All the evidence indicates that the explosiveness is inherent in the dark coating that forms on the metal. Attempts to analyze this coating were unsuccessful. No solvent was found that would remove the excess perchloric acid without reacting with the dark layer. When the activated surface was washed with water, the deposit was instantly hydrolyzed, giving an acid solution containing $Bi^{+++}$, $ClO_4^-$ and $Cl^-$ ions. Analyses of these solutions gave varying results, impossible of interpretation. For example, in one series of three analyses, the $Bi^{+++}$–$Cl^-$ ratios (in gram atoms) of the hydrolyzed products were 1:0.104, 1:0.185 and 1:0.084. This variation is doubtless due to the loss of hydrochloric acid by volatilization during the activation process, while the $Bi^{+++}$ was left behind as a perchlorate.

The over-all reaction, including the preliminary action, the formation of the dark coating, and its hydrolysis, was studied as follows. A piece of bismuth embedded in glass wool was placed in one arm of an inverted V-shaped tube, and a few cubic centimeters of concentrated perchloric acid were added to the other arm. The apparatus was then evacuated and sealed off. The acid was then run into the arm containing the bismuth and the apparatus heated until the dark coating appeared. The solution was then run back into the other arm, and the product exploded by a slight blow on the tube. After several failures, a series of several explosions was obtained without demolishing the tube. The white fumes formed condensed on the surface of the tube, and were subsequently found to contain bismuthyl chloride. The tube was opened, and the solution and deposit analyzed, giving a $Bi^{+++}$–$Cl^-$ ratio very close to 8:3. This indicates that the gross reaction may be represented as

$$8Bi + 24HClO_4 \longrightarrow 7Bi(ClO_4)_3 + BiCl_3 + 12H_2O$$

This equation, however, gives no information about intermediate reactions.

There remains the possibility that the explosion is due to salts of monovalent or divalent bismuth. The strongest evidence against such an assumption is that there appears to be no metallic bismuth in the explosion products.

## Summary

Various hypotheses are considered to account for the explosive reaction of bismuth with hot, concentrated perchloric acid. The explosiveness seems inherent in the dark layer formed on the bismuth during the heating. Owing to its instability, this product has not been separated, and no analysis has been possible.

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[Contribution from the Sterling Chemistry Laboratory of Yale University]

# The Reaction between Nitrous Oxide and Hydrogen on Platinum

By J. K. Dixon[1] and John E. Vance

The catalyzed reaction of hydrogen on nitrous oxide has recently been the subject of several investigations. The reaction affords a means of comparing the rates of reaction of hydrogen and deuterium,[2] and its behavior on different catalysts is interesting, particularly in view of the various relationships between the kinetics of the reaction and the adsorption of the two reacting gases.[3] At one extreme, hydrogen may be so strongly adsorbed by the catalyst that the rate of reaction is practically independent of the hydrogen pressure, and at the other extreme the primary process may be a decomposition of nitrous oxide on the catalyst so that the rate is largely independent of the nitrous oxide pressure, as is the case on a reduced silver surface.[3]

Between these two extremes have been found[4,5,6] cases in which the mechanism changes, depending upon which of the two gases is in excess. The reaction as reported here belongs to the first class and since it has been possible to establish the simple mechanism applying, it seems desirable to present the results.

The characteristics of the reaction on a platinum filament have been determined previously by static methods.[4,6] By using flowing gases we have been able to eliminate some of the un-

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[1] Sterling Fellow of Yale University, 1932–1933. Present address Calco Chemical Company, Bound Brook, New Jersey.

[2] H. W. Melville, *J. Chem. Soc.*, 797 (1934).

[3] For a review of the literature, see for example, Benton and Thacker, This Journal, **56**, 1300 (1934).

[4] Hinshelwood, *Proc. Roy. Soc.* (London), **A106**, 292 (1924).

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

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

certainty arising from the unreproducible character of static experiments and to obtain a satisfactory mechanism under certain conditions for the reaction on smooth platinum wires.

## Experimental

Hydrogen, nitrogen and nitrous oxide were obtained from tanks. Hydrogen was purified by passage over solid potassium hydroxide, copper at 450°, calcium chloride and finally phosphorus pentoxide. Nitrogen was purified by passing it over copper at 450°, through a concentrated solution of potassium hydroxide, then over solid calcium chloride and phosphorus pentoxide. Some impurity, which was possibly carbon dioxide, led to a poisoning of the catalyst unless the nitrogen was purified with alkali in the way described. Nitrous oxide was passed through a solution of concentrated sulfuric acid containing solid ferrous sulfate, then over solid potassium hydroxide and finally phosphorus pentoxide. Air was excluded from these systems at all times.

The catalyst consisted of 0.1-mm. diameter wire gauze with an apparent total area of 38 sq. cm., which remained unchanged in appearance after use.

Each gas passed through a flowmeter before mixing. The flowmeters were standardized a number of times, the results agreeing to ±2%. Overflows kept the pressure heads constant. Water vapor in the "off-gases" was collected in a phosphorus pentoxide weighing tube, which was connected to the outlet tube from the catalyst by means of an ungreased ground joint. Weighings were made to ±0.2 mg.

A Pyrex catalyst tube was inserted in a furnace made of a long, well-insulated silica tube equipped with double-wrapped heating wire. A chromel–alumel thermocouple was placed in an inset tube located at the middle of the catalyst. The couple was twice standardized against a Bureau of Standards calibrated platinum resistance thermometer. Catalyst temperatures were measured with an accuracy of 0.1° and controlled during an experiment to ±0.5°.

A bubbling tube containing water at a constant temperature was sealed in after the nitrogen flowmeter before the mixing point with the other gases. By means of a suitable arrangement of stopcocks, the nitrogen was passed through or around the saturator, as desired. Blank runs, with nitrogen passing through the saturator and with no hydrogen or nitrous oxide present, gave the amount of water added from the saturator.

The amount of decomposition of the nitrous oxide alone at one atmosphere pressure and the highest temperature used in any of the experiments was found to be less than 0.5%. Tests were made for the presence of reaction products other than water. The off-gases were passed through water and the resulting solution analyzed. The amount of ammonia, $NO_3^-$ or $NO_2^-$ formed was *less than* $10^{-5}$ times the amount of water formed. The rate of reaction of hydrogen and nitrous oxide in the reaction chamber without the catalyst was negligible at all temperatures.

## Results

It was found that duplicate experiments checked well as long as sufficient time was allowed for the catalyst to reach conditions of equilibrium. Since nitrous oxide was not passed over the platinum at night it was often necessary at the beginning of a day to allow the reaction to proceed for one or two hours under fixed conditions before the reaction velocity reached a constant value. Passage of hydrogen, nitrogen or a mixture of the two gases over the catalyst at night did not affect this phenomenon. Tests and experiments to find impurities in the gases were negative. No adequate explanation of the temporary change in activity has been deduced. On raising the temperature of the platinum the rate of reaction was first low and then rose to some higher value; on lowering the temperature the reverse was true. The temperature coefficient and reaction mechanism were the same no matter how the temperature variation was carried out.

TABLE I

THE RATE OF REACTION OF NITROUS OXIDE AND HYDROGEN ON PLATINUM WIRE. AREA 38 SQ. CM.

| Total flow rate, cc./min. | Av. pressures, atm. $P_{N_2O}$ | $P_{H_2}$ | $P_{H_2O}$ | Water formed mole/sec. $\times 10^6$ $\omega$ | Water added mole/sec. $\times 10^6$ | $\epsilon^{1/2}$ $\times 10^3$ |
|---|---|---|---|---|---|---|
| $t$, 259.4°; $K$, 87 | | | | | | |
| 92.4 | 0.204 | 0.206 | 0.000306 | 0.0385 | | 0.46 |
| 230.8 | .328 | .039 | .000180 | .0566 | | .51 |
| 134.1 | .434 | .179 | .000270 | .0493 | | .36 |
| 94.8 | .806 | .193 | .000788 | .1018 | | .41 |
| 69.4 | .710 | .334 | .000404 | .0808 | | .36 |
| | | | | | Av. | .42 |
| $t$, 333.0°; $K$, 11 | | | | | | |
| 233.3 | 0.0478 | 0.206 | 0.000394 | 0.0908 | | 1.39 |
| 90.3 | .210 | .200 | .00221 | .2605 | | 1.21 |
| 163.8 | .464 | .215 | .00261 | .580 | | 1.23 |
| 93.5 | .798 | .190 | .00678 | .892 | | 1.28 |
| 195.2 | .194 | .0468 | .00100 | .277 | | 1.29 |
| 61.0 | .188 | .806 | .00274 | .257 | | 1.25 |
| 192.6 | .196 | .213 | .00106 | .273 | | 1.24 |
| 91.2 | .204 | .199 | .0121 | .163 | 0.685 | 1.19 |
| 193.7 | .195 | .212 | .0107 | .228 | 1.32 | 1.36 |
| 164.1 | .466 | .217 | .00772 | .468 | 0.636 | 1.22 |
| 91.9 | .200 | .195 | .0120 | .183 | .673 | 1.27 |
| | | | | | Av. | 1.27 |
| $t$, 404.0°; $K$, 9.4 | | | | | | |
| 224.8 | 0.0503 | 0.217 | 0.00218 | 0.673 | | 3.97 |
| 119.2 | .0944 | .420 | .00657 | 1.192 | | 4.00 |
| 185.2 | .178 | .184 | .00718 | 1.807 | | 3.79 |
| 236.1 | .317 | .201 | .00893 | 2.880 | | 3.68 |
| 192.8 | .0930 | .0498 | .00288 | 0.756 | | 3.30 |
| 224.2 | .0527 | .219 | .01403 | .458 | 1.95 | 3.95 |
| | | | | | Av. | 3.78 |
| $t$, 470.9°; $K$, 4.5 | | | | | | |
| 221.0 | 0.0480 | 0.217 | 0.00706 | 2.947 | | 8.6 |

Table I represents the results of a typical series of some one hundred and fifty individual experiments. The temperature variation was in the order shown in the table. The average partial pressures of nitrous oxide, hydrogen and water in atmospheres, are shown in the table as calculated from the initial partial pressures and the amount of water formed. The partial pressure of nitrogen can be calculated from the data in Table I, since the total pressure was always one atmosphere. When water was added to the inlet gases the amount of water formed was calculated by taking the difference between the total found and the amount added in the corresponding blank run. Except for these less exact experiments with added water, the accuracy of the experiments was equal to or better than ±5% at the three highest temperatures. The amount of water formed and the constants in the table refer to the whole surface.

In order to obtain an equation which expresses the reaction velocity of hydrogen and nitrous oxide to form nitrogen and water as a function of the partial pressures of the gases, it is necessary to consider the results of certain adsorption studies. A review of the experiments of Benton and his collaborators, dealing with the adsorption of hydrogen by metals, shows that hydrogen is absorbed in an activated form on platinum above 250° even when the metal is in the form of a smooth wire. The rate of transformation of para to ortho hydrogen on metals at relatively high temperatures involves an activated form of the adsorbed gas. The activated form is atomic hydrogen.[7] We have found that nitrous oxide did not decompose at temperatures less than 470° which is in accord with previous observations of Cassel and Glückauf.[6] This leads to the conclusion that nitrous oxide is rapidly and reversibly adsorbed on platinum below about 500°. The amount of hydrogen adsorbed by platinum may, in a certain temperature interval, increase with temperature due to activated adsorption. The amount of nitrous oxide adsorbed should decrease with temperature up to 500°. Qualitatively at least the amount of hydrogen adsorbed should be considerably greater than that of nitrous oxide from 250 to 500°.

The formula expressing the rate of reaction is derived in a way described by Langmuir.[8] The rate of reaction in moles per second is $\omega$, the $\mu$'s are the rates at which the various gases strike the surface in moles per second, the $\theta$'s are the fractions of the surface covered with the gases, the $\alpha$'s are the accommodation coefficients and $\nu$'s the rates of evaporation in moles per second. The subscripts 1, 2 and 3 refer to hydrogen, nitrous oxide and water, respectively. The quantity, $\theta$, denotes the fraction of the surface free of gas. Reaction is assumed to take place when a nitrous oxide molecule from the gas collides with two hydrogen atoms occupying adjacent spaces of adsorption on the surface. It will be assumed for the present that the rates of condensation and evaporation of the hydrogen are of the same order of magnitude as the rate of reaction. The following equations are obtained in the usual way

$$\omega = \alpha_1\theta^2\mu_1 - \nu_1\theta_1^2 \tag{1}$$

$$\omega = \epsilon\mu_2\theta_1^2 \tag{2}$$

$$\nu_2\theta_2 = \alpha_2\mu_2\theta \tag{3}$$

$$\nu_3\theta_3 = \alpha_3\mu_3\theta \tag{4}$$

$$\theta + \theta_1 + \theta_2 + \theta_3 = 1 \tag{5}$$

Since the results are not sufficiently accurate to evaluate the slight influence of hydrogen exactly, it cannot be stated definitely that hydrogen atoms and not molecules are reactants. If the latter are involved, Equations (1) and (2) should be modified accordingly.

On solving, one finds

$$\left(\frac{\epsilon\mu_2}{\omega}\right)^{1/2} = 1 + \frac{1}{\theta_1}\,(\theta_2 + \theta + \theta_3) \tag{6}$$

Equation (6) reduces to a form which agrees with experimental data if $\theta$ and $\theta_2$ can be neglected in comparison with $\theta_3$ and the rate of reaction, $\omega$, is much less than $\alpha_1\theta^2\mu_1$. Measurements of Rowley and Bonhoeffer,[9] as well as of Bonhoeffer and Farkas,[10] indicate that $\alpha_1$ is greater than 0.1, which leads to a value of $\theta$ less than 0.01 if the rate of reaction is neglected. Equation (6), on the basis of the assumptions, reduces to

$$\epsilon^{1/2} = \left[1 + K\frac{p_{H_2O}}{p_{H_2}^{1/2}}\right]\left[\frac{\omega}{\mu_{N_2O}}\right]^{1/2} \tag{7}$$

which is the same equation as used to calculate constants in Table I, except in the latter $p_{N_2O}$ has replaced $\mu_{N_2O}$. Data in Table I indicate that $\theta_3/\theta_1$ decreases from approximately 0.5 at 470° to 0.1 at 260°.

If anomalies due to new forms of activated adsorption are neglected, $\theta_3$ and $\theta_1$ should decrease with an increase in temperature. There

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(7) Bonhoeffer, Farkas and Rummel, *Z. physik. Chem.*, **B21**, 225 (1933). See also Sherman and Eyring, THIS JOURNAL, **54**, 2661 (1932).

(8) See for example, *Trans. Faraday Soc.*, **17**, 621 (1922).

(9) Rowley and Bonhoeffer, *ibid.*, **28**, 242 (1933).

(10) Bonhoeffer and Farkas, *Z. physik. Chem.*, **B21**, 84 (1933).

should be some higher temperature or lower pressure region in which the surface is not completely covered where $\theta$ will no longer be negligible. The reaction might be concerned with an interaction of adsorbed nitrous oxide and adsorbed hydrogen, in which case Equations (1) to (7) would no longer apply and the reaction would be inhibited by hydrogen.[11] This would account for the marked inhibition by hydrogen observed by Cassel and Glückauf at very much higher temperatures and low pressures. In the case of a silver surface Benton and Thacker[3] have identified the mechanism as another extreme in which nitrous oxide is adsorbed and decomposed. When an intermediate type of catalyst such as aluminum oxide is used, the mechanism becomes more complicated, even though the results are quite reproducible, and the rate is dependent on the pressures of hydrogen and nitrous oxide.[12] It thus appears that a change in mechanism may result from a change in conditions or catalyst.

The rate constant $\epsilon$ may be used to calculate the activation energy of the reaction. A plot of $\epsilon$ *vs.* $1/T$ gives a straight line with a slope corresponding to an activation energy of 22.6 ± 1 kcal. This value must be corrected to obtain the activation energy corresponding to the theoretical Equation (7) since $\mu_{N_2O}$ changes with temperature while $p_{N_2O}$ was used in calculating $\epsilon$. This correction amounts to +0.5 kcal., making the energy of activation 23.1 ± 1 kcal.

A simple calculation appears to support the mechanism for the reaction on platinum as proposed above. The apparent area of the metallic surface was 38 sq. cm. Assuming a pressure of nitrous oxide of 0.20 atmosphere and a temperature of 606°K., the amount of nitrous oxide colliding with the surface is 2.06 moles per second. The activation energy of 23,100 calories may be used to calculate the fraction of the collisions which are effective, leading to a calculated rate of $1.1 \times 10^{-8}$ mole/sec. The actual rate observed for same pressure of nitrous oxide was $26.0 \times 10^{-8}$ mole/sec. This discrepancy is not extremely serious in view of the uncertainty involved in some of the relations between gases and surfaces. A few of the factors which would alter the calculated rate may be mentioned: (1) the apparent area is doubtless smaller than the actual area, making the calculated rate higher; (2) any orientation effects would reduce the calculated rate; (3) adsorption of inactive nitrous oxide on the hydrogen layer followed by adsorption on a bare spot with subsequent activation might increase the calculated rate; (4) activation in more than one degree of freedom would increase the rate of activation.

## Summary

The reaction of hydrogen and nitrous oxide on smooth platinum wire has been studied in the temperature range from 260 to 471° by a flowing method. The rate of the reaction is approximately proportional to the nitrous oxide pressure and nearly independent of the hydrogen pressure. Water inhibits the reaction slightly.

The results indicate that the reaction occurs when a nitrous oxide molecule with the observed energy of activation of 23,100 calories collides with the surface which is practically completely covered with hydrogen and water.

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[11] G. M. Schwab, "Katalyse," Verlag J. Springer, Berlin, Germany, 1931, p. 159.

[12] Unpublished data.