The MercurySensitized Reaction between Hydrogen and Nitrous Oxide

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The data were obtained for a solution at pH 7.70, buffered by a disodium phosphate-monosodium phosphate mixture. The R rates show almost exactly the same dependence upon catechol concentration (0.56 power) as upon hydroquinone concentration. The $1/t$ rates, which apply to the induction period region of development, vary with a somewhat higher power of the catechol concentration. The rate of the silver-catalyzed reaction of catechol with silver ions derived from a soluble silver salt, on the other hand *is directly proportional* to the catechol concentration. This, again, is the same result as that obtained previously in similar experiments with hydroquinone. The technique employed was the same as that described previously,[8] and the rate data are given in Table II.

Thus, a marked difference is observed, both

TABLE II. Rate of silver-catalyzed reduction of silver ions from solution. Solution: pH 7.58; Na₂SO₃, 0.0555M; AgNO₃, 0.0111M; gum arabic, 0.55 percent; total volume, 90 ml.

Catechol conc.	0.0104	0.0208	0.0416	0.0832
Rate	0.0156	0.0310	0.0627	0.117

with hydroquinone and catechol, between the silver-catalyzed reduction of silver ions from solution and the development of silver bromide grains. Adsorption of the reducing agent is not indicated for the first reaction, but is indicated for the second. This is true under conditions such that the pH is equal in both types of reaction, and the silver-ion concentration of the solution in the first type is equal to or of the same order of magnitude as the equilibrium silver-ion concentration supplied by silver bromide.

The Mercury-Sensitized Reaction between Hydrogen and Nitrous Oxide

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The mercury photo-sensitized reaction of nitrous oxide and hydrogen to produce nitrogen and water has been studied in the pressure range 10–500 mm. It is shown that hydrogen exerts only a minor influence on the rate. A mechanism has been postulated involving a sensitized decomposition of nitrous oxide into nitrogen and atomic oxygen at a rate roughly one thousand times the rate of reaction of hydrogen atoms with nitrous oxide. The atomic oxygen promotes chains by reaction with hydrogen, the chains are terminated by recombination of hydrogen atoms, on the wall at low pressure and mainly in the gas phase above 100 mm pressure under the experimental conditions.

D URING a study of the mercury-sensitized reaction between hydrogen and nitric oxide, Taylor and Tanford[1] concluded that nitrous oxide, if formed during the course of the reaction, could not accumulate in the system because of a rapid reaction with hydrogen atoms. This conclusion was contrary to the findings of Melville[2] in claiming an energy of activation for the reaction between nitrous oxide and hydrogen atoms of 15–20 kcal. Careful analysis of Melville's paper in conjunction with an earlier paper[3] on

the thermal reaction and especially in the light of other work on nitrous oxide[4] showed inconsistencies which called for further study.

EXPERIMENTAL

A low pressure quartz-mercury arc in the form of a flat spiral energized by a 5000-volt transformer carrying about 4.8 amp. in the primary, was used as the source of the resonance radiation. The lamp had an estimated yield of about 90 percent of its energy at 2537A. The reaction vessel was a stoppered quartz flask of about

[1] H. A. Taylor and C. Tanford, J. Chem. Phys. **12**, 47 (1944).
[2] H. W. Melville, Proc. Roy. Soc. **A146**, 737 (1934).
[3] H. W. Melville, Proc. Roy. Soc. **A142**, 524 (1933).
[4] W. H. Manning and W. A. Noyes, Jr., J. Am. Chem. Soc. **54**, 3907 (1932); J. K. Dixon, *ibid.* **56**, 101 (1934).

TABLE I. Pressure change in mm.

Time (min.)	Run 19 P_{N_2O} 28.6 P_{H_2} 28.9	Run 20 249.7 253.9	Run 36 19.8 19.9	Run 119 120.1 81.3
0.5	−0.2	−2.4	0	0
1	0.5	−2.7	0.1	−0.8
2	1.7	−2.1	1.1	1.7
4	3.7	−0.1	2.8	5.2
6	5.2	3.0	4.0	7.7
8	6.9	6.2	4.7	8.6
10	7.9	10.0		8.8
15	10.2	17.7		9.8
20	11.9	24.3		10.7
25	13.0	30.9		
30		36.1		
40		48.6		
50		56.1		
60		61.3		

250-cc capacity, carrying in its neck, placed horizontally, a boat filled with P_2O_5 to remove the water produced by the reaction. The vessel was submerged in a water bath, maintained at 39°C during a run and was connected to reservoirs of reactants, manometer, and pump system as well as to a gas analysis apparatus. After every two runs the flask was detached from the rest of the apparatus, washed, dried, and supplied with fresh P_2O_5.

Nitrous oxide was prepared by decomposition of ammonium nitrate under atmospheric conditions, the water and nitrous oxide being collected at the temperature of liquid nitrogen and then pumped to a good vacuum. The nitrous oxide was later volatilized from the water at −78°C into a large evacuated vessel. It was stored in this reservoir which was always open to a dry-ice trap.

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 at 95°C, the second at room temperature.

The products from two experiments were analyzed by removal from the reaction vessel with a Toepler pump through a trap immersed in liquid nitrogen and thence to a gas burette. Nitrous oxide was thus frozen out along with other possible gases present except nitrogen and hydrogen. The total volume of these latter being determined, the hydrogen was burned over copper oxide at 350°C and the residual gas measured as nitrogen. The contents of the trap was then vaporized and its volume measured.

No attempt was made to analyze this fraction further.

For a run, a known pressure of nitrous oxide and of hydrogen saturated with mercury vapor, was admitted to the reaction vessel and exposed to the lamp which had previously been allowed to attain its full intensity. The course of the reaction was followed by pressure readings on the manometer at suitable intervals.

RESULTS

In Table I are listed the pressure changes observed at various times in four typical experiments chosen to illustrate various characteristics. An induction period is characteristic of all runs. When the pressure of nitrous oxide is high, an initial increase in pressure is observed indicating that the initial slow pressure decrease in other runs is caused by a balancing of this increase by the normal decrease. When nitrous oxide containing mercury vapor but without hydrogen was exposed to the radiation under the same conditions a steady increase in pressure was observed. The initial pressure increase is thus accounted for and at the same time it should be noted that

TABLE II. Dependence of rate on total pressure.

Run	P_{N_2O} mm	P_{H_2} mm	Rate (mm/sec.)	Av. rate	K
27	10.0	11.3	0.0120		
21	9.5	10.7	0.0128	0.012$_4$	0.076
30	20.0	20.1	0.0152		
36	19.8	19.9	0.0151		
40	19.9	19.9	0.0146		
44	20.3	20.3	0.0157	0.015$_2$	0.091
17	28.0	28.9	0.0173		
19	28.6	28.9	0.0174		
24	26.1	26.0	0.0170		
25	26.8	25.3	0.0178		
46	26.9	25.8	0.0179	0.017$_5$	0.100
15	49.9	49.7	0.0186		
16	53.8	52.6	0.0196		
76	51.8	53.0	0.0206		
51	51.5	52.3	0.0212	0.020$_0$	0.111
22	99.1	106.8	0.0221		
C	100	100	0.0223	0.022$_3$	0.114
11	150.1	156.1	0.0236		
12	147.0	155.0	0.0230		
73	149.3	150.0	0.0236		
74	150.1	152.0	0.0237	0.023$_5$	0.106
7	247.3	248.8	0.0269		
20	249.7	253.9	0.0278	0.027$_4$*	0.108

* This value was corrected on the basis of a plot of rate as a function of total pressure to 0.025$_6$.

TABLE III. Dependence of rate on nitrous oxide.

Run	P_{N_2O}	P_{H_2}	Rate (mm/sec.)	Av. rate	K
57	10.1	100.9	0.0064	0.006₄	0.089
92	19.1	99.2	0.0095		
95	21.0	101.0	0.0094	0.009₅	0.088
56	30.7	100.4	0.0122		
88	29.9	102.0	0.0121		
89	29.5	103.8	0.0120		
94	31.1	99.1	0.0124	0.012₂	0.093
91	39.1	101.0	0.0147	0.014₇	0.103
87	49.1	100.2	0.0158	0.015₈	0.099
85	81.0	99.9	0.0208	0.020₈	0.113
C	100	100	0.0223	0.022₃	0.114
79	122.0	101.0	0.0240	0.024₀	0.116

the quenching efficiency of N₂O must be quite high. Again, when in a normal run with hydrogen present and the lamp turned off, there was observed a continued pressure decrease for from one to three minutes, it was obvious that the diffusion of water vapor to the drier was relatively slow when only small amounts were present. If therefore, the diffusion takes about two minutes it is to be expected that the pressure increase due to decomposition of nitrous oxide will evidence itself initially but with increasing amounts of water present a pressure decrease will predominate. The maximum rate of pressure change immediately following the induction period was taken as that most nearly representative of the water-forming reaction. This would of course be a minimum value.

A limitation on the amounts of nitrous oxide and hydrogen which could be used was observed and is illustrated partially by Run 119, a borderline case, where over 75 percent of the reaction (in terms of the final pressure change) is complete in five or six minutes. For still higher ratios of nitrous oxide to hydrogen an irregular pressure increase was observed for only one or two minutes after which no further pressure change occurred. Examination of the drier after such a run showed it to be densely caked and grey or black, quite unlike its appearance after a normal run. If this same drier were used again for a normal run, a rate was observed which was at least 15 percent below that of similar runs using fresh drier. The

ratio of nitrous oxide to hydrogen had therefore to be maintained below 1.3.

Table II shows the dependence of the rate for a 1:1 ratio of the gases as a function of the total pressure varying from 20 to 500 mm.

Table III shows the variation of the rate at constant hydrogen pressure with change in the nitrous oxide pressure from 10 to 125 mm. Comparison of Tables II and III shows a great similarity between the effect of total pressure and of nitrous oxide indicating that the change in nitrous oxide pressure is much more significant than a change in hydrogen. This is borne out by the data in Table IV for the dependence of the rate on hydrogen at constant nitrous oxide. Because of the limitation mentioned previously it was impossible to go below 75-mm hydrogen, the nitrous oxide pressure being 100 mm. The last three runs in Table IV were made after the apparatus had been dismantled and reassembled. They are self-consistent, the trend with changing hydrogen reproduces that of the earlier runs and they differ only in the magnitude of the rates. This is probably caused by a change in the light intensity resulting from a change in position of the lamp.

In Table V are presented the data for several runs with the new lamp setting in which the total pressure was maintained constant at about 200 mm while the ratio of the partial pressures was varied. Again the similarity in the trend of these rates, as the nitrous oxide pressure is changed, with those in Table III shows the prime influence of the nitrous oxide on the over-all rate.

The results of the analyses of the products from two runs are given in Table VI. The first was at

TABLE IV. Dependence of rate on hydrogen.

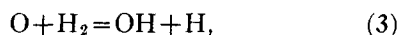| Run	P_{N_2O}	P_{H_2}	Rate (mm/sec.)	Av. rate	K
97	100.8	74.0	0.0215	0.021₅	0.100
96	99.2	119.9	0.0222		
103	99.5	118.0	0.0223		
101	99.7	120.7	0.0222	0.022₂	0.118
C	100	100	0.0223	0.022₃	0.114
98	100.6	153.9	0.0210	0.021₀	0.119
109	99.2	100.0	0.0263	0.026₃	0.143
104	99.7	166.8	0.0246	0.024₆	0.153
108	100.5	200.4	0.0230	0.023₀	0.146

TABLE V. Dependence of rate on pressure ratio.

Run	P_{N_2O}	P_{H_2}	Rate (mm/sec.)	K
117	40.6	157.9	0.0178	0.154
112	60.0	139.7	0.0212	0.149
110	80.3	122.2	0.0241	0.148
111	99.5	102.6	0.0263	0.143
118	111.2	90.6	0.0268	0.139
119	120.1	81.3	0.0275	0.138

TABLE VI. Analysis of products.

	I		II	
$P^0_{N_2O}$	101.2		100.8	
$P^0_{H_2}$	100.7		101.1	
	Calc.	Obs.	Calc.	Obs.
N_2	25.1 cc	25.4	13.4	14.5
H_2	2.0	2.2	13.4	13.7
N_2O	—	—	13.4	15.2

about 93 percent reaction, the second at about 50 percent. The discrepancy between the observed and calculated values for nitrous oxide in the second analysis might indicate the presence of another gas in the nitrous oxide fraction. However, the fact that both the hydrogen and nitrogen are also high casts doubt on this possibility. In any event nitric oxide was not found since no brown fumes formed when the nitrous oxide fraction was mixed with air.

DISCUSSION

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

$$Hg + h\nu = Hg^*, \tag{1}$$

$$Hg^* + H_2 = Hg + 2H, \tag{1}$$

$$Hg^* + N_2O = Hg + N_2 + O, \tag{2}$$

$$O + H_2 = OH + H, \tag{3}$$

$$H + N_2O = N_2 + OH, \tag{4}$$

$$OH + H_2 = H_2O + H, \tag{5}$$

$$2H + M = H_2 + M. \tag{6}$$
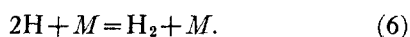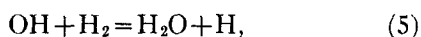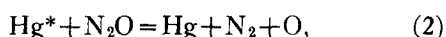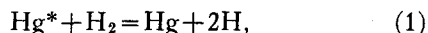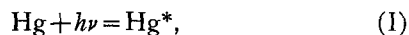
Reactions (1) and (1) constitute the well-known mercury-sensitized dissociation of hydrogen. Melville[2] assumed that nitrous oxide merely deactivates excited mercury and assigned to it a quenching diameter the same as for hydrogen. The observation of a rapid reaction in mercury-sensitized nitrous oxide by Taylor and Marshall,[5] which has been repeated here, as well as in the work of Manning and Noyes,[4] is contrary to this assumption. Noyes shows that the quenching diameter expressed as $(R_{Hg} + R_{N_2O})$ is 10A, an exceedingly large value relatively. Noyes concludes that reaction (2) seems to be the most probable initial step and Stearn and Eyring[6]

[5] H. S. Taylor and A. L. Marshall, J. Phys. Chem. 29, 1140 (1925).

[6] A. E. Stearn and H. Eyring, J. Chem. Phys. 3, 778 (1935).

have calculated the activation energy for the nitrous oxide dissociation to yield $N_2(^1\Sigma)$ and $O(^3P)$ to be only 50 kcal.

The subsequent reactions of the oxygen atoms are those well-established by the interpretation of hydrogen-oxygen systems. As will become obvious later, reaction (2) is the principal mode of destruction of the nitrous oxide but does not quite account quantitatively for the observed rates. This is the main reaction, and requires that the removal of hydrogen atoms from the system occurs chiefly by recombination. In reaction (6) M designates the third body which could be another hydrogen atom, a hydrogen molecule, a nitrous oxide molecule, or the wall of the vessel. It is expected that at least in the higher pressure range a gas phase recombination would be more probable; a wall reaction predominant at low pressures. Concerning the relative efficiencies of hydrogen and nitrous oxide as third bodies little can be said definitely. Melville has suggested that the possible reaction

$$2H + N_2O = H_2O + N_2$$
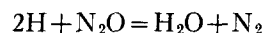
might favor nitrous oxide as being the more efficient. This reaction would however add another mode of removal of nitrous oxide to those pictured above and it is doubtful that the data are sufficiently accurate to warrant its inclusion with the added rate constant. It is not unlikely on the basis of the resonance structure of nitrous oxide that a collision with a hydrogen atom would be 'sticky' thus favoring it as a third body. It has been assumed in the subsequent analysis that the concentration of M may be replaced by the total initial pressure in the higher pressure range.

The removal of nitrous oxide by reaction (4) with a hydrogen atom was used by Melville in interpreting both the thermal and the photo-

chemical reactions. From his interpretation of the measured temperature coefficient he calculates the energy of activation to be 7.5 kcal. but promptly casts doubt on the value and suggests 15–20 kcal. as a more reliable value. Dixon[7] from a study of this reaction using hydrogen atoms from a discharge tube estimated a lower limit of the energy of activation as 10 kcal. Geib also found evidence[8] for a high E and it is found here that this reaction is slow. Some energy would however be available as residual energy in the production of hydrogen atoms from the excited mercury.

Evaluating the stationary concentrations of excited mercury, hydrogen, and oxygen atoms and hydroxyls, the over-all rate of disappearance of nitrous oxide is given by

$$-\frac{dP_{N_2O}}{dt} = \frac{k_2 I P_{N_2O}}{k_1 P_{H_2} + k_2 P_{N_2O}} + \frac{k_4 I^{\frac{1}{2}} P_{N_2O}}{(k_6 P)^{\frac{1}{2}}}$$

$$= \frac{K P_{N_2O}}{P_{H_2} + (k_2/k_1) P_{N_2O}} + \frac{K' P_{N_2O}}{(P_{H_2} + P_{N_2O})^{\frac{1}{2}}}.$$

The ratio of the quenching efficiencies of nitrous oxide and hydrogen for excited mercury, namely k_2/k_1, has a value of 6.4 based on Noyes' value of $100A^2$ for the quenching area of nitrous oxide and $6A^2$ for hydrogen when due allowance is made for the reduced masses of the two molecules. With this ratio known, the rate equation contains two constants. When the pressures of the two gases are equal as in Table II the first term on the right of the equation is constant and hence K' can be deduced from the rate differences. For partial pressures above 50 mm K' has an average value of 0.001. Using this value for K' the values of K given in the previous tables were obtained. The constancy of K in the higher pressure ranges is good. The higher value of the constant in runs numbered 104 and higher

is caused as previously mentioned by the changed position of the lamp. The general constancy is still good, all the pressures being above 50 mm.

That the failure of K to remain constant at lower pressures is probably caused by a wall recombination of hydrogen atoms is shown by the dependence of the rate differences in Table II between 10 and 20 mm, and between 20 and 25 mm, on the pressure of nitrous oxide rather than on its square root. For a wall combination, the rate of reaction (6) would not involve M and the second term on the right of the final rate equation would be $K'' P_{N_2O}$. K'' thus found has a value 0.0003 and K has the constant value 0.070 at 10, 20, and 25 mm (Table II). On the other hand, the drop in rate at low pressure may be due to incomplete quenching since the effect is also observed (Table III) at low nitrous oxide pressures.

The mechanism suggested is thus capable of accounting for the observed results. From the relative magnitudes of K and K' it is apparent that reaction (2) the decomposition of nitrous oxide by excited mercury is much more effective than (4) the reaction with hydrogen atoms which Melville considered the principal reaction. The mechanism is essentially the same as that which Melville proposed for the thermal reaction and thus the thermal and photo-sensitized reactions become correlated. Finally the observations by Taylor and Marshall as also by Melville that the photo-sensitized nitrous oxide-hydrogen reaction proceeds faster than the oxygen-hydrogen reaction receive explanation since the quenching efficiency of nitrous oxide is so high and the chain steps, essentially the same in both reactions are thus initiated more rapidly by oxygen atoms from nitrous oxide. When the nitrous oxide to hydrogen ratio is high the reaction of the oxygen atoms with mercury becomes significant and HgO deposits, driven by the water vapor stream on to the drier causing the discoloration and caking observed.

[7] J. K. Dixon, J. Am. Chem. Soc. 56, 101 (1934).
[8] See Geib, Ergeb. d. exakt. Naturwiss. 15, 44 (1936).