[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Reaction between Nitrous Oxide and Hydrogen on Alumina

By John E. Vance and J. K. Dixon¹

Introduction.-In a previous paper² a report was made on a study of the reaction of hydrogen and nitrous oxide on a platinum surface. That work indicated that the mechanism probably involved the reaction of a gaseous nitrous oxide molecule with two hydrogen atoms adsorbed adjacent to each other on the surface, the important process being the activation of the hydrogen. It was pointed out at that time that the reaction on platinum was of interest, particularly when considered in light of the results obtained on a reduced silver surface,3 for in the case of silver, it is the activation and decomposition of the nitrous oxide which form the primary steps in the mechanism. It was suggested that on surfaces of intermediate type, such as alumina, one might expect to find that the activation of both nitrous oxide and hydrogen are important. The results of the work reported here tend to fulfill this expectation.

Because of the weak adsorption of water on surfaces of platinum and silver, water has little effect on the rate of reaction of nitrous oxide and hydrogen on these catalysts; on alumina, however, where water is strongly adsorbed, the pressure of water vapor may be expected to be an important factor in the rate of reaction. In recent years alumina has become important industrially as a catalyst for dehydrogenations, for example, in the dehydrogenation of hydrocarbons in a temperature range of 400-700°. Consequently, any information related to the effect of water on the activation of hydrogen by alumina and on the activity of the latter in catalytic hydrogenation, particularly in this temperature range, should be of practical interest at this time.

Experimental

The catalyst used both in the kinetic and in the adsorption experiments was prepared from C. P. aluminum chloride. The salt was dissolved in distilled water and placed under a bell jar beside a beaker containing ammonium hydroxide. The alumina slowly precipitated as the ammonia gas dissolved in the solution of aluminum chloride. The alumina was filtered, washed thoroughly and dissolved in dilute nitric acid. This solution was filtered and the alumina precipitated as before. The final precipitate was washed by decantation for one month, filtered, dried and ignited at approximately 500° for one hour. The dehydrated alumina was without coloration and had a density of 3.1. The particles had a diameter of about 3 mm.

For the experiments on the reaction rate, the gases were drawn continuously from tanks, purified and passed through standardized flowmeters as described in the previous paper. The purification of hydrogen and nitrous oxide for the adsorption experiments was as before, but the hydrogen for these experiments was finally passed through liquid air and expanded into an evacuated storage flask. The nitrous oxide, after chemical purification, was frozen in liquid air and pumped several times before storage.

The catalyst tube for the rate experiments was the same as previously used. The temperature of the surrounding furnace was manually controlled to within $\pm 0.5^{\circ}$ and was measured by means of a chromel-alumel thermocouple standardized against a calibrated platinum resistance thermometer. As before, a water saturator, maintained at constant temperature, was placed in the nitrogen line before the catalyst tube, so that water could be added to the gases at will. The weight of the alumina used as catalyst was 2.5 g. After the gases had passed over the catalyst, they were passed through a phosphorus pentoxide weighing tube, whose weights, before and after an experiment, were recorded to ± 0.2 mg. After an experiment involving certain partial pressures of the three gases was concluded, and before another involving new pressures was made, the new mixture of gases was allowed to pass through the catalyst tube for a period of thirty or forty minutes before any measurement was made of the water formed. In a series of experiments, no trend was noticeable in the weights of water.

For the adsorption experiments, 50 g. of alumina was used, placed in a bulb of such volume that the free space remaining was 48.7 cc. The bulb was inserted into an electrically heated furnace whose temperature was maintained to within $\pm 1^{\circ}$. The capillary connection from this bulb to the stopcock gave an unheated volume of 0.3 cc. so that no cold space correction was required to obtain the desired accuracy. Through the stopcock the adsorption bulb was attached to a forevolume of 63.1 cc. with a constant volume manometer. The procedure in the adsorption experiments was to admit hydrogen or nitrous oxide to the evacuated forevolume, noting the temperature and pressure. Then the stopcock to the adsorption bulb, previously evacuated, was opened and the pressure and temperature again read. A simple calculation on the basis of the ideal gas laws gave the amount of gas adsorbed by the alumina. Following each isotherm, the alumina was evacuated by means of an oil and a diffusion pump. At the higher temperatures where activated adsorption of the hydrogen took place, or after water had been admitted to the alumina, it was necessary to evacuate the adsorption bulb for several days. In every case, the pressure over

⁽¹⁾ Sterling Fellow of Yale University, 1932-1933. Present address: Calco Chemical Division of American Cyanamid Company, Bound Brook. New Jersey.

⁽²⁾ J. K. Dixon and J. E. Vance. THIS JOURNAL, 57, 818 (1935).

⁽³⁾ A. F. Benton and C M. Thacker, *ibid.*, 56, 1300 (1934).

the alumina was reduced to 10^{-3} mm. or lower between adsorption experiments.

Adsorption of Hydrogen on Alumina.—Adsorption and desorption isotherms checked to within a few per cent. at 0° . Duplicate adsorption isotherms at 200° agreed to within only 30%. Because of the difficulty encountered in removing water and hydrogen from oxides, even over long periods of pumping, it is not surprising to find this variation. Plots of pressure *versus* the amount adsorbed were nearly linear at 0° and 200°. Adsorption equilibrium was established rapidly at these temperatures, there being no evidence, over several hours, of any activated adsorption such as might be characterized by a slow decrease in pressure. Heats of adsorption are derived from the data in Table I.

TABLE I

HEAT OF ADSORPTION OF HYDROGEN ON ALUMINA cc. H₂ adsorbed per g. = kP_{H_2} where P_{H_2} is in mm. Hg

Temp., °K.	k	Heat of adsorption, cal./mole
273	$1.26 imes10^{-4}$	2000
473	2.05×10^{-5}	

Since this heat of adsorption is higher than that expected for van der Waals adsorption, it is probably connected with a rapid type of activated adsorption.⁴ At 259° there was indication of activated adsorption as evidenced by a slow adsorption. Thus, although a negligible amount of gas was taken up in half an hour, there was a slight decrease at 145 mm. pressure amounting to 0.0031 cc./g. in twenty hours and 0.0038 in one hundred forty-eight hours. Since experiments at higher temperatures revealed larger amounts of adsorption, it is evident that some type of activated adsorption began to take place around 260° .

A considerable number of adsorption isotherms were nade in the same temperature range as in kinetic studies, namely, 396 and 455° . The amounts of gas adsorbed and the rates of adsorption at the two temperatures were roughly the same over a thirty-hour period of time, the adsorption amounting to only 0.008 to 0.015 cc. per g. of alumina. A plot of data which were obtained at 396° is shown in Fig. 1 and indicates a small amount of gas was adsorbed rapidly in the first fifteen to twenty minutes which was followed by slow adsorption. Although the data cannot claim high precision because of the small total adsorption, it is evident that addition of even a small amount of water decreased the rate and therefore water could be an important factor in the reaction.

In kinetic studies, the alumina was practically saturated with water at all times. From Fig. 1, it is found that a total of $0.2 \times 4.63 \times 10^{-6} = 2.32 \times 10^{-6}$ mole of hydrogen was adsorbed in 0.25 hour by 50 g. Assuming a linear rate of adsorption, the rate of adsorption of hydrogen was 0.06×10^{-6} mole per minute. This is to be compared with a yield at 403° in the reaction of hydrogen and nitrous oxide of 25×10^{-6} mole per minute for 3 g. at the same temperature. From this it is evident that the adsorption rate would have to be some 7000 times greater on a smaller fraction of the surface in order for this surface to be effective in maintaining the required reaction velocity. Nitrous oxide would have to clean up this surface as fast as the hydrogen is adsorbed. Although we have made no measurements on desorption rates, we are inclined to believe they are small, in which case our pressure decrease would not represent the difference between large adsorption and desorption rates, and thus we would be justified in assuming we have measured the rate of adsorption alone.

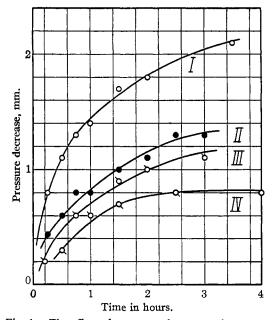


Fig. 1.—The effect of water on the rate and amount of adsorption of hydrogen by alumina at 396°: pressure of hydrogen, 145–150 mm.; weight of alumina, 50.7 g. The following amounts of water were on the alumina: I, none; II, 0.9 mg.; III, 11.6 mg.; IV, saturated. A decrease in pressure of 1 mm. corresponds to the adsorption of 4.6×10^{-6} mole of hydrogen.

Adsorption of Nitrous Oxide on Alumina.—Measurements were reproducible over a period of several months to within 20% of the total amount of nitrous oxide adsorbed. Adsorption and desorption curves checked to within a few per cent. from 0 to 259° , and plots of pressure *versus* the amount adsorbed were linear at temperatures from 100 to 333° ; at 0° the curves were concave to the pressure axis. At a pressure of 500 mm. of nitrous oxide, the following amounts of that gas were adsorbed, in cc. (N. T. P.) per gram of anhydrous alumina: 0°, 8.44; 100°, 0.996; 200°, 0.204; 259°, 0.109. In the temperature range where the adsorption plots are linear, one may easily calculate the heat of adsorption, in which case the result is 3500 calories per mole of nitrous oxide from 0 to 333° in the pressure range from about 10 to 500 mm.

There was no indication of activated adsorption of nitrous oxide, even at temperatures of 259 and 333°. However, at 259° nitrous oxide decomposed at a measurable rate when its pressure exceeded 400 mm., and at 333° it was not possible to evaluate the adsorption except when the rate of decomposition was reduced to a low value by saturating the surface with water vapor. Since the measurements showed measurable decomposition of nitrous oxide at 259° , it is concluded that activation of nitrous oxide at 259° , it measurements that low.

⁽⁴⁾ R. A. Beebe and H. M. Orfield, THIS JOURNAL, 59, 1627 (1937)

Experiments were performed which indicated that, even on a surface completely saturated with water, adsorption was only 20% less than on an unpoisoned surface at 200 and 259°. The pressure of water over the alumina in the kinetic experiments was of the same order of magnitude as in adsorption experiments where the surface was saturated, *i. e.*, 1–10 mm.; hence it seems reasonable to conclude that the adsorption of nitrous oxide was not affected by water more than 20% during reaction with hydrogen. Adsorption of nitrous oxide was rapid in all cases, therefore, attempts to evaluate the effect of water on the rate of adsorption were not feasible.

Decomposition of Nitrous Oxide on Alumina.-It seemed desirable to determine where nitrous oxide decomposition began on alumina under conditions similar to those obtaining in the reaction with hydrogen. In one method of studying this point, 44 cc. per minute of nitrous oxide and 65-125 cc. per minute of dry nitrogen were passed over the alumina at 480°. There was less than 2% of oxygen in the off-gas. With a temperature of 475° and with the nitrogen saturated with water, the percentage of oxygen amounted to less than 0.2. This corresponds to around 2% decomposition of the nitrous oxide. The other procedure was to determine the slow pressure increase with time in static adsorption experiments in order to permit an evaluation of the rate of decomposition. With 15.7 mg. of water on 50 g. of alumina, the rate of decomposition at 259° was 0.72×10^{-6} mole per minute. Increase in the amount of water to 52 mg. halved the rate of decomposition, and saturation decreased it 25 times (Fig. 2), making the rate of decomposition about 0.03×10^{-6} for a surface saturated with water, which was the condition obtaining in the kinetic experiments. This is to be compared with an estimated value of 25.5×10^{-6} mole per minute of water formed in the reaction of hydrogen and nitrous oxide on 50 g. of alumina The rate of decomposition of nitrous oxide alone is thus too slow to account for the observed reaction

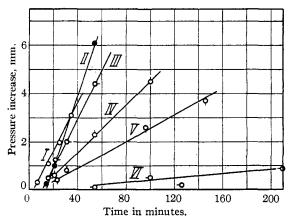


Fig. 2.—The effect of water on the rate of decomposition of nitrous oxide on alumina at 259°. Curves I, II, III, IV and VI show the effect at a pressure of 500 mm., curve V is at 150 mm. The following amounts of water were on the alumina: I. none; II, 1.1 mg.; III, 15.7 mg.; IV, 52.3 mg.; V, 15.7 mg.; VI, saturated. The slope of curve III corresponds to a decomposition rate of 0.1 nm./min. or 0.72×10^{-6} mole/min. in 111 cc.

rate. In the presence of hydrogen, however, less activation would be required, and the surface would probably be capable of activating the nitrous oxide at a rate sufficient to maintain the observed reaction rate.

The data which are plotted in Fig. 2 also indicate that the rate of decomposition is nearly proportional to the nitrous oxide pressure and is not critically affected by water vapor pressure. This is interpreted to mean that most of the adsorbing surface and not just a few active centers are active in nitrous oxide decomposition. Data in the absence of hydrogen thus indicate that in the presence of hydrogen one may make the reasonable assumption that the amount of nitrous oxide adsorbed and its rate of activation are approximately proportional to the pressure and that the amount of adsorption and rate of activation of nitrous oxide are not critically affected by water vapor. even up to saturation with the latter.

Results of the Kinetic Experiments.—The reaction rate appeared to be reproducible over the period of study to within $\pm 3\%$ at 472° and $\pm 5\%$ at 333° . Experiments were invariably made in duplicate and in most cases the experiments were repeated many times after intervening changes of temperature and pressure conditions, so that considerable confidence could be placed in the reproducibility of the data. Table II summarizes the average values of the weight of water formed by the reaction, the weight of water added to the entering gases, the pressures of nitrous oxide, hydrogen and water and the total flow of gases. In each instance, the pressure represents the average of the inlet and outlet pressure.

The extent of reaction which took place varied somewhat, but in general was kept low; at 333 and 403° the maximum fraction of decomposition was 5% and at 472° , 10-20%. The fraction decomposed may be found by dividing the pressure of water vapor formed, by the pressure of hydrogen or nitrous oxide, whichever is the smaller. The fact that the reaction proceeded to a greater extent at the highest temperature does not seem to have affected the kinetics of the reaction. This may be checked in the following way: at a constant pressure of hydrogen of approximately 0.2 atm., the ratio of the weight of water formed with a pressure of nitrous oxide of 0.05 atm. to that formed with a pressure of nitrous oxide of 0.45 atm. is 2.10 at a temperature of 403° , while the same ratio at 472° is 2.35. Similarly, with a constant pressure of nitrous oxide of about 0.2 atm., the ratio of the weight of water formed when the pressure of hydrogen is 0.05 atm. to the weight of water formed when the pressure of hydrogen is 0.2 atm. is 1.20 at 403° and 1.06 at 472°.

		2	.5 g. of alumin	um oxide		
No. of	Wt. H ₂ O formed.	H ₂ O added.	N ₂ O	Average pressures, atm.	H ₂ O	Average flow, cc./min.
expts.	moles/min. × 10 ⁶	moles/min. × 10 ⁶	Temperature	- 403°	1110	ee./ mitt.
6	19.6		0.0502	0.213	0.00107	224
0 3	23.0		, 116	.204	.00174	161
3 15	23.0 23.7		.203	. 197	.00312	93
15 6	23.7 39.6		.455	.203	.00312	166
	39.0 40.4		.400	.192	.00292	95
6	40.4 20.4		. 198	.0445	.00129	194
4 3	19.2		. 194	.0890	.00123	98
$\frac{3}{2}$	31.4		.316	.674	.00643	60
2 4	26.6		. 190	.791	.00535	61
	9.8	53.7	. 201	. 200	.0158	93
$\frac{4}{6}$	9.8 20.7	55.9	.458	.200	.00967	166
0	20.7	00.9			.00907	100
			Temperature	e, 333°		
2	6.2		.457	.207	.000457	166
2	5.7		.804	. 196	.00074	94
2	5.1		.326	.674	.00103	60
			Temperature	e, 472°		
8	77.5		.0471	.212	.00422	225
$\overline{2}$	97.8		. 113	. 160	.00749	160
9	101		. 113	. 198	.00777	160
9	101		. 187	. 183	.0129	96
11	138		. 190	.204	.00882	191
4	183		. 447	. 188	.0134	167
5	94.1		. 188	.040	.00600	192
2	85.5		.0888	. 0845	.00507	207
5	94.8		.097	. 403	.01000	11 6
9	96.7		. 097	.433	.0109	109
5	40.0	176	. 090	.0835	.0227	211
2	87.5	14.1	.092	.404	.0121	117
2	84.1	27.4	.093	. 404	.0144	118
2	70.8	55.9	.093	. 401	.0189	118
4	79.3	34.4	.096	. 424	.0164	112
3	75.6	48.5	.097	. 426	.0191	112
2	90.8	116.0	. 190	. 204	. 0203	194
3	122	28.5	. 191	. 203	.0114	192
2	112	56.3	. 191	.204	.0143	193
2	103	77.5	.190	. 203	.0163	193
3	91.5	105	. 191	. 203	.0190	194

TABLE II	
----------	--

REACTION OF HYDROGEN AND NITROUS OXIDE ON ALUMINA

Discussion

As a first approximation, it seemed reasonable to make an attempt to set up an equation for the kinetics of the reaction using average partial pressures and assuming that the average pressure of each gas exists over the entire catalyst, thus avoiding the difficulties involved in integrating the differential rate equation over the length of the catalyst.

An examination of the data at the two higher temperatures, where the data are more complete and the results more accurate, reveals a striking similarity between the kinetics at the two temperatures. From experiments made with nearly constant pressures of water vapor and hydrogen, but with nitrous oxide pressures of 0.20 and 0.46 atm., it may be concluded that the rate of formation of water varies as the 0.66 power of the nitrous oxide pressure. If one then plots the rate of water formation divided by $P_{\rm NiO}^{2/3}$ against the reciprocal of the pressure of water, reasonably straight lines are obtained at constant hydrogen pressure, and from these data it can be shown graphically that the hydrogen pressure must enter as the 0.33 to 0.66 power. The exponent appears to be 0.66 at 333°, 0.5 at 403° and 0.33 at 472°. If ω = moles of water formed per minute and if $P_{\rm NiO}$, $P_{\rm H}$, and $P_{\rm HiO}$ denote the corresponding partial pressures in atmospheres, then

$$\omega = k_1 P_{N_{2O}}^{2/3} \times P_{H_2}^{n_2} + \frac{k_2 P_{N_{2O}}^{2/3} P_{H_2}^{n_2}}{P_{H_{2O}}}$$
(1)

where n_2 depends on the temperature and k_1 and k_2 are constants, whose values are given in Table III.

Although this equation may not necessarily be unique in describing the data, it appears to have the advantage of simplicity. An equation made up of only one term, but still having two constants and of well-known form

$$\omega = \frac{k_1 P_{\rm N20}^{2/8} P_{\rm H2}^{n_2}}{1 + K_2 P_{\rm H20}} \tag{2}$$

where n_2 is between 0.33 and 0.66 as before, does not fit the data as well as equation (1). The average deviation for equation (2) is 0.41 as compared with 0.28 for equation (1) at 472°. This suggests that the reaction does not involve a simple interaction of hydrogen and nitrous oxide inhibited by water on a single type of surface.

The kinetic expression (1) suggests that the reaction involves the activation and reaction of adsorbed hydrogen and nitrous oxide, and that the reaction is retarded by water vapor because the water is strongly adsorbed and thus covers a part of the active surface. It is also possible to explain the use of two constants in the kinetic expression as the result of two reactions, one on alumina which water inhibits, and one on hydrated alumina unaffected by water, the constants k_2 and k_1 , respectively, being involved. Activation energies E_{k_1} and E_{k_2} differ by 5700 cal., which might be due to the heat of desorption of water from the alumina.

The exponent for the hydrogen pressure decreases with temperature from 0.66 to 0.33 between 333 and 472°. This indicates an increase in the effective covering of the surface by hydrogen, whether the surface is hydrated or unhydrated, as the temperature increases. For equilibrium the reverse should be true. If the rate of adsorption were the controlling factor, the facts could be accounted for, thus making a definite interpretation of the kinetic equation somewhat hazardous. Experimentally, however, the time taken to reach a constant rate of water formation, which could be reproduced from time to time over several months, was of the order of ten to thirty minutes, hence the over-all slow hydrogen adsorption over twenty-four hours or more was evidently not an important factor in reaction.

The data do not permit any conclusion as to whether hydrogen reacts in the atomic form.

Temperature Coefficient.—Since the reaction rate involves the two constants, k_1 and k_2 (shown in Table III), the logarithms of both these constants have been plotted against the reciprocal of the absolute temperature in order to obtain the apparent activation energies E_{k_1} and E_{k_2} of the two processes which are presumably involved. The values are $E_{k_1} = 30.0$ kcal. and $E_{k_2} = 35.7$ kcal. as shown in Table III.

TABLE III

VALUES OF THE RATE CONSTANTS AND ACTIVATION ENER-GIES IN THE REACTION OF HYDROGEN AND NITROUS OXIDE ON ALUMINA

	ω	$= k_1 P_{N_2O}^{n_1} \times P$	$\frac{m_{2}}{m_{2}} + \frac{k_{2}P_{N_{2}O}^{n_{1}} \times P_{H_{2}O}}{P_{H_{2}O}}$	$P_{\mathrm{H}_2}^{n_2}$	
°Ċ.	n2	k_1	k_2	E_{k_1} , kcal.	E_{k_2} , kcal.
333	0.66	$3.0 imes 10^{-6}$	$1.24 imes 10^{-8}$		
403	. 50	44.0×10^{-6}	29.9×10^{-8}	30.0	35.7
472	. 33	300×10^{-6}	340×10^{-8}		

Activation energies for the catalytic decomposition of nitrous oxide, and for the reaction of nitrous oxide and hydrogen, are assembled in Table IV. If we neglect the difference between the true and apparent activation energies, due to lack of sufficient data on heats of adsorption, it seems significant to us that the values for the two reactions are $29,000 \pm 6000$ calories per mole, with the exception of the value for the reaction of hydrogen and nitrous oxide on silver which is 16,000 calories lower. The latter catalyst is the only one in which the rate of reaction is not a function of the nitrous oxide pressure, for in this case the slow process is the interaction of hydrogen with adsorbed oxygen atoms formed by nitrous oxide decomposition on the surface. It appears that nitrous oxide interacts with the adsorbed hydrogen, lowering the activation energy by 9000 calories on a platinum catalyst. The energy for both reactions also appears to decrease as the ease of oxidation and reduction of the metal in the catalyst increases, although this is not necessarily the only factor involved. The weakening of the N–O bonds in nitrous oxide resulting from adsorption permits the reaction to set in at a lower temperature and with lower activation energy.

Recent reports⁵ indicate that the activity of alumina in dehydrogenation of hydrocarbons is

⁽⁵⁾ O. Beeck, H. P. A. Groll and J. Burgin, U. S. Patent 2,131,089, Sept. 27, 1938.

Reaction partners	Catalyst	Author	Activation energy
Nitrous Oxide	Pt	Hinshelwood"	32500
	Au	Hinshelwood	29000
	CuO	Schwab ^b	24000
	MgO	Schwab ^b	29000
	CuO-MgO	$Schwab^b$	22400
Hydrogen + Nitrous Oxide	Ag	Benton and Thacker ³	13000
	Pt	Vance and Dixon ²	23100
	Al_2O_8 (hyd.)	Vance and Dixon	30000
	Al_2O_3 (anh.)	Vance and Dixon	35700

TABLE IV			
THE DECOMPOSITION OF NUTBOUR ON IT	D ar		

" C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," first edition, Cambridge University Press, 1926, p. 186. ^b G. M. Schwab, "Katalyse vom Standpunkt der chemischen Kinetik," J. Springer, Berlin, 1931, p. 212.

enhanced by addition of small amounts of water or hydrogen sulfide up to around 3%. Under these conditions, our results suggest that the surface which would be active in reaction of hydrogen with nitrous oxide would be around 15% of the "unhydrated" form and 85% "hydrated." It is conceivable that the "unhydrated" form is more active in carbon-carbon cracking than the hydrated form, and since both forms might catalyze dehydrogenation, then addition of water suppresses the undesired carbon-carbon cracking. Since the temperature coefficients for k_1 and k_2 are not too widely different, the explanation of the beneficial action of the water observed at 472° might apply at temperatures as high as 600 to 700°.

Summary

The reaction of nitrous oxide and hydrogen 1. has been studied at 330, 403 and 472° on aluminum oxide in a flowing system. Reaction was limited to about 10% at the highest temperature to permit use of average pressures in setting up a kinetic expression.

2. Rates and amounts of adsorption for hydrogen and nitrous oxide on the same aluminum oxide were measured from 0 to around 400°.

3. Nitrous oxide is adsorbed reversibly and instantaneously up to 250° where it begins to undergo decomposition at a rate proportional to its pressure. Saturation of the alumina with water reduced the rate 25-fold. Rate of decomposition of nitrous oxide alone was 850 times less than the rate of reaction with hydrogen.

4. Adsorption of hydrogen is reversible and

instantaneous up to 250° where a slow activated adsorption becomes measurable. Between 300 and 400°, there appears to be a rapid initial adsorption followed by a very slow process, both of which are critically affected by the addition of a small amount of water vapor. The average measured rate of adsorption in the first fifteen minutes was 2700 times less than the rate of reaction with nitrous oxide, thus suggesting that the latter cleans up the most active surface for adsorption of hydrogen at the rapid rate which is required to maintain the observed reaction velocity.

5. The rate of water formation is proportional to the two-thirds power of the nitrous oxide pressure and to a fractional power of the hydrogen pressure which varies from 0.66 at 333° to 0.33 at 472°. A reasonably good kinetic expression involving two constants has been fitted to the data which suggests that part of the reaction between nitrous oxide and hydrogen takes place on an unhydrated alumina surface inhibited by water and the remainder on a completely hydrated surface uninhibited by water.

6. The apparent activation energies on the hydrated and "anhydrous" surfaces are 30.0 and 35.7 kcal. per mole, respectively. The difference is attributed in part to the heat of adsorption of water.

7. The apparent activation energies of the decomposition of nitrous oxide and of the reaction between nitrous oxide and hydrogen on various catalysts were compared and shown to have a certain similarity.

NEW HAVEN, CONN.

RECEIVED OCTOBER 3, 1940