

THE Hg(¹P₁) SENSITIZED PHOTOLYSIS OF N₂ AND CO

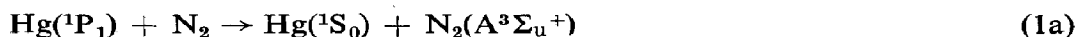
R. SIMONAITIS and JULIAN HEICKLEN

Department of Chemistry and Ionosphere Research Laboratory, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)

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SUMMARY

The Hg(¹P₁) sensitized photolysis of CO and CO-O₂, CO-N₂, N₂-CO₂-NO, and N₂-N₂O-NO mixtures were studied at 25°C. Hg(¹P₁) sensitization of CO leads to small amounts of CO₂ and C₃O₂, and this is taken as evidence for some CO(a³Π) production. The CO₂ quantum yield increases markedly in the presence of O₂, but the enhancement can be explained entirely by the oxidation of vibrationally excited CO. The Hg(¹P₁) sensitization of N₂ can proceed by three paths:



The relative importance is $k_{1a}/k_1 = 0.28$ and $k_{1b}/k_1 > 0.50$, where $k_1 \equiv k_{1a} + k_{1b} + k_{1c}$.

INTRODUCTION

The study of N₂(A³Σ_u⁺) reactions is of interest in regards to the earth's upper atmosphere where N₂(A³Σ_u⁺) is produced by nitrogen atom recombination. The chemistry of CO(a³Π) is of interest in the atmospheres of Mars and Venus, where one of the principal ultra-violet emissions observed by the Mariner 6 and 7 space probes was the Cameron bands of CO¹. The CO(a³Π) is produced in these atmospheres by the photoelectron dissociative excitation of CO₂ and photodissociative excitation of CO₂.

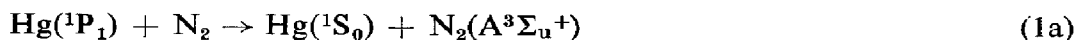
N₂(A³Σ_u⁺) is a component of "active" nitrogen, and this has been used as a source of this state for laboratory studies²⁻⁷. In this way both chemical interactions and total quenching constants with other gases have been measured. Investigation of the reactions of N₂(A³Σ_u⁺) in "active" nitrogen is complicated,

however, by the presence of other reactive species. Another source of $N_2(A^3\Sigma_u^+)$ for laboratory studies has been the photolysis of N_2O at 1470 \AA^{8-10} . Again, this method has the complication that additional reactive intermediates are present. Recently sensitization techniques have been developed which minimize the complications. Setser and his coworkers¹¹⁻¹⁴ have produced and studied $N_2(A^3\Sigma_u^+)$ by sensitization with $Ar(^3P)$ atoms, and Callear and Wood¹⁵ have used Kr and Xe sensitization.

$CO(a^3\Pi)$ has been produced by direct irradiation¹⁶⁻¹⁹, as well as by Xe sensitization²⁰ and Ar sensitization^{11,14} in the vacuum ultra-violet. More recently an electric discharge²¹ as well as controlled electron bombardment²² have been used to produce $CO(a^3\Pi)$. From all of these studies the lifetime of $CO(a^3\Pi)$ as well as quenching coefficients for this state with other gases have been measured.

Liuti *et al.*²³ have observed CO_2 and C_3O_2 formation in the $Hg(^1P_1)$ sensitized photolysis of CO. They have ascribed the formation of these products to the reaction of $CO(a^3\Pi)$ with ground state CO. However, quantum yield measurements were not made, hence it was not possible to ascertain whether $CO(a^3\Pi)$ production was an important process.

Since the experiments of Liuti *et al.*, Granzow *et al.*^{24,25} have obtained results that suggest that $Hg(^1P_1)$ photosensitization of N_2 and CO can produce $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$, respectively. If so, then this method would be a convenient and clean source of these states for laboratory studies. However, the kinetic evidence obtained by Granzow *et al.* is consistent with several possible routes for $Hg(^1P_1)$ deactivation. For N_2 these are:



and for CO these are:



where \neq indicates vibrational excitation. Granzow *et al.* favored reactions (1a) and (2a) as the dominant processes based on selection rule considerations.

In this paper we present results on the $Hg(^1P_1)$ photosensitization of CO, both in the absence and presence of O_2 and N_2 , and of $Hg(^1P_1)$ photosensitization of N_2 in the presence of CO, CO_2 , N_2O and CO_2 -NO mixtures. These experiments were designed to (i) determine the relative importance of the primary processes (1a)-(1c) and (2a)-(2c), and (ii) obtain relative rate coefficients for the physical and chemical quenching of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ by various gases.

EXPERIMENTAL

Procedure and apparatus

The experiments utilized conventional static photochemical techniques. The reaction vessel was a cylindrical quartz cell 5 cm in diameter and 10 cm long. For experiments at elevated temperatures, the cell was enclosed in a wire-wound aluminium furnace. The temperature was regulated to $\pm 1^\circ\text{C}$ by a Cole-Parmer Proportio Null Regulator Series V300.

The gases were saturated with Hg vapor at room temperature and mixed directly in the cell. After irradiation, the gases non-condensable at -196°C were collected in a Toepler pump and the products (O₂ or CO, depending on the experiment) were analyzed by gas chromatography using a 10 ft \times 1/4 in. column packed with Linde 5A molecular sieves. The gases condensable at -196°C were collected separately and analyzed for CO₂, when appropriate, by gas chromatography with an 18 ft \times 1/4 in. column packed with Porapak Q.

1849 Å radiation was obtained from a Hanovia flat-spiral mercury resonance lamp (No. Z1400-013) filtered through γ -irradiated LiF windows. The lamp was placed in an aluminium housing, which was flushed with N₂ in order to remove the O₂. With this arrangement, the relative intensity of the 2537 Å line compared to the 1849 Å line was 3% when the optical density of the LiF windows at 2537 Å was 4.

The actinometry utilized was the mercury sensitized decomposition of N₂O. For this system $\Phi\{\text{N}_2\} = 1.41^{26}$.

Materials

N₂O (Matheson) was purified by degassing and passing over ascarite to remove CO₂. The N₂ (Air Products Research Grade) was purified by passage over traps maintained at -196°C . The only impurity detected was O₂ (5 p.p.m.). The CO (Matheson) was passed slowly over traps filled with glass wool in order to remove the CO₂ and iron carbonyl; the CO₂ remaining was 2 p.p.m. CO₂ (Matheson, bone dry) was purified by degassing. O₂ was purified by passage over traps at -196°C . NO (Matheson) was distilled at -186°C and degassed at -196°C .

Hg(¹P₁) PHOTSENSITIZATION OF CO*Results*

The results for the Hg(¹P₁) photosensitized oxidation of CO are presented in Table I. Experiments were done at 25 and 275°C. In the absence of O₂, CO₂ and C₃O₂ were produced, the latter as a yellow-brown polymer on the cell windows. The quantum yield of CO₂ formation, $\Phi\{\text{CO}_2\}$, is nearly independent of the CO pressure and is about 0.007 at 25°C and 0.0018 at 275°C. The slight drop in $\Phi\{\text{CO}_2\}$ at 25°C as [CO] decreases from 440 to 63 Torr is due to competing fluorescence of Hg(¹P₁)²⁵.

TABLE I

Hg(³P₁) SENSITIZED PHOTOLYSIS OF CO IN THE PRESECE OF O₂

[CO]/[O ₂]	[CO] (Torr)	[O ₂] (Torr)	I _a (mTorr/min ^a)	Irradiation time (min)	Φ(CO ₂)
Temp. = 25°C					
∞	63	0.0	8.70	90	0.0056
∞	440	0.0	6.90	117	0.0080
∞	445	0.0	8.70	122	0.0070
400	438	1.10	24.5	62	0.037
218	437	2.00	24.5	30	0.053
152	443	2.90	24.5	30	0.059
54.5	446	8.20	24.5	32	0.120
54.0	438	8.10	24.5	10	0.129
53.0	438	8.30	24.5	60	0.108
31.8	430	13.5	24.5	10	0.178
Temp. = 275°C					
∞	107	0.0	1.90	120	0.0017 ^b
∞	200	0.0	1.90	120	0.0015 ^b
∞	440	0.0	1.90	95	0.0021 ^b
∞	440	0.0	1.90	20	0.0020 ^b
172	447	2.60	1.67	33	0.124
166	340	2.05	2.06	30	0.160
150	100	0.68	1.67	31	0.130
141	430	3.05	2.06	60	0.132
126	430	3.40	2.06	60	0.154
119	102	0.85	2.06	61	0.194
118	55	0.46	2.06	60	0.15
92	440	4.80	2.06	30	0.205
82	107	1.30	2.06	37	0.210
43	52	1.20	1.67	36	0.255
32.8	427	13.0	2.06	37	0.370
28.8	101	3.50	2.06	30	0.41

^a Units are in mTorr/min at 25°C, regardless of the temperature of the experiment.

^b There is about a 50% uncertainty in these values.

With O₂ present, the [CO]/[O₂] ratio was kept high to minimize direct photosensitization of O₂ and excited O₂ formation by energy transfer from Hg(³P₁). When O₂ is present no evidence for C₃O₂ polymer formation was obtained. Liuti *et al.*²³ also found that when a small amount of O₂ was present, C₃O₂ formation was eliminated. At 25°C, neither the CO pressure nor the absorbed intensity, I_a, was varied, but the O₂ pressure ranged from 1.10 to 13.5 Torr and the irradiation time was varied by a factor of six. Φ{CO₂} increased by a factor of ~25 as [CO]/[O₂] dropped from infinity to 32.

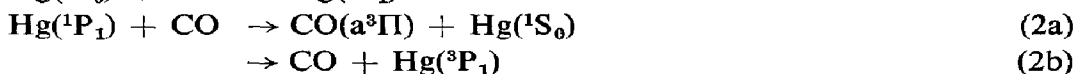
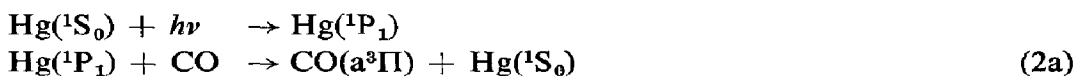
In our earlier studies²⁷ on the Hg(³P₁) photosensitized oxidation of CO it was found that experiments at 25°C could be done only in the presence of an oxygen atom scavenger in order to prevent the formation of O₃ which in turn attacks Hg to produce HgO, thus inhibiting the photolysis due to Hg consumption. In the present experiments, the photolysis rate decreased by only about 15% as the

irradiation time was extended by a factor of six. Presumably, either O₃ is not produced, or the mercury pressure remains sufficient to absorb all the 1849 Å radiation even though HgO formation occurs. At 275°C, the rate of photolysis is independent of irradiation time even at 2537 Å, because at this temperature, both O₃ and HgO are unstable.

At 275°C we found a significant dark reaction occurring between O₂ and CO to give CO₂. A fairly substantial correction had to be applied to Φ{CO₂}, amounting to as much as 50% in the worst case, though 20–30% was more typical. The total pressure, mostly CO, was varied from 53 to 450 Torr and [CO]/[O₂] from 28.8 to 172. Φ{CO₂} increased by a factor of more than 200 as [CO]/[O₂] dropped from infinity to 28.8

Discussion

In the absence of O₂, the possible reactions are:



The carbon atom adds to CO to produce C₃O₂. Reaction (3) is an overall reaction and includes the passage of Hg(³P₁) to Hg(³P₀) as an intermediate in CO[≠] production²⁷. This mechanism leads to the simple result:

$$\Phi_0\{\text{CO}_2\} = k_{2a}k_{4a}/k_2k_4 \quad (I)$$

where $k_2 \equiv k_{2a} + k_{2b} + k_{2c}$ and $k_4 \equiv k_{4a} + k_{4b} + k_{4c}$. The subscript "0" on Φ{CO₂} indicates the value in the absence of O₂. It is 0.007 at 25°C and 0.018 at 275°C and corresponds to $k_{2a}k_{4a}/k_2k_4$ at those temperatures.

In the presence of O₂, a number of additional reactions need to be considered.

These are:





where O_2^* represents electronically excited O_2 . For simplicity all the vibrationally excited CO^\neq molecules are considered kinetically indistinguishable, though the mechanism of formation undoubtedly affects the vibrational level distribution.

The carbon atom produced in reaction (4a) is assumed to always produce CO_2 in the presence of O_2 . If CCO is produced from carbon atom addition to CO, it probably oxidizes to $\text{CO} + \text{CO}_2$, so the net effect is the same. Even if the assumption is incorrect, it hardly makes any difference since the amount of CO_2 produced as a result of reaction (4a) is relatively small in the presence of O_2 . O_2^* can also lead to CO_2 production, but its contribution has been shown to be negligible for $[\text{CO}]/[\text{O}_2] > 20$ in our previous study²⁷.

The fate of the oxygen atom is to react with either CO in reaction (10) or O_2 in reaction (11). At 275°C, reaction (11) is of no consequence since O_3 is unstable and redissociates. However at 25°C, reaction (11) can be of some significance. Its rate coefficient is²⁸ $2.0 \times 10^8 \text{ M}^{-2} \text{ sec}^{-1}$. For reaction (10), the high-pressure limiting second-order rate constant is $1.1 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C²⁹. This value underestimates the importance of reaction (10) because it may not be completely in the second-order regime. Nevertheless, reaction (10) accounts for the removal of at least 40% of the oxygen atoms even at the most unfavorable conditions. Most of the time it removes a much higher percentage. Even if the removal is by reaction (11), O_3 may react with CO to produce CO_2 ³⁰, so that the net effect is the same as removal by reaction (10). Consequently we ignore reaction (11). At worst this will introduce only a 25% error in a few points, but the analysis of the data is greatly facilitated.

The mechanism outlined above leads to a complex expression for $\Phi\{\text{CO}_2\}$. However, simplifications can be made by considering the relative rate constants. The ratio k_2/k_6 is not known, but Granzow *et al.*^{25, 31} have found that N_2 and CO quench $\text{Hg}(^1\text{P}_1)$ with equal efficiency which suggests that both molecules quench with unit efficiency. If so, then k_2/k_6 must be close to or greater than one. The ratios k_3/k_7 and k_4/k_8 are, respectively, 0.31³² and 1.3¹⁴. Thus for our experimental conditions $k_2[\text{CO}] \gg k_6[\text{O}_2]$, $k_3[\text{CO}] \gg k_7[\text{O}_2]$, and $k_4[\text{CO}] \gg k_8[\text{O}_2]$. The situation with regards to reactions (5) and (9) is different, however. The ratio k_5/k_9 is 0.07 at 25°C and 0.025 at 275°C²⁷. Thus $k_9[\text{O}_2]$ is not negligible compared to $k_5[\text{CO}]$.

Including the above considerations, *i.e.* C always produces CO_2 , the production of CO_2 from O_2^* is negligible, reaction (11) is negligible, and $k_6[\text{O}_2]$, $k_7[\text{O}_2]$, and $k_8[\text{O}_2]$ are respectively negligible compared to $k_2[\text{CO}]$, $k_3[\text{CO}]$, and $k_4[\text{CO}]$, leads to the rate law:

$$\Phi\{\text{CO}_2\} = \frac{2k_{2a}k_{9a}[\text{O}_2]}{k_2k_4[\text{CO}]} + \frac{2k_{9a}[\text{O}_2]}{(k_5[\text{CO}] + k_9[\text{O}_2])} \left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{(k_{2b} + k_{2c})}{k_2} \right\} \quad (\text{II})$$

if all the quadratic terms in [O₂]/[CO] are deleted.

The quantity $\Phi'\{\text{CO}_2\}$ is $\Phi\{\text{CO}_2\}$ in excess of that produced as a result of reactions (4a) and (6b).

$$\Phi'\{\text{CO}_2\} \equiv \Phi\{\text{CO}_2\} - 2\Phi_0\{\text{CO}_2\} - 2k_{6b}[\text{O}_2]/k_2[\text{CO}] \quad (\text{III})$$

In computing the last term, k_{6b}/k_2 was assumed equal to one, which is probably an overcorrection. Both correction terms are small ($\leq 10\%$) compared to $\Phi\{\text{CO}_2\}$ and only lead to minor alterations.

The first term on the right-hand side of eqn. (II) is the contribution from CO(a³Π) reacting directly with O₂ *via* reaction (8a). It cannot be important since $k_{8a}/k_4 < 1$,^{14,19} and [CO]/[CO₂] > 30. Thus this term must contribute less than 20% of the total to $\Phi\{\text{CO}_2\}$. Omitting this term and inverting leads to the result:

$$\Phi'\{\text{CO}_2\}^{-1} = \left(\frac{k_9}{2k_{9a}} + \frac{k_5[\text{CO}]}{2k_{9a}[\text{O}_2]} \right) \left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{(k_{2b} + k_{2c})}{k_2} \right\}^{-1} \quad (\text{IV})$$

Plots of $\Phi'\{\text{CO}_2\}^{-1}$ vs. [CO]/[O₂] are shown in Figs. 1 and 2 for the data at 25 and 275°C, respectively. The data at 25°C are well fitted by a straight line of slope 0.121 and intercept 8.0. At 275°C, there is more scatter in the data, but they can be fitted reasonably by a straight line of slope 0.044 and intercept 1.6. The fact that there is no apparent curvature in the plots is experimental justification for omitting the quadratic terms in [O₂]/[CO]. The ratio of slope to intercept gives $k_5/k_9 = 0.015$ at 25°C and 0.027 at 275°C. The latter value agrees exactly with that found at 275°C when CO^z was produced by Hg(³P₁) sensitization²⁷. However, the value at 25°C is a factor of 4.7 smaller than found for Hg(³P₁) sensitization²⁷. At least part of the discrepancy can be attributed to the neglect of reaction (11) in the analysis, as well as to uncertainty in the data. Reaction (11) is of some importance

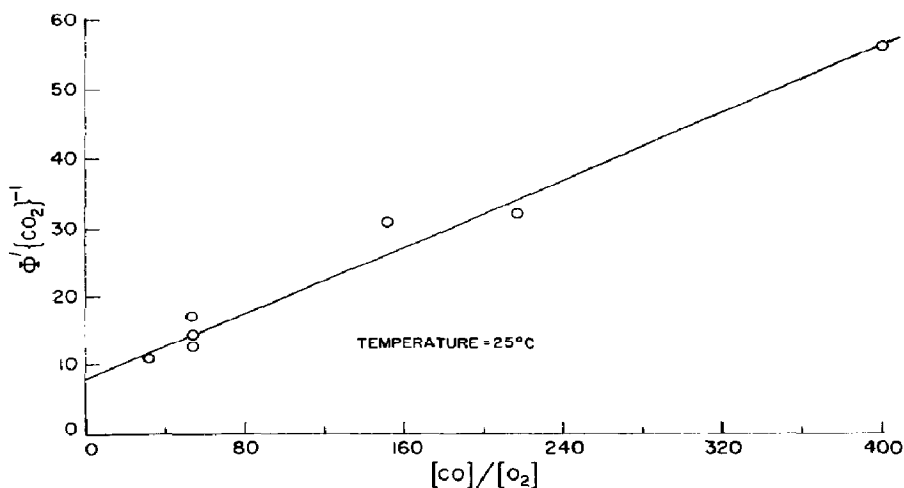


Fig. 1. Plot of $\Phi'\{\text{CO}_2\}^{-1}$ vs. [CO]/[O₂] in the Hg(¹P₁) photosensitization of CO-O₂ mixtures at 25°C.

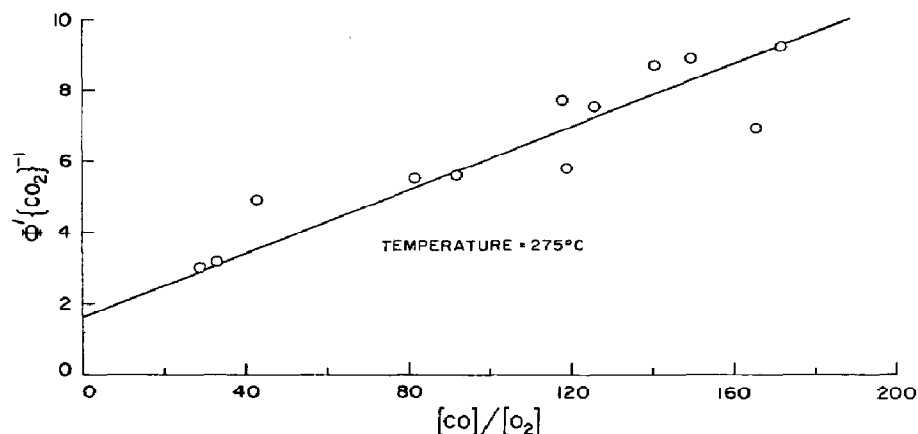


Fig. 2. Plot of $\Phi\{\text{CO}_2\}^{-1}$ vs. $[\text{CO}]/[\text{O}_2]$ in the $\text{Hg}(^1\text{P}_1)$ photosensitization of $\text{CO}-\text{O}_2$ mixtures at 275°C .

at $[\text{CO}]/[\text{O}_2] \sim 30$. If this reaction had been included the values of $\Phi\{\text{CO}_2\}^{-1}$ would have been reduced about 25%, and the intercept reduced almost a factor of two, thus reducing the disparity between k_5/k_9 in this and the previous study. Another reason for the discrepancy may be that the vibrational energy distribution and thus the reactivity of CO^\neq is different in the two studies. This would be expected if CO^\neq is produced by sensitization from either $\text{Hg}(^1\text{P}_1)$ or $\text{CO}(a^3\Pi)$.

If the quantity $(k_{2a}k_{4b}/k_2k_4 + (k_{2b} + k_{2c})/k_2)$ is near unity, then twice the slope and intercepts of the Figs. give k_5/k_{9a} and k_9/k_{9a} respectively. Thus at 275°C , $k_5/k_{9a} = 0.088$ and $k_9/k_{9a} = 3.2$ in exact agreement with that found in the $\text{Hg}(^3\text{P}_1)$ studies²⁷. At 25°C , $k_5/k_{9a} = 0.24$ in exact agreement with that found for $\text{Hg}(^3\text{P}_1)$, but $k_9/k_{9a} = 16$, which is a factor of 4.8 larger, for the reasons discussed above. Consequently either $k_{4b} \simeq k_4$ or $k_{2a}/k_2 \ll 1$. In either case, CO^\neq is produced efficiently in the $\text{Hg}(^1\text{P}_1)$ sensitization of CO . The similarity of the rate coefficient ratios for $\text{Hg}(^1\text{P}_1)$ and $\text{Hg}(^3\text{P}_1)$ sensitization suggests that the principal path of $\text{Hg}(^1\text{P}_1)$ sensitization is to produce $\text{Hg}(^3\text{P}_1)$ as an intermediate *via* reaction (2b).

The values for the rate coefficient ratios are summarized in Table II.

TABLE II

SUMMARY OF RATE COEFFICIENT DATA

Ratio	Value	Temp. ($^\circ\text{C}$)	Source
$k_{2a}k_{4a}/k_2k_4$	0.007	25	Eqn. (I)
$k_{2a}k_{4a}/k_2k_4$	0.018	275	Eqn. (I)
k_5/k_9	0.015	25	Eqn. (IV) Fig. 2
k_5/k_9	0.070	25	Ref. 27
k_5/k_9	0.027	275	Eqn. (IV), Fig. 2
k_5/k_9	0.025	275	Ref. 27

TABLE II (continued)

Ratio	Value	Temp. (°C)	Source
$\frac{k_9/2k_{9a}}{\left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{k_{2b} + k_{2c}}{k_2} \right\}}$	8.0	25	Eqn. (IV), Fig. 1
$\frac{k_9/2k_{9a}}{\left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{k_{2b} + k_{2c}}{k_2} \right\}}$	1.6	275	Eqn. (IV), Fig. 2
$\frac{k_5/2k_{9a}}{\left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{k_{2b} + k_{2c}}{k_2} \right\}}$	0.12	25	Eqn. (IV), Fig. 1
$\frac{k_5/2k_{9a}}{\left\{ \frac{k_{2a}k_{4b}}{k_2k_4} + \frac{k_{2b} + k_{2c}}{k_2} \right\}}$	0.044	275	Eqn. (IV), Fig. 2
$k_1k_4k_{12}/k_{1a}k_{4a}k_{12a}$	260	25	Eqn. (VI), Fig. 3
$k_1k_{12}k_{13}/k_{1a}k_{4a}k_{12a}$	46	25	Eqn. (VI), Fig. 3
k_{13}/k_4	0.18	25	Eqn. (VI), Fig. 3
k_{1a}/k_{1b}	0.25	25	Eqns. (VII)-(X)
k_{1a}/k_1	0.28	25	$k_{1b}/k_1 = 0.9$
k_{1b}/k_1	>0.5	25	Eqn. (XI)

Hg(¹P₁) PHOTSENSITIZATION OF N₂-CO MIXTURES

Results

In order to ascertain the relative importance of reactions (1a), (1b) and (1c), the Hg(¹P₁) photosensitization of N₂-CO mixtures was examined. The products were CO₂ and C₃O₂, but only the CO₂ was measured, since C₃O₂ was detected as a

TABLE III

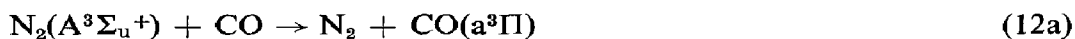
Hg(¹P₁) SENSITIZED PHOTOLYSIS OF N₂-CO MIXTURES AT 25°C

[N ₂]/[CO]	[CO] (Torr)	[N ₂] (Torr)	<i>I</i> ₀ (mTorr/min)	Irradiation time (min)	10 ⁴ Φ {CO ₂ }
64.0	8.0	508	196	62	3.10
63.0	8.0	499	196	300	3.40
59.0	8.5	503	196	960	3.14
46.0	9.0	409	193	121	4.30
17.0	30.0	510	173	60	11.0
15.3	33.0	502	193	120	9.1
14.5	34.5	501	196	60	13.1
4.80	106	504	196	60	20.0
3.40	117	397	348	60	25.0
2.27	153	347	348	60	28.8
1.70	209	356	193	60	39.0

yellow-brown polymer on the cell windows. The results for $\Phi\{\text{CO}_2\}$ are shown in Table III. The N_2 pressure was always in excess and held at 356–508 Torr. $\Phi\{\text{CO}_2\}$ increased from 3.1×10^{-4} to 3.9×10^{-3} as $[\text{N}_2]/[\text{CO}]$ dropped from 64 to 1.7. The increase, however, is not as rapid as would be expected for a simple competition for $\text{Hg}(^1\text{P}_1)$ between N_2 and CO .

Discussion

The reactions of pertinence here are reactions (1)–(5) as well as:



The quenching of $\text{N}_2(\text{A}^3\Sigma_u^+)$ by N_2 is immeasurably slow^{8,15} and can be ignored. Also the rate coefficient for reaction (12) is 2×10^{-12} cm³/sec for $\text{N}_2(\text{A}^3\Sigma_u^+, v = 0)$ ^{9,15} or 2.4×10^{-11} cm³/sec for $\text{N}_2(\text{A}^3\Sigma_u^+, v = 1)$ ^{7,14,15}. Thus the quenching of $\text{N}_2(\text{A}^3\Sigma_u^+)$ by Hg is also negligible, since that rate coefficient is 1.4×10^{-11} cm³/sec⁶, and the Hg pressure is $\leq 10^{-4}$ of the CO pressure.

The fate of the carbon atom, CO^* , or $\text{Hg}(^1\text{P}_1)$ can be ignored since none of these species lead to CO_2 production in this system. Young and St. John⁶ have stated that reaction (12a) proceeds, but Callear and Wood¹⁵ found no evidence for $\text{CO}(\text{a}^3\Pi)$ formation *via* reaction (12a) in a single experiment. Reaction (12a) is 0.15 eV exoergic for the $v = 0$ levels of both $\text{N}_2(\text{A}^3\Sigma_u^+)$ and $\text{CO}(\text{a}^3\Pi)$. Consequently it is both energy and spin allowed. The reverse reaction would be 100 times slower because of the energy barrier. Callear and Wood¹⁵ also found no evidence for the back reaction, but Taylor and Setser¹⁴ and Slinger and Black¹⁹ report that at least part of the quenching of $\text{CO}(\text{a}^3\Pi)$ produces $\text{N}_2(\text{A}^3\Sigma_u^+)$. However, the rate coefficient for total quenching of $\text{CO}(\text{a}^3\Pi)$ by N_2 is 1×10^{-11} cm³/sec¹⁴. This value is sufficiently large so that the bulk of the deactivation must occur by reaction (13).

For simplicity we ignore the reverse of reaction (12a). In effect this simplification is incorporated as an apparent reduction in the forward rate coefficient.

The reaction mechanism leads to the following rate law

$$\Phi\{\text{CO}_2\}^{-1} = \left(\frac{k_4}{k_{4a}} + \frac{k_{13}[\text{N}_2]}{k_{4a}[\text{CO}]} \right) \left(\frac{1 + k_1[\text{N}_2]/k_2[\text{CO}]}{k_{2a}/k_2 + k_{1a}k_{12a}[\text{N}_2]/k_2k_{12}[\text{CO}]} \right) \quad (V)$$

The rate coefficient ratio $k_1/k_2 = 1.0$ ^{24,25,31}. Thus $k_1[\text{N}_2]/k_2[\text{CO}] \gg 1$ for $[\text{N}_2]/[\text{CO}] > 5$. If, for $[\text{N}_2]/[\text{CO}] > 5$, k_{2a}/k_2 is also negligible, then eqn. (V) reduces to:

$$\Phi\{\text{CO}_2\}^{-1} = \left(\frac{k_4}{k_{4a}} + \frac{k_{13}[\text{N}_2]}{k_{4a}[\text{CO}]} \right) \frac{k_1k_{12}}{k_{1a}k_{12a}} \quad (VI)$$

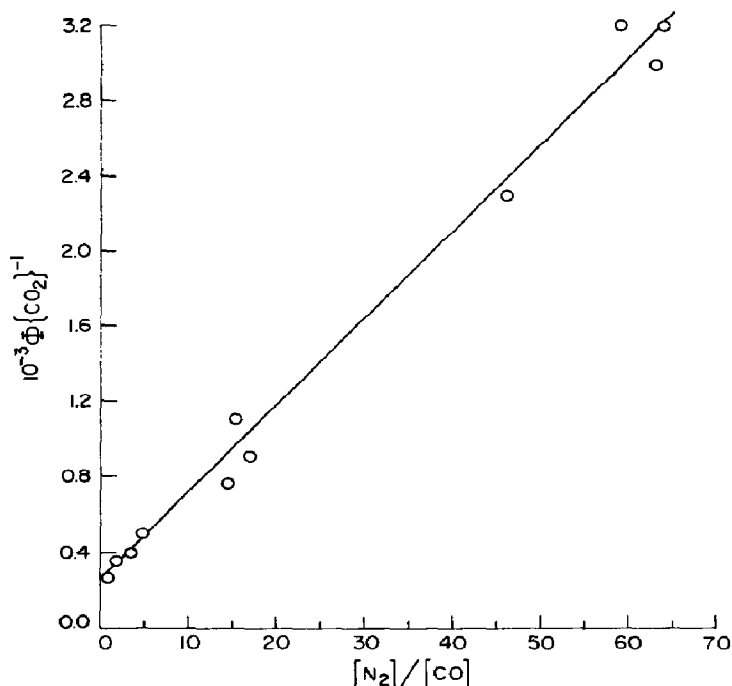


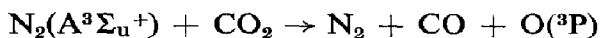
Fig. 3. Plot of $\Phi\{\text{CO}_2\}^{-1}$ vs. $[\text{N}_2]/[\text{CO}]$ in the Hg(¹P₁) photosensitization of N₂-CO mixtures at 25° C.

Figure 3 is a plot of $\Phi\{\text{CO}_2\}^{-1}$ vs. $[\text{N}_2]/[\text{CO}]$. The plot is linear, thus justifying the assumption that k_{2a}/k_2 is negligible. The intercept gives $k_1k_4k_{12}/k_{1a}k_{4a}k_{12a} = 260$, and the slope gives $k_1k_{12}k_{13}/k_{1a}k_{4a}k_{12a} = 46$. The ratio of slope to intercept gives $k_{13}/k_4 = 0.18$, more than a factor of two higher than the value of 0.07 given by Taylor and Setser¹⁴. However, the value of k_4 reported by Slanger and Black¹⁹ is a factor of two lower than that of Taylor and Setser. If the Slanger and Black value is used, then the two values for k_{13}/k_4 are in good agreement. Furthermore our value has the virtue of corresponding to a direct measurement of the ratio.

Hg(¹P₁) PHOTSENSITIZATION OF N₂ IN THE PRESENCE OF CO₂-NO MIXTURES

Results

Campbell and Thrush²⁻⁴ have obtained evidence that N₂(A³Σ_u⁺) formed in "active" nitrogen by three body recombination of N atoms dissociates CO₂ with relatively high efficiency:



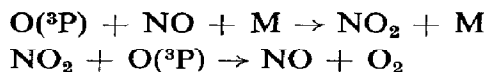
On the other hand Becker *et al.*³³ have studied the recombination of N atoms in the presence of CO₂ in the large Bonn reactor. They found no NO β or γ band emission, which would have been observed if the above reaction proceeded to produce O(³P).

TABLE IV

Hg(¹P₁) SENSITIZED PHOTOLYSIS OF N₂ IN THE PRESENCE OF CO₂ AND NO

[N ₂] (Torr)	[CO ₂] (Torr)	[NO] (Torr)	I _a (mTorr/min)	Irradiation time (min)	Φ{CO}	Φ{O ₂ }
43	1.25	0.0	11.2	60.0	~0.012	~0.002
41	1.20	0.015	11.2	60.0	~0.017	<0.002
500	10.0	0.014	15.1	27.0	-	0.012
515	21.0	0.0	5.7	90.0	0.023	-
506	20.0	1.3	5.7	91.0	0.042	-
500	21.0	1.1	5.7	90.0	0.045	-

In order to test for the above reaction, the Hg(¹P₁) sensitization of N₂-CO₂ mixtures was examined, the ratio [N₂]/[CO₂] being kept large to minimize Hg(¹P₁) sensitization of CO₂. The results are in Table IV. Trace amounts of NO were introduced to aid the O(³P) atom combination *via*²⁶:

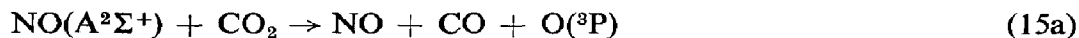


The quantum yields of CO and O₂ are small. Presumably they can be completely accounted for by the direct sensitization of CO₂, since the quenching of Hg(¹P₁) by N₂ and CO₂ is probably of about equal efficiency and the Hg(¹P₁) sensitization of CO₂ leads to dissociation 48% of the time³⁴. Thus we conclude that the N₂(A³Σ_u⁺) sensitized decomposition of CO₂ is unimportant in our system, if it occurs at all.

With more NO present, the sensitization of NO can occur:



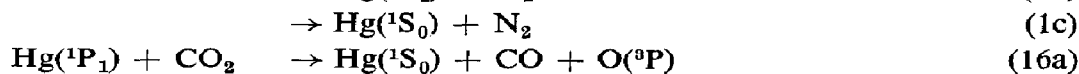
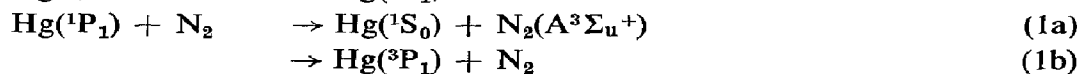
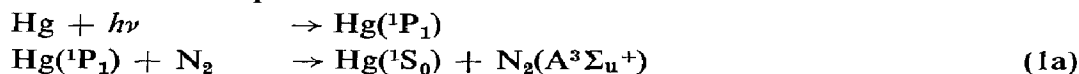
This is a well known reaction and occurs with about unit efficiency^{15, 35}. It can then be followed by the NO(A²Σ⁺) sensitized decomposition of CO₂^{36, 37}:

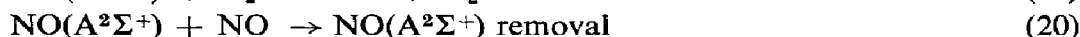
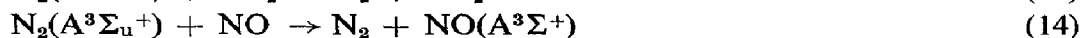
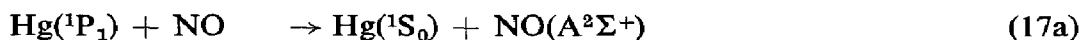


The results in Table IV show that at the elevated NO pressures Φ{CO} is measurably increased. This increase is attributed to reaction (15a).

Discussion

The reactions of pertinence here are:





This mechanism predicts the rate law:

$$(\Phi\{\text{CO}\} - \Phi_0\{\text{CO}\})/\Phi_0\{\text{CO}\} = \alpha(k_{17a}[\text{NO}] + \beta k_{1a}[\text{N}_2])/k_{16}[\text{CO}_2] \quad (\text{VII})$$

where

$$\Phi_0\{\text{CO}\} \equiv k_{16}[\text{CO}_2]/(k_1[\text{N}_2] + k_{16}[\text{CO}_2] + k_{17}[\text{NO}]) \quad (\text{VIII})$$

$$\alpha \equiv k_{15a}[\text{CO}_2]/(k_{15}[\text{CO}_2] + k_{19}[\text{N}_2] + k_{20}[\text{NO}]) \quad (\text{IX})$$

$$\beta \equiv k_{14}[\text{NO}]/(k_{14}[\text{NO}] + k_{18}[\text{CO}_2]) \quad (\text{X})$$

Since k_{17} is probably not larger than k_1 , $\Phi_0\{\text{CO}\}$ is essentially $\Phi\{\text{CO}\}$ in the absence of NO. The fractions α and β can be computed readily from known rate constant ratios.

The ratios k_{15a}/k_{15} , k_{19}/k_{15} , k_{20}/k_{15} and k_{18}/k_{14} are 0.17³⁷, <0.0025³⁵, 0.50^{35, 37}, and <0.001^{7-9, 14, 15}, respectively. Thus for the runs in Table IV with CO₂ pressures of about 20 Torr, $(\Phi\{\text{CO}\} - \Phi_0\{\text{CO}\})/\Phi_0\{\text{CO}\} = 1.0$, $\alpha = 0.16$, and $\beta = 1.0$. Consequently $(k_{17a}[\text{NO}] + k_{19}[\text{N}_2])/k_{19}[\text{CO}_2] = 6.2$. Now it is extremely unlikely that k_{17a}/k_{16} can be much greater than unity, so that $k_{17a}[\text{NO}]/k_{16}[\text{CO}_2]$ is negligible. Thus $k_{19}/k_{16} = 0.25$. Since $k_{16}/k_1 = 0.931$, then $k_{1a}/k_1 = 0.28$.

Hg(¹P₁) SENSITIZED PHOTOLYSIS OF N₂-N₂O MIXTURES

Results

The previously discussed experiments have given the results that $k_{1a}/k_1 = 0.28$. The dominant quenching process of Hg(¹P₁) by N₂, however, is still open. To examine this question we have studied the Hg(¹P₁) photosensitization of N₂ in the presence of small amounts of N₂O. The expectation is that if Hg(³P₁) is produced by reaction (2b), the Hg(³P₁) will be quenched by N₂O to give N₂ and O(³P). However, reaction (1c) should not lead to O(³P) production, even if highly vibrationally excited N₂ is produced.

The results for the Hg(¹P₁) photosensitization of N₂ in the presence of N₂O are presented in Table V. The only product observed was O₂. Small amounts of NO were added to catalyze the O(³P) atom combination in order to minimize wall losses. In one experiment NO was not added and $\Phi\{\text{O}_2\}$ was greatly reduced. The ratio $[\text{N}_2]/[\text{N}_2\text{O}]$ was maintained at ≥ 21.2 to minimize photosensitization of

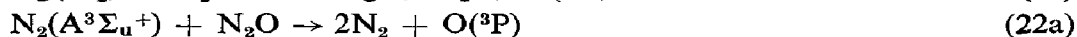
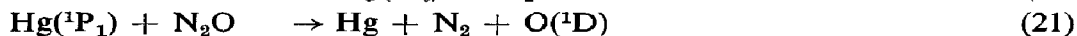
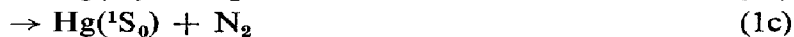
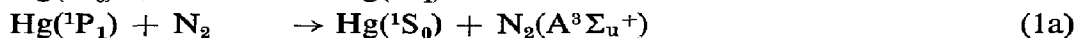
TABLE V
Hg(¹P₁) SENSITIZED PHOTOLYSIS OF N₂-N₂O MIXTURES

[N ₂]/ [N ₂ O]	[N ₂ O] (Torr)	[NO] (mTorr)	I _a (mTorr/min)	Irradiation time (min)	Φ{O ₂ }
[N ₂] = 513 ± 20 Torr					
660	0.80	9	15.1	25.0	0.27
297	1.70	10	13.7	25.0	0.30
293	1.80	0	13.7	26.0	0.065
278	1.80	12	13.7	25.0	0.30
278	1.80	26	13.7	25.0	0.32
266	2.00	15	15.1	25.0	0.39
50.2	10.0	13	15.1	25.0	0.35
49.6	10.0	11	15.1	25.0	0.34
22.4	22.0	17	15.1	25.0	0.46
21.2	24.0	20	13.7	25.0	0.36
[N ₂] = 205 ± 7 Torr					
191	1.10	12	5.7	60.0	0.15
172	1.15	11	11.2	25.0	0.13
[N ₂] = 102 ± 3 Torr					
103	1.00	11	4.30	25.0	0.13
95	1.10	13	4.30	60.0	0.13
27.0	3.70	11	4.30	60.0	0.15
26.7	3.75	12	11.2	25.0	0.15
[N ₂] = 48 ± 1 Torr					
50	0.99	11	4.65	62.0	0.057
47	1.00	14	11.2	25.0	0.047

N₂O by Hg(¹P₁). Experiments were performed at N₂ pressures of approximately 500, 200, 100 and 50 Torr. At 500 Torr of N₂, Φ{O₂} declines slightly as [N₂]/[N₂O] increases, but Φ{O₂} decreases by almost a factor of seven as the N₂ pressure is reduced from 500 to 50 Torr at a given [N₂]/[N₂O] ratio.

Discussion

In the Hg(¹P₁) photosensitization of N₂ in the presence of N₂O, the following reactions need to be considered:



The O(¹D) atom is deactivated readily by collision with N₂ to produce O(³P) which either combines to produce O₂ or is lost on the wall. There is some loss of Hg(¹P₁) by radiation and this can be up to 20% at 50 Torr of N₂²⁵. However, at high N₂ pressures, both the radiation loss of Hg(¹P₁) and the wall loss of O(³P) should be minimal and $\Phi\{O_2\}$ rises. Reaction (21) proceeds with unit efficiency²⁶, as does reaction (23)³⁸. However, since $k_{21}/k_1 = 0.9^{31}$ and $[N_2]/[N_2O] \geq 21.2$, reaction (21) is negligible.

The mechanism then predicts that:

$$\Phi\{O_2\} \leq (k_{1b}/k_1 + k_{1a}k_{22a}/k_1k_{22})/2 \quad (XI)$$

Since $k_{1a}/k_1 = 0.28$, reaction (1a) can account for $\Phi\{O_2\} = 0.14$ at most, but $\Phi\{O_2\}$ reaches ~ 0.4 under some conditions. Thus $k_{1b}/k_1 \geq 0.50$.

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