = 0.17$  rather than  $k_{2a}/k_2 = 1.0$ .

Equation (ii) reduces to an expression compatible with the data for  $\Phi\{N_2\}$  if  $k_4[CO_2] \ll k_3[NO]$  at all  $[CO_2]/[NO]$  ratios. Then eqn. (ii) becomes

$$\Phi\{N_2\} = \frac{k_{1a}}{k_1} + \frac{k_{2a}}{k_3} \left( \frac{k_{1c}}{k_1} + \frac{k_{2b}[CO_2]}{k_1[NO]} \right) \quad (\text{iv})$$

where

$$\Phi\{N_2\} \equiv \bar{\Phi}\{N_2\}(1 + k_2[CO_2]/k_1[NO]) \quad (\text{v})$$

Equation (iv) predicts that  $\Phi\{N_2\}$  is constant at very high  $[NO]/[CO_2]$  ratios, that  $\Phi\{N_2\}$  changes as  $[NO]/[CO_2]$  drops, and that eventually  $\Phi\{N_2\}$  again becomes constant at very low  $[NO]/[CO_2]$  ratios. This behavior is observed in Fig. 2.

A plot of  $\Phi\{N_2\}$  vs.  $[CO_2]/[NO]$  should be linear with the slope and intercept equal to  $k_{2b}k_{3a}/k_1k_3$  and  $k_{1a}/k_1 + k_{1c}k_{3a}/k_1k_3$ , respectively.  $\Phi\{N_2\}$  was computed from eqn. (v) using  $k_2/k_1 = 2.0$  as obtained above, and the appropriate plot is shown in Fig. 6. The plot is reasonably linear and has an intercept of 0.022 (10 points) and a slope of  $6.4 \times 10^{-3}$ . The value of  $k_{1a}/k_1 + k_{1c}k_{3a}/k_1k_3$  obtained by Cohen and Heicklen<sup>4</sup> was 0.17, but this was based on the assumption that  $k_{2a} = k_2$ . Our results give  $k_{2a}/k_2 = 0.17$ , hence Cohen and Heicklen's value may be recalculated to be 0.033 in fair agreement with our value of 0.022.

In the photolysis of NO alone at 2139 Å,  $\Phi\{N_2O\}$ , as well as  $\Phi\{N_2\}$ , was determined. Figure 3 shows a plot of  $\Phi\{N_2\}/\Phi\{N_2O\}$  vs.  $[NO]$ . The quantum yield ratio increases from about 1.7 to about 3.0 as  $[NO]$  increases from 0 to 350 Torr. The increase is not large and may not be real. It brackets the average value of 2.2 found in a previous study<sup>3</sup> in which a combination of 2144 and 2265 Å radiation was used.

Strausz and Gunning<sup>10</sup> studied the  $Hg(^3P_1)$  sensitized photolysis of NO, which gives  $NO(a^4\Pi)$ . Since the  $a^4\Pi$  state is one of the two possibilities for  $NO^*$ , these results are pertinent. They found that  $\Phi\{N_2\}/\Phi\{N_2O\}$  decreases rapidly with

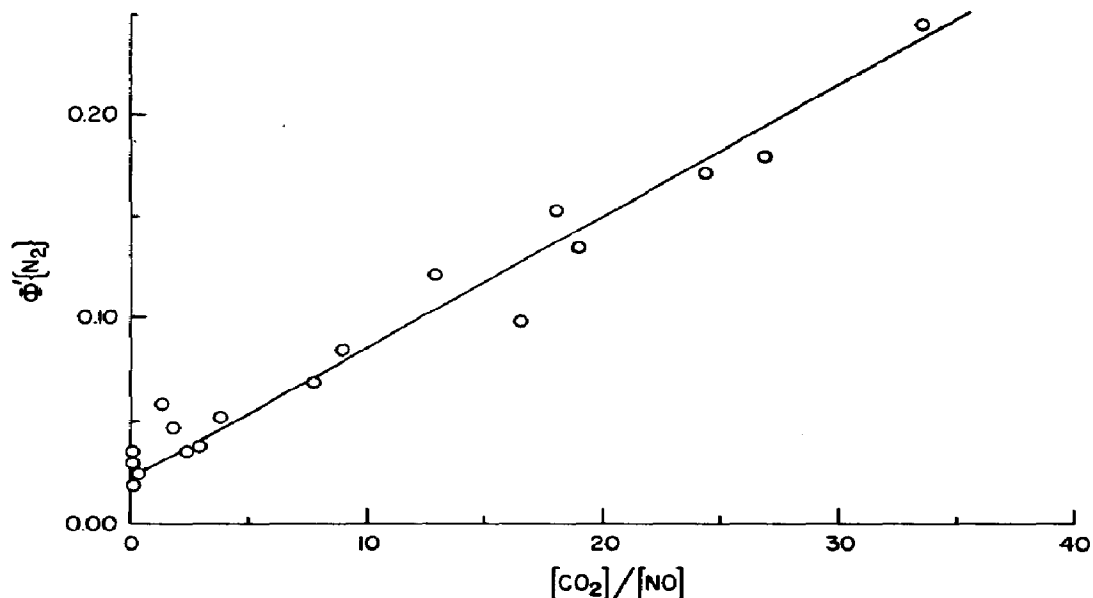
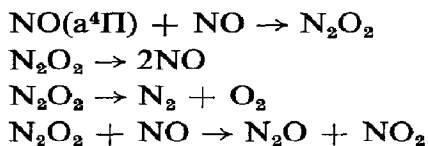


Fig. 6. Plot of  $\Phi' \{N_2\} \equiv \Phi \{N_2\} (1 + 2.0[CO_2]/[NO])$  vs.  $[CO_2]/[NO]$  in the photolysis of NO in the presence of  $CO_2$  at 2139 Å and 25°C.

increasing  $[NO]$ , contrary to our results. They explained their findings via the scheme



For the two studies to be compatible, there are three possibilities. The first is that  $NO^*$  is highly vibrationally excited ground electronic state of NO and not  $NO(a^4\Pi)$ . The second is that  $k_{1c}/k_1$  is negligibly small, so that in the absence of  $CO_2$ , no  $NO^*$  is produced. However, in this case, the ratio  $\Phi\{N_2\}/\Phi\{N_2O\}$  should be different in the presence of  $CO_2$ . Unfortunately we do not have the appropriate experimental results (because of analytical difficulties) with  $CO_2$  present.

The third possibility is that all the results may be explained by a common scheme with the differences resulting from the amount of energy input. Such a scheme is the following



where NO' may be any of the reactive states of NO. This scheme predicts that

$$\frac{\Phi\{\text{N}_2\}}{\Phi\{\text{N}_2\text{O}\}} = \frac{k_{6a} + k_{7a}[\text{NO}]}{k_{6b} + k_{7b}[\text{NO}]} \quad (\text{vi})$$

If  $k_{7b}[\text{NO}] \ll k_{6b}$ , then eqn. (vi) reduces to

$$\Phi\{\text{N}_2\}/\Phi\{\text{N}_2\text{O}\} = k_{6a}/k_{6b} + k_{7a}[\text{NO}]/k_{6b} \quad (\text{vii})$$

Equation (vii) fits our data and conforms to the plot in Fig. 3. The intercept of the plot gives  $k_{6a}/k_{6b} = 1.7$  and the slope gives  $k_{7a}/k_{6b} = 3.7 \times 10^{-3} \text{ Torr}^{-1}$ . In the  $\text{Hg}(^3\text{P}_1)$  sensitized experiments, the total available energy (4.89 eV) is considerably less than with 2139 Å radiation (5.80 eV). Therefore reaction (6b) would be much less likely, and if  $k_{6b} \ll k_{7b}[\text{NO}]$ , eqn. (vi) reduces to

$$\Phi\{\text{N}_2\}/\Phi\{\text{N}_2\text{O}\} = k_{7a}/k_{7b} + k_{6a}/k_{7b}[\text{NO}] \quad (\text{viii})$$

If, also  $k_{7a} \ll k_{7b}$ , then eqn. (viii) is the rate law found by Strausz and Gunning<sup>10</sup> for the  $\text{Hg}(^3\text{P}_1)$  sensitized experiments.

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#### REFERENCES

- 1 A. V. Kleinberg and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, 101 (1955) 1031.
- 2 J. J. McGee and J. Heicklen, *J. Chem. Phys.*, 41 (1964) 2974.
- 3 J. Heicklen, *J. Phys. Chem.*, 70 (1966) 2456.
- 4 N. Cohen and J. Heicklen, *J. Phys. Chem.*, 71 (1967) 558.
- 5 N. Basco, A. B. Callear and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, A260 (1961) 459.
- 6 R. Young and R. Sharpless, *Disc. Faraday Soc.*, 33 (1962) 228.
- 7 H. Broida and T. Carrington, *J. Chem. Phys.*, 38 (1963) 136.
- 8 A. B. Callear and I. W. M. Smith, *Trans. Faraday Soc.*, 59 (1963) 1720.
- 9 R. Simonaitis, R. I. Greenberg and J. Heicklen, *Intern. J. Chem. Kinetics*, in press.
- 10 O. P. Strausz and H. E. Gunning, *Canad. J. Chem.* 39 (1961) 2549.