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The Kinetics of Reaction between Nitrous Oxide and Hydrogen at a Silver Surface

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In previous reports it has been shown that the order of magnitude of the rate of reaction between oxygen and hydrogen[1] or carbon monoxide[2] at silver surfaces is roughly equal to the rate at which the reducing gas collides with the (measured) adsorbed oxygen with the necessary joint activation energy. Of the reactants in these cases only oxygen was appreciably adsorbed. It was hoped that the interaction of nitrous oxide and hydrogen would be an analogous case for which the above hypothesis might be tested.

For the homogeneous reaction a few experiments by Hinshelwood[3] gave rates roughly equal to what would be expected for decomposition of nitrous oxide alone. In the more extended work of Melville[4] at 550 to 700° the rate was found to be greater in presence of hydrogen; it was proportional to the pressure of nitrous oxide and nearly independent of that of the hydrogen. A chain reaction was indicated. On a gold wire at 704 to 880° Hutchison and Hinshelwood[5] found that the rate increased with the pressure of each reactant, but more and more slowly, so that no further effect was obtained above 300 to 500 mm. On a platinum wire, which strongly adsorbs hydrogen, the rate at 234 to 307° appeared[3] to be proportional to the pressure of nitrous oxide and inversely proportional to that of the hydrogen. Up to 500° this conclusion was confirmed by Cassel and Glückauf.[6] Above this temperature, however, there was a sharp decrease in rate which was attributed to retardation by oxygen resulting from decomposition of the nitrous oxide.

Our results show that on silver at 60 to 180° the mechanism of reaction consists of a primary decomposition of nitrous oxide, followed by interaction of hydrogen with the resulting adsorbed oxygen. The decomposition of nitrous oxide at temperatures as low as 60° was wholly unexpected in view of the numerous studies of the last decade on the reaction at much higher temperatures at surfaces of platinum,[7] gold,[8] and metallic oxides.[9] In general the rate of decomposition has been found proportional to the pressure of nitrous oxide; only on platinum and a few oxides was it retarded by the oxygen produced.

Experimental Methods

Apparatus.—Reaction kinetics were measured by the flow method. Purified mixtures of nitrous oxide and hydrogen, separately metered by capillary flowmeters, were passed upward through the catalyst at atmospheric pressure at a constant total rate of 50 cc. (0°, 760 mm.) per minute, and the water formed in the reaction was periodically collected and weighed in glass-stoppered weighing tubes filled with magnesium perchlorate. The cylindrical Pyrex catalyst bulb carried a central well to accommodate the copper–constantan thermocouple for potentiometric measurement of temperature. The catalyst was held in place with glass wool in the narrow annular space surrounding the well. To ensure uniformity of temperature two concentric coils of aluminum wire were embedded in the catalyst. Blank runs without the silver showed that up to at least 245° there was no catalysis due to the glass walls or to aluminum, nor any homogeneous reaction. The catalyst bulb was maintained at the desired temperatures by means of suitable liquids boiling under regulated pressures. Since the primary requirement was dissipation of excess heat, the bulb was immersed in the liquid rather than in the vapor. With these arrangements no temperature gradient could be detected at different heights within the catalyst.

The entering gases could be mixed with any desired concentration of water vapor by by-passing them through two thermostated saturators. A by-pass around the catalyst bulb was also provided.

Electrolytic hydrogen was prepared and freed from oxygen, carbon dioxide and water in the usual manner. Nitrous oxide in tanks intended for anesthesia was passed through a washing tower containing a sulfuric acid solution of ferrous sulfate, and then through bulbs containing glass wool, soda lime and calcium chloride. Before entering the catalyst the mixtures were finally dried over magnesium perchlorate. After entering the purifying lines the gases came in contact, in addition to these reagents, only with glass and "Lubriseal" stopcock grease.

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(1) Benton and Elgin, THIS JOURNAL, **51**, 7 (1929).

(2) Benton and Bell, *ibid.*, **56**, 501 (1934).

(3) Hinshelwood, *Proc. Roy. Soc.* (London), **A106**, 292 (1924).

(4) Melville, *ibid.*, **A142**, 524 (1933).

(5) Hutchison and Hinshelwood, *J. Chem. Soc.*, **128**, 1556 (1926).

(6) Cassel and Glückauf, *Z. physik. Chem.*, **B19**, 47 (1932).

(7) Hinshelwood and Prichard, *J. Chem. Soc.*, **127**, 327 (1925); Cassel and Glückauf, *Z. physik. Chem.*, **B9**, 427 (1930); **B17**, 380 (1932); van Praagh and Topley, *Trans. Faraday Soc.*, **27**, 312 (1931); Schwab and Eberle, *Z. physik. Chem.*, **B19**, 102 (1932); Lüke and Fricke, *ibid.*, **B20**, 357 (1933).

(8) Hinshelwood and Prichard, *Proc. Roy. Soc.* (London), **A108**, 211 (1925).

(9) Shah, "Proc. 15th Indian Sci. Cong.," 1928, p. 170; *Chem. Abs.*, **25**, 2907 (1931); Schwab and Schultes, *Z. physik. Chem.*, **B9**, 265 (1930); Schwab, Staeger and v. Baumbach, *ibid.*, **B21**, 65 (1933).

Catalyst.—The finely divided silver was prepared by cautious reduction with hydrogen, up to 100°, of precipitated silver oxide by the method previously described.[10] It was then heated in a stream of hydrogen for four hours at 132°. Of the product thus obtained, a representative sample of 9.594 g. was used for the kinetic studies, and the remainder (46.36 g.) reserved for the adsorption measurements. Subsequently, between Runs 18 and 19 (see below), both portions were heated in hydrogen at 210° for four hours.

Procedure and Calculations.—Each run was continued until a constant rate was attained, as evidenced by agreement (within 0.1–0.2 mg.) of four or five weighings of the water formed in ten-minute intervals over a period of two hours or more. For thirty minutes before and after each run pure hydrogen was passed over the catalyst at the temperature of the run.

"Check" runs were made alternately throughout the investigation. The marked changes in activity of the catalyst thus revealed were corrected for by selecting a particular run in each series as standard, and adding to, or subtracting from, the yields in the other runs the percentage amount necessary to bring the checks into agreement. Since conditions were purposely chosen to give small percentage conversions, the reaction kinetics are derivable, without appreciable error, on the basis of the average of the entering and exit partial pressures of each gas.

All volumes are expressed in cc. at 0° (760 mm.), and all pressures in mm. of mercury at 0°.

Reaction Kinetics

All runs are numbered in the order in which they were made. The results at 60° with hydrogen in excess are shown in Table I. Column 2 gives the entering rate of flow of nitrous oxide; the remainder of the 50 cc./min. was hydrogen. The values in Column 3 are the averages of the entering and exit pressures of nitrous oxide. The last two columns show the yield observed at the steady state, and the same corrected for changes in the activity of the catalyst. Since the time required to reach a steady state had continuously increased in Runs 1 to 7, hydrogen alone was passed over the catalyst for four hours at 84° before Run 8. As can be seen from Table I this treatment was accompanied by a marked increase in activity; in Run 12 a conversion of 100% was obtained. On the whole the data leave no doubt that at 60° the rate of reaction is independent of the pressure of nitrous oxide.

TABLE I

EFFECT OF PRESSURE OF NITROUS OXIDE AT 60°

Run	N_2O, cc./min.	Av. pN_2O, mm.	Yield, mg. obs.	H_2O/10 min., corr.
1	5.00	71.0	3.64	(4.2)
2	2.50	33.6	3.70	4.3
3	5.00	71.1	3.60	(4.2)
4	1.25	15.0	3.82	4.1
5	5.00	70.9	4.17	4.2
6	7.50	108.5	4.42	4.1
7	5.00	71.2	4.88	(4.2)
8	5.00	64.4	10.7	(11.6)
9	5.00	64.2	11.6	11.6
10	2.50	26.7	11.4	11.5
11	5.00	63.7	11.4	(11.6)
12	1.25	9.3	10.6	
13	5.00	64.0	11.5	(11.6)
14	7.50	104.1	11.2	11.3

A series at 60° with nitrous oxide in excess is detailed in Table II. While the rapid decrease in activity limits the quantitative significance of these results, it is clear that the rate increases with increasing hydrogen pressure.

TABLE II

NITROUS OXIDE IN EXCESS AT 60°

Run	H_2, cc./min.	Av. pH_2, mm.	Yield, mg. H_2O/10 min. obs.	corr.	calcd., Eq. 1
15	5.00	74.6	1.31	(1.21)	
16	2.50	37.1	0.80	0.77	0.77
17	5.00	73.9	1.21	1.21	1.19
18	7.50	110.9	1.53	1.9	1.52
19	5.00	74.0	0.75	(1.21)	

At this point, after long treatment with hydrogen at 60° had failed to restore the activity, the

TABLE III

NITROUS OXIDE IN EXCESS AT 160–180°

Run	H_2, cc./min.	Av. pH_2, mm.	Yield, mg. H_2O/10 min. obs.	corr.	calcd., Eq. 1
		Temperature, 160°			
20	5.00	72.3	2.82	(3.91)	
21	1.25	17.9	1.02	1.2	1.22
22	5.00	72.0	3.91	3.91	3.84
23	7.50	107.9	4.90	4.83	5.36
24	5.00	71.4	4.03	(3.91)	
25	2.50	35.5	2.23	2.19	2.17
26	5.00	71.1	3.93	(3.91)	
		Temperature, 170°			
27	5.00	68.8	5.00	4.97	5.60
28*	5.00	69.8	3.93	(3.91)	
29	1.25	17.5	1.59	1.64	1.67
30*	5.00	72.2	3.65	(3.91)	
31	7.50	106.0	7.05	7.99	7.95
32*	5.00	71.1	3.25	(3.91)	
33	2.50	34.5	2.74	3.16	3.12
34*	5.00	71.7	3.53	(3.91)	
		Temperature, 180°			
35	5.00	68.5	6.49	7.6	7.5
36*	5.00	71.4	3.11	(3.91)	
37*	5.00	71.1	2.94	(3.91)	
38	7.50	101.2	8.58	10.4	10.4
39*	5.00	70.6	3.52	(3.91)	

* Check runs at 160°.

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(10) Benton and Elgin, THIS JOURNAL, **48**, 3027 (1926).

catalyst was sintered in a stream of hydrogen for four hours at 210°. The effect of hydrogen pressure on the conversion was then studied at 160, 170 and 180°, with the results given in Table III. Nitrogen, which is certainly not adsorbed by the catalyst, is assumed to be without effect on the conversion. The influence of the other product, water, is shown in Table IV. These last measurements were made at 90°, since the activity of the catalyst at 160–180° became inconveniently high shortly after Run 39. In each case the entering gas consisted of 5 cc. per min. of hydrogen and 45 of nitrous oxide, plus the water equivalent to the values in Column 2. The latter were determined by direct weighings of the water from the gas stream by-passed around the catalyst. Because of the small conversions the average pressure of hydrogen was substantially constant (74 mm.). It is evident that at 90° water strongly retards the reaction.

TABLE IV

EFFECT OF WATER VAPOR AT 90°

Run	Entering H_2O, mg./10 min.	Av. pH_2O, mm.	Yield, mg. H_2O/10 min.	
			obs.	corr.
40	0.0	3.13	3.35	1.25
42	1.46	3.90	1.25	0.80
43	0.0	1.17	1.25	1.25
44	3.29	6.75	0.72	0.75
45	0.0	1.09	1.17	1.25

Tests with Nessler's solution in runs at 60° and at 160° failed to detect any ammonia in the exit gases.

The results in Tables I–IV suggest an equation for the rate of reaction in the form

$$Y = k\bar{p}_H/(1 + a\bar{p}_W) \qquad (1)$$

where Y is the yield in mg. of water per ten minutes, $\bar{p}_H$ and $\bar{p}_W$ are the averages of the entering and exit partial pressures of hydrogen and water, respectively, and k and a are constants at a given temperature. In absence of entering water vapor, $\bar{p}_W = {}^1/_2 \times Y/10 \times 22.4/18 \times 750/50 = 0.933\ Y$, where the nearly constant barometric pressure has been taken as 750 mm. Hence the above reaction equation may be put in the form $\bar{p}_H/Y = 1/k + (0.933\ a/k)Y$. On a plot of $\bar{p}_H/Y$ *versus* Y, the best straight lines drawn through the observed points gave the following values for the constants at temperatures of 60, 160, 170 and 180°, respectively: $k = 0.045$, 0.076, 0.104, 0.14; $a = 1.6$, 0.116, 0.059, 0.046. The yields calculated by inserting these values in Eq. 1 are given in the last column of Tables II and III. On the whole the agreement is good, except in a few cases where large corrections for change in activity were necessary. Because of the intervening heat treatment of the catalyst, the values of k and a at 60° are not comparable with those at the higher temperatures.

On a plot of log k *versus* $1/T$ the points at 160–180° fall on a nearly straight line. The energy of activation thus calculated is 13 kcal., and is probably accurate within 10%.

Adsorption of Water Vapor

The larger sample of silver used for adsorption studies had been given the same preliminary treatment as the catalyst. The values recorded here are the volumes in cc. (0°, 760 mm.) taken up by the 46.36 g. sample.

Water Vapor.—After equilibrating the sample with mixtures of water vapor and either nitrous oxide or hydrogen, the adsorbed water plus that in the free space was swept out, collected and weighed. The volume of the free space was determined with hydrogen, which is not appreciably adsorbed under the conditions used.[10] In this way the "nitrous oxide-covered" surface was found to adsorb 1.6 cc. of water at 180° and 250 mm., 1.8 cc. at 160° and the same pressure, and 8.0 cc. at 60° and 60 mm. In experiments with hydrogen as diluent the bare surface adsorbed only 1.0 cc. at 160° and 250 mm. These results, which are qualitatively similar to those obtained by Benton and Elgin[1] for "oxygen-covered" and bare silver surfaces, are clearly consistent with the retarding influence of water on the catalysis. While a number of complete isotherms were determined with a view to a quantitative comparison of the values of a in the equation $V_{\text{ads.}} = V^\circ ap/(1 + ap)$ with the a in the kinetic equation given above, the method was insufficiently accurate for these small adsorptions.

Decomposition of Nitrous Oxide

The behavior of this gas in contact with silver was studied in closed system in an apparatus of the type described by Pease.[11] It can safely be assumed that the nitrogen used as reference gas was not adsorbed. Between runs the sample was treated with hydrogen for several hours at about 200° and then evacuated.

At 160° no immediate adsorption of nitrous oxide occurred. Instead the pressure in the system rose gradually from the calculated free-

(11) Pease, THIS JOURNAL, **45**, 1197 (1923).

space value at zero time and continued to increase slowly for many hours, but ultimately became substantially constant. The percentage increase of pressure ranged from 26 to 37, as compared with the theoretical 50% for decomposition into nitrogen and oxygen or into nitrogen and nitric oxide, or 25% if nitrogen and nitrogen dioxide were formed. Formation of nitric oxide or nitrogen dioxide as the *principal* reaction is incompatible with previous studies of the decomposition, both homogeneous and catalyzed, over a wide range of higher temperatures. Production of very small quantities of the dioxide, either directly or through oxidation of nitric oxide, is not excluded.

From the difference between the theoretical and observed final pressures the amount of oxygen adsorbed could be calculated, or at least an upper limit for the adsorption in case the decomposition of nitrous oxide was not quite complete. Typical values are given in Table V. In each run the successive amounts of nitrous oxide were introduced without removing the accumulated products of the previous decomposition. Run 1 refers to our 46.36 g. sample; in Run 2 and subsequent runs another sample (Ag_{II}, 47.70 g.) was used. The initial and final pressures in the free space may be obtained by multiplying the values in Columns 2 and 3, respectively, by 37.0 (Run 1) or 37.3 (Run 2). The theoretical increase of pressure and, therefore, the calculated adsorptions of oxygen in Table V would be somewhat less if any nitrogen dioxide was formed, or if, as is probable,[12] the original nitrous oxide contained 2 to 3% of inert gas.

TABLE V

DECOMPOSITION OF NITROUS OXIDE AT 160°

Run	Total N_2O in, cc.	Final vol. in free space, cc.	O_2 adsorbed, cc.	Total time, hr.
1a	4.58	6.10	0.77	1.5
1b	6.31	8.62	.85	10
1c	10.65	13.82	2.16	17
1d	13.06	16.44	3.15	21
2a	7.53	9.54	1.76	21
2b	10.37	13.10	2.46	25
2c	14.99	19.34	3.15	29

The accumulation of adsorbed oxygen markedly inhibited the rate of decomposition. Thus, for example, with nearly equal pressures of nitrous oxide, the average rate for the first ten minutes in Run 1c was about 0.01 cc. per min., as compared with 0.08 in Run 1a. For an initially bare surface (Ag_{II}) the rate at which oxygen appeared in the gas phase increased with the pressure of nitrous oxide, as shown in Table VI. When the inhibition by oxygen is taken into account, the apparent one-half order with respect to nitrous oxide would probably become first order.

TABLE VI

RATE OF DECOMPOSITION AS FUNCTION OF PRESSURE

Init. pN_2O, mm.	$\Delta P = pO_2$, after		$k = (\Delta P/t)^2/pN_2O$	
	5	10 min.	5	10 min.
281	27	34	0.104	0.041
184	19	25	.078	.034
485	34	42	.095	.036

In a subsequent study[13] of the adsorption of oxygen as such, Ag_{II} at 160° took up altogether about 9 cc. of this gas, of which 4 to 5 cc. was adsorbed almost instantaneously even at pressures of the same order as the average oxygen pressures built up in the present work. With 5 cc. present on the surface the rate of *desorption* of oxygen was only 0.004 cc. per hour. Accordingly, in the decomposition of nitrous oxide we would have expected no oxygen to appear in the gas phase until after an adsorption of at least 5 cc. had accumulated. Actually gaseous oxygen appeared at once, and even after many hours the adsorption amounted to only 1 to 3 cc. The supposition that large quantities of adsorbed oxygen were present initially, having escaped removal in the preliminary treatment with hydrogen, appears inadmissible in the light of our earlier studies on this system. The amount of adsorbed oxygen might be kept down to small values, in spite of a high rate of adsorption, if some almost equally rapid process occurred by which it was removed from the surface. The only conceivable process of this kind is reaction with nitrous oxide; the experiments show, however, not only that the accumulation of adsorbed oxygen strongly *retards* the decomposition of nitrous oxide, but that the total rate of disappearance of the latter is negligibly small compared to the expected rate of adsorption of oxygen. In view of the facts observed, we can find no means of escape from the following conclusions: (1) the primary decomposition of nitrous oxide results in gaseous nitrogen and an adsorbed oxygen atom which may react with another molecule of nitrous oxide to give *gaseous* oxygen and nitrogen; (2) the oxygen atoms (or possibly oxides of nitrogen),

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(12) Compare Bennett, *J. Phys. Chem.*, **34**, 1137 (1930); van Arkel and Beek, *Pharm. Weekblad*, **69**, 469 (1932).

(13) Benton and Drake, THIS JOURNAL, **56**, 255 (1934).

presumably occupying the most active spots, inhibit the ordinary activated adsorption of oxygen; (3) nitrous oxide does not react readily with oxygen held as ordinary activated adsorption; (4) the ordinary activated adsorption probably does not consist of atoms. Such a mutual inhibition as indicated in (2) and (3) might well give rise to large apparent changes in activity as noted in the catalytic experiments with hydrogen.

With Ag_{II} at 60° there was an immediate adsorption of about 0.1 cc. of nitrous oxide, followed by a slow and barely detectable increase in pressure, in one case for example, equivalent to 0.06 cc. in four hours. The fact that nitrous oxide was being decomposed very slowly was proved by a dynamic experiment (at 61°) in which this gas at atmospheric pressure was passed over Ag_{II}, nitrous oxide and oxygen in the exit gas being removed by a trap at $-183°$ and pyrogallol solution, respectively, and the nitrogen collected in a buret over water. Decomposition proceeded more and more slowly and finally came to an end, with a total of 14.5 cc. (0°, 760 mm.) of nitrogen collected. The equivalent 7.3 cc. of oxygen was probably retained by the catalyst only in part.

Conclusion

It is clear that the interaction of nitrous oxide and hydrogen in our catalytic experiments involved a primary decomposition of nitrous oxide, followed by reaction of hydrogen with the resulting adsorbed oxygen. Such a mechanism was perhaps to be expected, since any nitrous oxide adsorbed on silver would doubtless be oriented with the nitrogen atoms toward the gas phase and thus in a position unfavorable for interaction with gaseous hydrogen. Our absolute rates of reaction at the lower temperatures were of the same order, per gram of catalyst similarly prepared, as those observed by Benton and Elgin[10] for the hydrogen–oxygen reaction. As a further proof of this correspondence we found that when a mixture of 2.5 cc. per minute of oxygen and 47.5 of hydrogen was suddenly substituted for one of $5N_2O:45H_2$, after the latter had reached a steady conversion over Ag_{II} at 61°, the rate of water formation changed only from 7.4 to 11.3 mg. per five minutes.

The amount of reactive oxygen on the surface at the steady state was evidently nearly the same regardless of the pressure of nitrous oxide. On the assumption that in the catalytic reaction the successful fraction of all collisions of gaseous hydrogen with adsorbed oxygen is given by the factor $e^{-13,000/(RT)}$ (any difference between the true and observed activation energies being disregarded), the observed value of the reaction constant k at 160° would require an oxygen-covered surface of only 12 sq. cm. at the steady state. This would mean an adsorption[13] of 5.4×10^{-4} cc. of oxygen by the catalyst, equivalent to 0.0026 cc. on the larger (46.36 g.) sample. Even if the true activation energy were as large as 16,000 cal. (the value obtained for the hydrogen–oxygen reaction), an adsorption by the catalyst of only 0.019 cc. of oxygen would be indicated. It is evident either that an extremely small fraction of the surface is occupied during the catalysis by oxygen in a suitably reactive form, or that the simple collision hypothesis is inadequate. In view of the complexities of the reaction detailed analysis at this time appears unwarranted.

Summary

In contact with reduced silver at 60 to 180° the rate of interaction of nitrous oxide and hydrogen is found by the flow method to be expressible by the equation $Y = k\bar{p}_H/(1 + a\bar{p}_W)$, where Y is the "steady-state" rate, $\bar{p}_H$ and $\bar{p}_W$ are the average partial pressures of hydrogen and water vapor, respectively, and k and a are constants. From the change of k with temperature an activation energy of 13 kcal. is calculated.

Measurements of the adsorption of water vapor are consistent with its observed retarding effect on the reaction.

Nitrous oxide is not appreciably adsorbed as such, but slowly decomposes to form nitrogen and oxygen, the latter being slowly adsorbed and retarding further decomposition. This fact, as well as direct comparison of catalytic rates when oxygen is substituted for nitrous oxide, shows that the catalytic reaction involves a primary decomposition of the nitrous oxide, followed by interaction of hydrogen with the resulting adsorbed oxygen.

Some decomposition product of nitrous oxide, presumably adsorbed oxygen atoms, markedly inhibits the ordinary activated adsorption of oxygen—a fact which suggests that the latter may be molecular rather than atomic.

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