The Mercury-photosensitized Reaction of Hydrogen with Nitric Oxide

Kohji TADASA,* Naomi IMAI, and Tetsuo INABA

Faculty of Liberal Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591

(Received June 9, 1975)

The Hg-photosensitized reaction of a mixture of H_2 and NO has been studied mainly at room temperature. The quantum yield of the H_2O formation is nearly unity, independent of the pressures of both H_2 and NO. The quantum yield of the N_2 formation is proportional to the NO pressure, while that of N_2O decreases with the NO pressure; both of them are independent of the H_2 pressure. In order to interpret the results concerning the H_2O formation, the following process is proposed:

(i) $NO_3 + NO \longrightarrow 2NO_2$

$NO_2 + HNO \longrightarrow OH + 2NO$

$OH + HNO \longrightarrow H_2O + NO$

in addition to the well-established H_2O-forming process:

(ii) $2HNO \longrightarrow H_2O + N_2O$

NO_2, one of the reactants in Process (i), is formed by the chain process proposed by Arden and Phillips:

(iii) $H + NO + M \longrightarrow HNO + M$

$HNO + 2NO \longrightarrow N_2 + H + NO_3$

The (ii) and (iii) processes also coincide with the results of the N_2O and N_2 formations respectively.

In this laboratory, the effect of nitric oxide on the photochemical decomposition of formaldehyde has been studied.[1] The photolysis of formaldehyde has been known to proceed by means of the free-radical-chain mechanism, where the hydrogen atom is one of the chain carriers. The addition of nitric oxide to the photolysis was found to cause an inhibition of the chain decomposition of formaldehyde. In order to elucidate the kinetics of the inhibited photolysis, it is desirable to study reactions containing the hydrogen atom and nitric oxide. Thus, in this work, the mercury-photosensitized reaction of a mixture of hydrogen and nitric oxide was investigated. This photosensitized reaction has already been studied by several workers,[2-5] but no satisfactory interpretation has been given for the kinetics of the overall reaction.

Experimental

Materials. The nitric oxide and hydrogen used were obtained from the Takachiho Kagaku Co., Ltd.; they had research-grade purities of 99.6% and 99.95% respectively. They were used without further purification.

Apparatus. A cylindrical reaction cell of quartz was used; it had a volume of 262 ml. The lamp used was a 2537-source of a spiral type.

Procedure. The reactants, H_2 and NO, were successively expanded into the reaction vessel, in which they were then kept for more than two hours in order to reach the diffusion equilibration and then saturated with mercury for the same period at room temperature. Most runs were carried out at room temperature with 15-min irradiation (0.2—2% conversion). One series of runs, however, was carried out at various temperatures up to 250 °C. For all the experiments, the absorbed light intensity was approximately the same. Its value was determined to be 8.3×10^{-7} einstein l^{-1} min^{-1} by propane actinometry, assuming the quantum yield of hydrogen to be unity at a low intensity, a low temperature, a high propane pressure, and a very low conversion.[6]

Analysis. The mixture of decomposition was then separated and collected by means of cold traps (at −78 °C, for H_2O and −196 °C for N_2O) and a Toepler gauge (N_2), and analyzed quantitatively by means of a gas-chromatograph. The water, one of the products, was converted to hydrogen by treating it with the sodium evaporated as a thin layer onto the surface of a glass trap; then its amount was determined (though the measurement was not very accurate). The hydrogen and nitrogen were analyzed on a 2 m Molecular Sieve 5A column at room temperature, and the nitrous oxide, on a 4 m Porapak Q column at room temperature. Identification was achieved by using IR and a mass spectrometer.

Results

The products of the Hg-photosensitized reactions were N_2, N_2O, H_2O, and unidentified nitrogen oxides

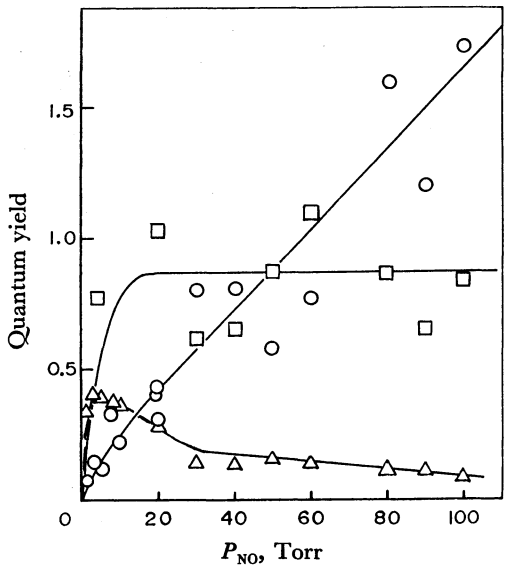

Fig. 1. Plot of quantum yield *vs.* NO pressure.
T=room temperature, P_{H_2}=20 Torr, irradiation time=15 min.
○: N_2, △: N_2O, □: H_2O.

* Present address: Department of Agricultural Chemistry Faculty of Agriculture, University of Shinshu, Ina City, Nagano-ken 396.

TABLE I. Hg-PHOTOSENSITIZED REACTION OF H_2 WITH NO
$I_a = 8.3 \times 10^{-7}$ Einsteins l^{-1} min^{-1}

Temp (°C)	Reactant (Torr)[a]		Irr. time (min)	Product (Torr)[a]			Quantum Yield		
	H_2	NO		H_2O	N_2	N_2O	ϕ_{H_2O}	ϕ_{N_2}	ϕ_{N_2O}
25	20	1	15	—	0.018	0.082	—	0.078	0.36
	20	3	15	0.18	0.034	0.092	0.78	0.148	0.40
	20	5	15	—	0.030	0.090	—	0.130	0.39
	20	8	15	—	0.072	0.088	—	0.31	0.38
	20	10	15	—	0.052	0.086	—	0.23	0.37
	20	20	15	0.24	0.066	0.063	1.04	0.29	0.27
	20	20	15	—	0.092	—	—	0.40	—
	20	20	15	—	0.099	—	—	0.43	—
	20	30	15	0.14	0.19	0.029	0.61	0.83	0.126
	20	40	15	0.15	0.19	0.027	0.65	0.83	0.117
	20	50	15	0.20	0.13	0.030	0.87	0.58	0.130
	20	60	15	0.25	0.18	0.029	1.09	0.78	0.126
	20	80	15	0.20	0.37	0.018	0.87	1.61	0.078
	20	90	15	0.15	0.28	0.018	0.65	1.22	0.078
	20	100	15	0.19	0.40	0.010	0.83	1.74	0.044
25	10	20	15	0.24	0.12	0.045	1.04	0.52	0.20
	20	20	15	0.26	0.13	0.045	1.13	0.57	0.20
	50	20	15	0.27	0.12	0.065	1.17	0.52	0.28
	80	20	15	0.22	0.08	0.060	0.97	0.35	0.26
	100	20	15	0.29	0.10	0.070	1.26	0.44	0.30
50	20	20	20	0.16	0.095	0.075	0.93	0.55	0.44
	20	20	20	0.14	0.065	0.070	0.81	0.38	0.41
75	20	20	20	0.15	0.055	0.075	0.84	0.32	0.44
100	20	20	20	0.17	0.080	0.085	1.00	0.46	0.49
	20	20	20	0.15	—	0.075	0.86	—	0.44
150	20	20	20	0.16	0.087	0.080	0.96	0.50	0.46
	20	20	20	0.15	0.055	0.073	0.84	0.32	0.42
200	20	20	20	0.17	0.050	0.070	0.96	0.29	0.41
	20	20	20	0.14	—	0.063	0.84	—	0.37
250	20	20	20	0.15	0.050	0.060	0.87	0.29	0.35

a) Pressure in the cell at room temperature.

which might react with mercury in the system. After some runs, some of a white solid was found trapped in the cold U tube. On heating *in vacuo*, it turned yellow and released mercury. Strausz *et al.*[3] found a similar substance in their experiment and identified it as predominantly $Hg_2(NO_2)_2$. Because of the reaction of NO_2 with Hg both in the reaction cell and in the analysis part, the amount of NO_2 could not be measured.

The experimental results are listed in Table 1.

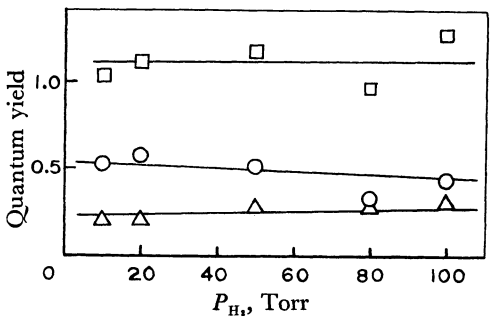

Fig. 2. Plot of quantum yield *vs* H_2 pressure.
T=room temperature, P_{NO}=20 Torr, irradiation time=15 min.
○: N_2, △: N_2O, □: H_2O.

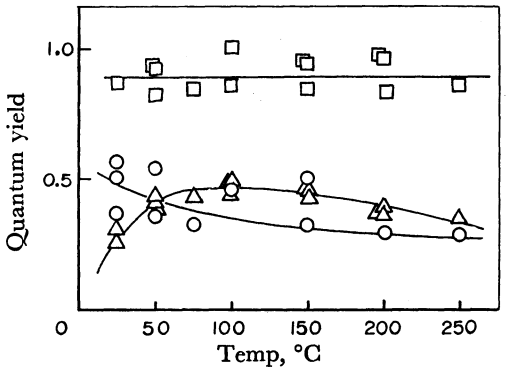

Fig. 3. Temperature dependencies of quantum yield.
P_{NO}=20 Torr, P_{H_2}=20 Torr, irradiation time=20 min.
○: N_2, △: N_2O, □: H_2O.

Figure 1 shows the effect of the NO pressure on each product formation, while Fig. 2 shows that of the H_2 pressure. These figures indicate the quantum yield of H_2O formation to be nearly unity over wide pressure ranges of reactants except for the low NO pressure range, though the accuracy of the quantitative analysis of H_2O is very low. Figure 3 shows the temperature dependencies of the yields of the products.

Discussion

The mercury-photosensitized reaction of H_2 has been studied by many workers. The primary reactions of the photosensitization were found to be as follows:[7]

$$Hg + h\nu(2537\,Å) \longrightarrow Hg^* \quad (1)$$

$$Hg^* + H_2 \longrightarrow HgH + H \quad (2)$$

$$\longrightarrow Hg + 2H \quad (3)$$

where $Hg^*=Hg(6^3P_1)$. In the presence of NO, Hg* should be largely quenched by NO, because of its high quenching cross section[8]:

$$Hg^* + NO \longrightarrow NO^* \quad (4)$$

where $NO^*=NO(^4\Pi)$.[9]

Since the formation of H_2O, which is a measure of the rate of the primary steps, as will be described later, is constant against the amount of H_2 and NO, the following step should occur:

$$NO^* + H_2 \longrightarrow HNO + H \quad (5)$$

The hydrogen atoms formed by (2), (3) or (5) should combine with NO as:

$$H + NO + M \longrightarrow HNO + M \quad (6)^{10}$$

The HgH radicals were shown to react with NO very rapidly[5]:

$$HgH + NO \longrightarrow Hg + HNO \quad (7)$$

One Hg* atom, therefore, leads to the formation of two HNO species.

It is well known that the HNO species combine with each other as:

$$2HNO \longrightarrow N_2O + H_2O \quad (8)^{2,3,10,11}$$

This reaction, however, is probably not the main reaction of HNO under the present conditions, since the N_2O yield is quite low compared with that of H_2O.

In the study of the H_2–NO pyrolysis at 500 °C carried out in this laboratory,[12] it was suggested that most of the HNO species react as:

$$2HNO \longrightarrow 2OH + N_2$$

and that the OH radicals thus formed react as:

$$OH + H_2 \longrightarrow H_2O + H$$

resulting in the H_2O–N_2 ratio in the product of 2:1. In this study at room temperature, however, the N_2 formation is of the first order in NO pressure and the H_2O formation is of the zeroth order in NO pressure, showing that they are formed by reactions different from those in the pyrolysis.

Since the H_2O quantum yield equals unity within the limits of experimental error over wide pressure ranges of the reactant gases, the rate of H_2O formation seems to exhibit that of the primary process. On the other hand, N_2 may be supposed to be formed by the chain reaction containing NO, because its quantum yield exceeds unity and its formattion is of the first-order with respect to NO.

Arden and Phillips have proposed that HNO induces the chain disproportionation of NO to N_2 and NO_2.[13]

$$HNO + 2NO \longrightarrow N_2 + H + NO_3 \quad (9)$$

$$NO_3 + NO \longrightarrow 2NO_2 \quad (10)$$

These reactions do not consume the HNO, however, since H atoms formed by (9) regenerate the HNO by means of (6). Thus, N_2 is formed by the chain reaction carried out by means of (6) and (9). Strausz and Gunning[3] has proposed a HNO–NO reaction scheme alternative to (9):

$$HNO + 2NO \longrightarrow N_2 + HNO_3\dagger$$

If it is followed by this reaction:

$$HNO_3 + NO \longrightarrow HNO + NO_3$$

it leads to the same results as (9).

As the mechanism of H_2O formation, when the NO pressure is not low, the following reactions may be proposed in addition to (8):

$$NO_2 + HNO \longrightarrow OH + 2NO \quad (11)$$

$$OH + HNO \longrightarrow H_2O + NO \quad (12)$$

Thus, one H_2O molecule is formed by consuming two HNO species by means of (11) and (12) as well as (8). The rate of the H_2O formation should equal that of the absorption of the light quanta:

$$R_{H_2O} = I_a \quad (I)$$

This has been clearly proved by the results, $\phi_{H_2O}=1$, shown in Figs. 1 and 2. This equation is not affected by the occurence of the chain disproportionation of NO carried out by means of (6) and (9).

The H_2O formation by this reaction:

$$OH + H_2 \longrightarrow H_2O + H$$

instead of (12) seems to be improbable at low temperature, since its activation energy is 5.2 kcal mole^{-1} ($E_{12}\sim0$).[14] If this reaction, nevertheless, occurrs appreciable, the H atom would be regenerated and (6) and (11) would follow it. In this case, H_2O would be formed by the chain reaction, and, accordingly, ϕ_{H_2O} should depend on the H_2 pressure; this is not consistent with the results shown in Fig. 2.

Accepting the reaction scheme (1)—(12), the rates of N_2 and N_2O formations in the steady state may be expressed as:

$$R_{N_2} = k_9[HNO][NO]^2 \quad (II)$$

and:

$$R_{N_2O} = k_8[HNO]^2 \quad (III)$$

where [HNO] can be obtained from this equation:

$$I_a = k_8[HNO]^2 + k_{11}[NO_2][HNO] \quad (IV)$$

From Rate Equations (II) and (III), we obtain:

$$\phi_{N_2}^{1/2}/\phi_{N_2O}^{1/4} = k_9^{1/2}[NO]/I_a^{1/4}k_8^{1/4} \quad (V)$$

This equation is tested in Fig. 4, which shows that this relation holds, although the plots do not fall on a straight line very clearly.

If $R_8 \ll R_{12}(=R_{11})$ (this reaction holds when [NO] is not low), the first term on the right-hand side of Eq. (IV) can be neglected. Thus,

$$\phi_{N_2} = k_9[NO]^2/k_{11}[NO_2] \quad (VI)$$

and

† This reaction was shown experimentally to be of the first order with respect to both HNO and NO, while (9) is of the first order with respect to HNO and of the second order with respect to NO.

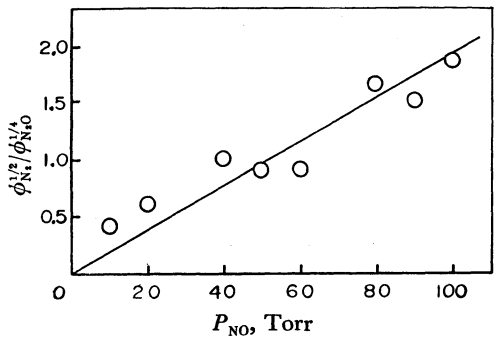

Fig. 4. Plot of $(\phi_{N_2}^{1/2}/\phi_{N_2O}^{1/4})$ value *vs.* NO pressure.
T=room temperature, P_{H_2}=20 Torr

$$\phi_{N_2O} = k_8 I_a / k_{11}^2 [NO_2]^2 \qquad \text{(VII)}$$

As NO_2 is consumed by the reaction with Hg,

$$NO_2 + Hg \longrightarrow (1/2)Hg_2(NO_2)_2$$

its concentration could not be measured. If $[NO_2]$ is assumed to be proportional to the added NO pressure, $\phi_{N_2} \propto [NO]$ and $\phi_{N_2O} \propto I_a/[NO]^2$. Figures 1 and 2 seem to indicate these relations to hold, even though very roughly.

Figure 3 shows that ϕ_{H_2O} does not vary, while ϕ_{N_2} decreases and ϕ_{N_2O} reaches a maximum, with the rise in the temperature to 250 °C. These tendencies are quite the same of those in the CH_2O–NO photolysis.[1] The decrease in the rate of the termolecular reaction (9) is supposed to cause the decrease of ϕ_{N_2} at higher temperatures. The increase of ϕ_{N_2O} with the temperature up to 100°C may be attributed to the occurence of Reaction (13):

$$HNO + NO \longrightarrow N_2O + OH \qquad (13)$$

in addition to (8). At temperatures higher than 100°C, Reaction (14) takes place:

$$2HNO \longrightarrow 2OH + N_2 \qquad (14)$$

Thus, HNO is consumed by (14) and (12) to a great extent, so that the rate of the N_2O formation by (8) and (13) should decrease above 100°C. It was suggested that these reactions occur in the H_2–NO[12] and CH_2O–NO[15] pyrolyses. The latter reaction, especially, was indicated to be predominant compared with (8) at 400 and 500 °C in these experiments. The occurence of these reactions, however, does not affect the (I) relation. Consequently, ϕ_{H_2O} holds constant over the temperature range examined.

References

1) K. Tadasa, N. Imai, and T. Inaba, to be published.
2) H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944). M. Z. Hoffman and R. B. Bernstein, *J. Phys. Chem.*, **64**, 1753 (1960). R. Atkinson and R. J. Cvetanović, *Can. J. Chem.*, **51**, 370 (1973).
3) O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, **60**, 347 (1964).
4) A. B. Callear and P. M. Wood, *J. Chem. Soc., Faraday II*, **68**, 302 (1972).
5) A. B. Callear and P. M. Wood, *Trans. Faraday Soc.*, **67**, 3399 (1971).
6) R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959).
7) A. B. Callear and R. E. M. Hedges, *Trans. Faraday Soc.*, **66**, 605, 615 (1970).
8) J. R. Bates, *J. Amer. Chem. Soc.*, **54**, 569 (1932).
9) R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Phys. Chem.*, **63**, 2082, (1959). M. Z. Hoffman and R. B. Bernstein, *ibid.*, **64**, 1769 (1960). O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, **39**, 2549 (1961). G. Karl, P. Kraus, J. C. Polanyi, and L. W. M. Smith, *J. Chem. Phys.*, **46**, 244 (1967).
10) P. Harteck, *Ber.*, **66**, 423 (1933).
11) L. Phillips, *J. Chem. Soc.*, **1961**, 3082. K. A. Wilde, *Combust. and Flame*, **13**, 173 (1969).
12) K. Tadasa, N. Imai, and T. Inaba, This Bulletin, **47**, 2979 (1974).
13) E. A. Arden and L. Phillips, *J. Chem. Soc.*, **1964**, 5118.
14) J. L. Franklin, *Ann. Rev. Phys. Chem.*, **18**, 261 (1967).
15) K. Tadasa, N. Imai, and T. Inaba, This Bulletin, **47**, 548 (1974).