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## The Mercury-Sensitized Reaction Between Hydrogen and Nitric Oxide

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The reaction of hydrogen atoms with nitric oxide has been studied by mercury sensitization of various mixtures of hydrogen and nitric oxide to produce nitrogen and water. The rate at constant nitric oxide pressure is proportional to the hydrogen at low hydrogen pressures, the effect diminishing at higher concentrations. With a given hydrogen concentration nitric oxide is almost without effect until an excess is present when it shows a retardation. At constant total pressure a maximum rate occurs with a particular excess of hydrogen. A mechanism based on HNO radicals has been postulated. These radicals decompose by a wall reaction to give nitrous oxide which is rapidly reduced to nitrogen.

THE homogeneous reaction between nitric oxide and hydrogen<sup>1</sup> is approximately third order, proceeding at measurable speed only above 700°C. The apparent activation energy of 49 kcal. coupled with a high rate constant makes it impossible to reconcile a termolecular mechanism similar to those for the reactions of nitric oxide with oxygen, chlorine, and bromine. The high rate constant alone would suggest a chain mechanism and the tests for such chains already applied<sup>1b</sup> are not unequivocal. From the complexity of the hydrogen-oxygen reaction taken in conjunction with the many similarities between nitric oxide and oxygen it would be surprising if the nitric oxide-hydrogen reaction was not relatively complex, probably involving hydrogen atoms originating either at a surface as in the hydrogen-oxygen reaction or in the gas phase by thermal dissociation of molecules as in the homogeneous para-ortho conversion. That

hydrogen atoms will react with nitric oxide has been demonstrated by Harteck<sup>2</sup> who showed the production of a yellow deposit at liquid air temperature of the formula (HNO)<sub>n</sub> which decomposed at higher temperatures. It seemed advisable, therefore, to study more carefully the kinetics of the hydrogen atom reaction.

### EXPERIMENTAL

Hydrogen atoms were produced by mercury sensitization. To this end a low pressure quartz-mercury arc, spiral in form and energized with a 0.265-kva transformer, was clamped alongside a cylindrical quartz reaction vessel connected to reservoirs of reactants, a manometer, and pump system. The reaction vessel and lamp were enclosed and temperature equilibrium at about 100°C was reached with the lamp operating before the reaction began. The lamp has an estimated yield of about 90 percent of its energy at 2537Å.

<sup>1</sup> (a) C. N. Hinshelwood and T. E. Green, *J. Chem. Soc.*, p. 730 (1926); (b) J. W. Mitchell and C. N. Hinshelwood, *ibid.*, p. 378 (1936).

<sup>2</sup> P. Harteck, *Ber.* 66, 423 (1933),

TABLE I. Pressure change in cm.

Time (min.)	Expt. 41 $P_{H_2} = 7.65$ $P_{NO} = 10.0$	Expt. 46 $10.2$ $10.0$	Expt. 50 $10.05$ $5.4$
2	0.45	0.8	0.85
4	1.4	1.9	1.9
6	2.35	3.0	2.9
8	3.35	4.1	3.75
10	4.3	5.1	4.45
12	5.25	6.1	5.05
14	6.05	7.1	5.5
16	6.85	7.95	5.85
18	7.6	8.75	6.05
20	8.3	9.55	6.25
25	9.75	11.3	6.65
30	10.55	12.6	7.05
35	10.8	13.55	7.4
40	10.95	13.95	7.65
50	11.15	14.25	7.8

Since water is one of the products of reaction and since it was simplest to follow the rate by pressure change, a large initial lag in pressure change until the vessel was saturated with water vapor was obviated by saturating the system initially with water. It was found that this did not affect the time needed for the completion of the reaction.

Nitric oxide was prepared from nitrosyl-sulfuric acid by treating its solution in sulfuric acid with mercury. Tank hydrogen was purified from oxygen by passage over hot platinized asbestos and was saturated with mercury vapor by bubbling through two traps containing mercury, the first one hot, the second at room temperature.

The products of some runs were analyzed by removal from the reaction vessel with a Toepler pump through a trap immersed in liquid nitrogen. The volume of the gases, nitrogen and hydrogen, thus withdrawn was measured. They were then burned over copper oxide at 325°C and the volume of the residual nitrogen determined. The liquid nitrogen around the trap was replaced with dry ice and the volume of gas released

measured. Only in experiments with excess nitric oxide was any gas released. Hence this volume was taken to be residual nitric oxide indicating that no ammonia is formed during the reaction. The residual contents of the trap diluted with water always had a pH of seven, showing absence of basic and acidic nitrogen compounds.

## RESULTS

In Table I are listed the actual pressure changes as a function of time for three typical experiments. A very brief initial induction period is succeeded by a fairly steady rate over many minutes. This maximum rate has been taken as the rate for the known initial partial pressures of the reactants.

Table II shows the variation of this rate with varying partial pressures of hydrogen at constant nitric oxide pressure. While the rate is approximately proportional to the hydrogen at low

TABLE III. Dependence of rate on nitric oxide.

Expt.	$P_{H_2}$ (cm)	$P_{NO}$ (cm)	Rate (cm/min.)	$k$
50	10.05	5.4	0.51	1.49
52	11.6	8.05	0.51	1.40
46	10.2	10.0	0.54	1.63
47	10.15	20.95	0.28	1.11
51	10.05	24.4	0.27	1.17

pressures, this effect is considerably diminished at high pressures. Thus the relative increase in rate between experiments 42 and 41, the latter at twice the hydrogen pressure of the former, is markedly greater than the relative increase in rate between runs 41 and 43 where the hydrogen ratio is almost three to one. The constant  $k$  in this and subsequent tables will be discussed later.

The dependence of the rate on nitric oxide at constant hydrogen pressure is shown in Table III. It will be seen that there is little change in rate until nitric oxide and hydrogen are present in equal amounts but that an excess of nitric oxide has a retarding effect.

Since from the above it appears that the total pressure as well as the partial pressures of the reactants has an effect on the rate, a series of runs was made at constant total pressure with varying proportions of hydrogen and nitric oxide. The data are presented in Table IV.

TABLE II. Dependence of rate on hydrogen.

Expt.	$P_{NO}$ (cm)	$P_{H_2}$ (cm)	Rate (cm/min.)	$k$
42	9.9	3.7	0.28	1.61
45	10.15	4.65	0.34	1.67
41	10.0	7.65	0.48	1.70
46	10.0	10.2	0.54	1.63
44	10.4	10.6	0.58	1.68
40	10.2	20.3	0.76	1.70
43	10.3	21.1	0.75	1.66

Inspection of these data shows a maximum in the rate where the ratio of hydrogen to nitric oxide is slightly greater than two to one. This means that, for this particular total pressure, the rate is empirically dependent on a power of the hydrogen pressure and a power of the nitric oxide pressure which is a little less than one-half that of the hydrogen pressure.

Several runs not included in the above tables are given in Table V; their significance will appear in the discussion later.

The results of the gas analysis of the final products from three runs on completion of the runs are given in Table VI. The calculated results are on the basis of complete reduction of one mole of nitric oxide by one mole of hydrogen to produce nitrogen and water.

Experiments performed to test the effect of the radiation on mercury-saturated moist nitric oxide in the absence of hydrogen, showed that a reaction occurred slowly whose products con-

TABLE IV. Dependence of rate on composition at constant total pressure.

Expt.	$P_{H_2}$ (cm)	$P_{NO}$ (cm)	Rate (cm/min.)	$k$
63	14.65	1.25	0.20	1.01
58	12.55	2.45	0.35	1.21
61	11.85	3.20	0.40	1.25
62	9.90	5.00	0.41	1.21
60	9.80	5.45	0.41	1.21
59	8.50	6.65	0.41	1.28
68	7.50	7.45	0.36	1.21
66	6.95	7.95	0.36	1.27
69	6.35	8.90	0.31	1.19
67	3.70	11.35	0.20	1.22
64	2.15	13.15	0.10	1.04
65	1.25	13.45	0.06	1.03

tained brown nitrogen tetroxide and nitrogen. The former was never observed in the presence of excess hydrogen and is probably negligible. However, such a reaction could account for the small amount of residual nitric oxide and the excess of nitrogen observed in the above analysis of the mixture containing excess nitric oxide. The slowness of this reaction, however, should not affect the interpretation of the observed maximum rate of pressure change as the rate of the reaction producing nitrogen and water. Finally, in the other two runs in Table VI the fact that the hydrogen observed exceeds the calculated may be attributed to the order in which the gases entered the reaction vessel,

TABLE V.

Expt.	$P_{H_2}$ (cm)	$P_{NO}$ (cm)	Rate (cm/min.)	$k$
48	13.10	5.25	0.56	1.50
49	12.50	5.25	0.53	1.44
53	5.95	5.30	0.41	1.50
54	5.10	5.15	0.41	1.62
55	10.30	4.85	0.45	1.33
56	16.95	5.85	0.54	1.32
57	23.25	5.55	0.53	1.21
71	7.10	9.70	0.32	1.17
72	8.40	16.05	0.29	1.15
73	27.75	8.05	0.53	1.09
74	5.55	3.40	0.31	1.20
75	10.15	9.00	0.37	1.10
76 <sup>a</sup>	7.90	8.50	0.41	1.37
77	9.30	7.85	0.43	1.31
78	10.30	7.05	0.46	1.32
79	6.90	6.40	0.33	1.14
81	10.05	8.35	0.38	1.12
87 <sup>b</sup>	11.95	11.55	0.59	1.70

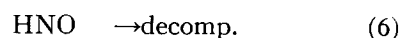
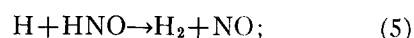
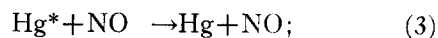
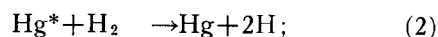
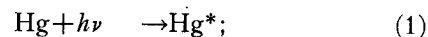
<sup>a</sup> Reaction vessel cleaned on outside and flamed while evacuated.

<sup>b</sup> Reaction vessel cleaned inside and out.

hydrogen being always the last, leaving the possibility of some hydrogen in the capillary connecting tubes which never entered into the reaction vessel or perhaps that the rapidity of reaction made uncertain the initial hydrogen pressure reading which may thus be slightly low.

## DISCUSSION

The following mechanism is suggested to account for the above observations:



Reactions (1) and (2) constitute the well-known mercury sensitized dissociation of hydrogen.

TABLE VI.

	$P_{H_2}$ 10.30	$P_{NO}$ 7.05	$P_{H_2}$ 6.55	$P_{NO}$ 7.45	$P_{H_2}$ 11.95	$P_{NO}$ 11.55
	obs.	calc.	obs.	calc.	obs.	calc.
N <sub>2</sub> cc	7.30	7.35	8.2	6.8	11.6	11.9
H <sub>2</sub> cc	7.00	6.70	—	—	1.6	0.8
NO cc	—	—	0.05	1.85	—	—

TABLE VII. Reaction of nitrous oxide and hydrogen.

Expt.	$P_{H_2}$ (cm)	$P_{N_2O}$ (cm)	Rate (cm/min.)
91	10	4.95	0.30
92	10	1.60	0.20

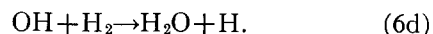
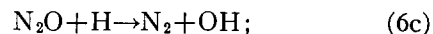
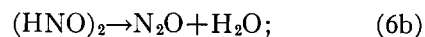
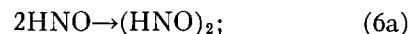
Reaction (3) is in accord with the very efficient quenching of mercury fluorescence by nitric oxide observed by Bates<sup>3</sup> and also by Noyes<sup>4</sup> who shows that practically no chemical change ensues from such quenching.

Reaction (4) follows from the findings of Harteck<sup>2</sup> in experiments at low temperature. The association of a two-body collision is analogous to the two-body formation of  $HO_2$  from H and  $O_2$  based on the similarity of  $O_2$  and NO. The possibility of the formation to any appreciable extent of OH and N, or of NH and O in reaction of H and NO is ruled out by the fact that no ammonia could be discovered among the products. This would also validate current estimates of the bond strengths of OH and NH in comparison with that of NO.

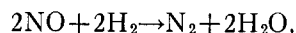
Harteck's observation of a stable compound  $(HNO)_n$  at liquid air temperatures, identified by him as similar to the intermediate obtained in ammonia oxidation and which decomposed at  $-95^\circ C$  into nitrous oxide and water, suggests that the compound was probably nitramide or its isomer hyponitrous acid. Smallwood<sup>5</sup> has shown that nitric oxide catalyzes the recombination of hydrogen atoms produced in a discharge tube. He states that over 99 percent of the nitric oxide was recovered unchanged and suggests reactions (4) and (5) to account for the observation. Work in this laboratory by Dr. O. C. Wetmore has also shown that no nitrogen is produced when nitric oxide is allowed to react with hydrogen atoms drawn from a discharge tube. That considerable amounts of nitrogen and water are found in the photosensitized system can only be attributed to the difference in the experimental conditions. In the latter, the system is static and hydrogen atoms are being continuously formed. In the discharge-tube reactions, the system is dynamic. If only a small fraction of the HNO produced

decomposed into nitrous oxide and water and most of it reacted with hydrogen atoms, the decomposition could be negligible in the flow system but cumulative in the static system.

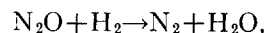
A possible mechanism for the decomposition of HNO may be the following:



Although these reactions may be considered as speculative they are not without foundation. Melville<sup>6</sup> gives the energy of activation of reaction (6c) as 15–20 kcal. If this were so the reaction would be relatively slow. Taylor and Marshall,<sup>7</sup> however, found that the mercury sensitized reaction between hydrogen and nitrous oxide proceeds much more rapidly than that between hydrogen and oxygen. It appears that nitrous oxide should be reduced as fast as it is formed. To test this the rate of reaction between nitrous oxide and hydrogen was measured under conditions exactly similar to those previously. The results of two runs are presented in Table VII. An average rate for the nitric oxide reaction at a hydrogen pressure of 10 cm is 0.45 cm/min. From the over-all reaction



such a rate of pressure change corresponds to 0.30 cm/min. of nitric oxide reacting, or, from the above mechanism to the formation of 0.15 cm/min. of nitrous oxide. Now the over-all nitrous oxide reaction is



whence the observed rate of pressure change is equal to the rate of disappearance of nitrous oxide. The observed rate of disappearance of nitrous oxide even at 1.60 cm is thus faster than its rate of production in the nitric oxide reaction, indicating that it cannot accumulate in the system. The hydrogen atoms required for reaction (6c) balance those produced in (6d) and conse-

<sup>3</sup> J. R. Bates, J. Am. Chem. Soc. **54**, 569 (1932).

<sup>4</sup> W. A. Noyes, Jr., J. Am. Chem. Soc. **53**, 514 (1931).

<sup>5</sup> H. M. Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929).

<sup>6</sup> H. W. Melville, Proc. Roy. Soc. **A146**, 737 (1934).

<sup>7</sup> H. S. Taylor and A. L. Marshall, J. Phys. Chem. **29**, 1140 (1925).

quently there is no disturbance of the stationary atom concentration in the system. Even if the above mechanism is incorrect the fact remains that nitrous oxide cannot accumulate in the system and unless the actual mechanism involves hydrogen atoms or HNO radicals in such a way as to disturb the stationary concentrations of these as calculated later the mechanism of nitrous oxide reduction is not relevant here.

The over-all decomposition of HNO is expressed in reaction (6) as a first-order reaction since the subsequent analysis will show this is in agreement with the observed data whereas a second-order rate is not. The first-order rate suggests that the reaction occurs on the surface.

From reactions (1), (2), and (3) the stationary concentration of excited mercury atoms is given by

$$P_{Hg^*} = I / (k_2 P_{H_2} + k_3 P_{NO}),$$

where  $I$  is the intensity of the light absorbed. The stationary concentration of hydrogen atoms given by reactions (2), (4), and (5) after eliminating HNO by reactions (4), (5), and (6) must be obtained from a quadratic equation in  $P_H$ . Comparison of various approximate solutions of this equation with the experimental results shows that the simplest and soundest approximation will be of the form

$$P_H = (AP_{NO} + B) / P_{NO},$$

where  $A$  and  $B$  are taken as constants, whereas  $B$  would actually be the difference of two approximately equal terms involving  $P_{Hg^*}$ ,  $P_{H_2}$ , or  $P_{NO}$ . With this value of  $P_H$ , the over-all rate of disappearance of nitric oxide as measured by  $k_6 P_{HNO}$  is found to be:

$$\begin{aligned} -dP_{NO}/dt &= k_6 P_{HNO} = k_6 \frac{2k_2 P_{Hg^*} P_{H_2}}{2k_6 P_H + k_6} \\ &= \frac{2k_2 k_6 P_{Hg^*} P_{H_2} P_{NO}}{(2k_5 A + k_6) P_{NO} + 2k_5 B} \\ &= \frac{k P_{H_2} P_{NO}}{\left( P_{H_2} + \frac{k_3}{k_2} P_{NO} \right) (P_{NO} + K)}, \end{aligned}$$

where

$$k = 2k_6 I / (2k_5 A + k_6)$$

TABLE VIII.

Time (min.)	Expt. 41 $k$	Expt. 46 $k$	Expt. 50 $k$
2	0.51	0.78	0.81
4	1.10	1.10	1.05
6	1.14	1.13	1.06
8	1.25	1.17	0.96
10	1.25	1.10	0.86
12	1.33	1.25	0.80
14	1.20	1.21	0.66
16	1.29	1.08	0.56
18	1.32	1.08	0.35
20	1.37	1.15	0.36
25	1.44	1.16	0.32
30	1.22	1.13	0.40
35	0.55	1.16	0.46
40	0.42	0.69	0.46
50	0.63	0.34	0.20

and

$$K = 2k_5 B / (2k_5 A + k_6).$$

According to Bates<sup>8</sup> the number of effective collisions per second at unit pressure between activated mercury atoms and nitric oxide molecules is  $1.25 \times 10^{-7}$  while for hydrogen the value is  $1.13 \times 10^{-7}$ . Hence  $k_3/k_2 = 1.1$ .

Experiments at a total pressure of 15 cm (Table IV) show that at this pressure the rate of reaction is a maximum when the ratio of hydrogen to nitric oxide is slightly greater than two. This condition is satisfied in the above rate equation when  $K = 4.5$ . Hence

$$\text{rate} = k \frac{P_{H_2} P_{NO}}{(P_{H_2} + 1.1 P_{NO})(P_{NO} + 4.5)}$$

A value for  $k$  according to this equation has been calculated for each experiment and is listed in the previous tables. The rate used in the calculation is the maximum rate of pressure change and this has been taken as the rate for the initial pressures. This tends to give high values for  $k$  on account of the induction period since when the maximum rate is actually attained, some reaction has already occurred. Since the induction effect is approximately constant, these values of  $k$ , though high, may be used for comparative purposes. That the rate expression does give constant values for  $k$  throughout a given run is nevertheless shown in Table VIII where the  $k$  values corresponding to the pressure

<sup>8</sup> J. R. Bates, J. Am. Chem. Soc. 52, 3825 (1930); 54, 569 (1932).

data in Table I are listed. In order to eliminate the effect of the induction period the rate equation was integrated from point to point during a run giving:

$$k(t_2 - t_1) = 2(x_2 - x_1) + (b - a + 4.5) \ln \frac{a - x_1}{a - x_2} + 4.5 \ln \frac{b - x_1}{b - x_2},$$

where  $a$  and  $b$  are the initial pressures of hydrogen and nitric oxide, respectively, and  $x$ , measured by  $\frac{2}{3}$  pressure change, is the amount decomposed in time  $t$ . The constancy is excellent save when hydrogen is in excess. This is to be attributed, not to any difference in the chemical behavior when hydrogen is in excess, but merely to the approximation which has been used in determining the stationary hydrogen atom concentration and naturally as the reaction progresses the effective excess of hydrogen increases and the approximation becomes worse as shown by the falling trend in experiment 50. The maximum value of the constant is nevertheless significant.

Inspection of the  $k$  values in Tables II, III, and IV shows good constancy in each set. In Table II the average deviation from the mean is well within experimental error. In Table III there is greater deviation. However, for slow rates the experimental accuracy is less, being

for a rate of 1 mm per min. only about 25 per cent. In Experiments 47 and 51 the low  $k$  value may be due to the presence of excess nitric oxide involving its reaction with water.

The variation of the constant from one set to another may appear significant. When all the experiments are grouped together in the order in which they were performed it is seen that the variation is a gradual decrease down to experiment 75. The variation cannot be attributed to differences in pressure or in the proportions of the reactants since individual experiments which were performed within one set are frequently repeated within another set and the  $k$  value found is in agreement with the average for the set. It must be concluded that the variation is due to a decrease in the illumination in the reaction vessel because of a mercury deposit on the inside and dust accumulation outside. The vessel and lamp were enclosed until after run 75. Inspection showed this condition to be true. When the outside of the reaction vessel was cleaned and flamed (see Table V) the value of  $k$  rose from 1.10 to 1.37. After the vessel had been cleaned thoroughly inside and out, run 87 showed a  $k$  value of 1.70 in agreement with the high values found in the earliest runs.

The apparent variation in the  $k$  values is thus mechanical, reflecting a variation in  $I_{\text{abs}}$  and it must be concluded that the suggested mechanism will account for the observations made.