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KINETICS AND MECHANISM OF THE HYDROGENATION OF CYCLOPROPANE OVER A NICKEL-SILICA-ALUMINA CATALYST

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The hydrogenation of cyclopropane has been investigated by a static method over a commercial nickel-silica-alumina isomerization catalyst between 56 and 100°. At 75° the rate expression for the reaction is $-dp/dt = k p_{C_3H_6}^{0.3} / p_{H_2}^{0.1}$, with an activation energy of 15.2 kcal./mole. Adsorption isotherms were determined for hydrogen between 0 and 400°, and for cyclopropane at 0 and 32.3°. By assuming the rate-determining step in the catalytic hydrogenation to be the reaction between adsorbed cyclopropane and an adsorbed hydrogen atom, the observed kinetic law has been interpreted in a manner consistent with the adsorption data. The reaction of the catalyst with carbon monoxide was investigated, and the chemical nature of the catalyst is discussed briefly.

Ciappetta and Hunter³ found that silica-alumina containing *ca.* 5% nickel effectively catalyzes the isomerization of saturated hydrocarbons under high pressures (25 atm.) in the presence of hydrogen. It was suggested that the isomerization activity is due to compound formation between the nickel and hydrous aluminum silicate. However, hydrocracking is the primary reaction at atmospheric pressure, a result that suggests that the isomerization activity is due largely to the experimental circumstances. The present research was undertaken to investigate the nature of this commercial isomerization catalyst under laboratory conditions in order to compare its properties with those of other supported nickel catalysts. In this paper we report the kinetics and mechanism of the hydrogenation of cyclopropane and also some adsorption characteristics of this complex catalyst.

Experimental

Materials.—The catalyst used in this work was the one designated by Ciappetta and Hunter^{3a} as SA-5N-VII-D and was supplied by The Atlantic Refining Company. Cylinder cyclopropane and propane from The Matheson Company were purified by pumping on the solid and subsequent fractional distillation. In the hydrogenation studies, cylinder hydrogen was purified by passage through charcoal, calcium chloride, palladized asbestos at 300°,

ascarite, magnesium perchlorate and a liquid nitrogen trap. For the adsorption measurement, the hydrogen was further purified by diffusion through a palladium thimble. Oxygen and iron carbonyl were removed from cylinder carbon monoxide by passage over activated copper turnings at 400°; water and carbon dioxide were removed by magnesium perchlorate and ascarite, and a final drying was effected by a Dry Ice-acetone trap. The silica-alumina was from the Davison Chemical Co.

Apparatus and Procedure.—A U-type Vycor-glass tube connected with a buret, a mercury manometer and a high vacuum line was used for the adsorption measurements. A sample of the nickel-silica-alumina catalyst was placed in the middle of the U-tube and reduced by the standard activation technique used by Ciappetta and Hunter,^{3a} *i.e.*, at 530° for 16 hours with a hydrogen flow rate of 6 liters/hour. After degassing the catalyst at 530° for 3 hours, a known volume of adsorbate was introduced into the catalyst vessel, which was kept at a desired temperature by means of an electric furnace or by a suitable constant temperature bath. The pressure of the gas in the adsorption vessel was read manometrically after a certain time of contact. The adsorbed amounts were determined from a knowledge of the dead space volume (approximately 60 cc.) for helium. A 10-g. sample of catalyst was used for hydrogen adsorption; in the cyclopropane adsorption work 3 g. of the catalyst that had been used for hydrogen adsorption were employed.

A cylindrical Pyrex reaction vessel of 211 cc. was used for the hydrogenation of cyclopropane. This reactor was connected with a capillary manometer and a high vacuum line and was equipped with a thermocouple well. The entire reaction volume could be enclosed by a removable jacket in which organic liquids were boiled to control the temperature. Mixtures of hydrogen and cyclopropane, prepared and mixed with a Töpler pump, were introduced into the reactor, and pressure readings were taken. The volume change due to hydrogenation was negligible compared with the total volume of the vessel. A 0.2-g. catalyst sample, reduced *in situ* by the standard technique, was found suitable for

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(3) (a) F. G. Ciappetta and J. B. Hunter, *Ind. Eng. Chem.*, **45**, 147 (1953); (b) **45**, 155 (1953); (c) F. G. Ciappetta, *ibid.*, **45**, 159 (1953); (d) **45**, 162 (1953).

the measurement of the reaction rates under the experimental conditions.

For the reaction of the catalyst with carbon monoxide a 1.90-g. catalyst sample, contained in a Pyrex tube equipped with a pre-heating coil, was reduced *in situ* by the standard technique and then treated with purified carbon monoxide at 50° for 84 hours. A flow rate of carbon monoxide of approximately 200 cc./min. was used. The resulting nickel carbonyl was decomposed at 300° in a weighed Pyrex tube equipped with a pre-heating coil and with standard taper joints to facilitate its removal.

The unreduced catalyst was analyzed for nickel by dissolving 0.5-g. samples in hydrofluoric acid and a few drops of sulfuric acid, evaporating to remove silica, complexing the aluminum as the tartrate, and precipitating nickel dimethylglyoxime.

Experimental Results

Adsorption of Hydrogen.—In order to see the extent of reduction, the catalyst, prepared by the standard activation technique, was allowed to contact with hydrogen for two weeks at 530° in a closed system. It was found that the pressure of hydrogen decreased slowly over this period. It was presumed that complete reduction was unattainable under the standard technique used, although the magnitude of the final static reduction indicated the catalyst was already more than 99% reduced. Regardless of the possibly incomplete reduction, the rate of hydrogen adsorption was immeasurably fast and reversible between 0 and 300°.

Adsorption isotherms were determined on this catalyst at 0, 100, 200 and 300° and at equilibrium pressures from a few mm. up to 800 mm. The results are shown in Fig. 1 by the solid lines.

After the above measurements the catalyst was reduced in hydrogen at 600° for 16 hours. No further static reduction could be detected in this case. Adsorption isotherms were also determined on this highly reduced catalyst at 0, 100, 200, 300 and 400° and at equilibrium pressures from a few mm. up to 900 mm. The results are shown in Fig. 1 by the dotted lines.

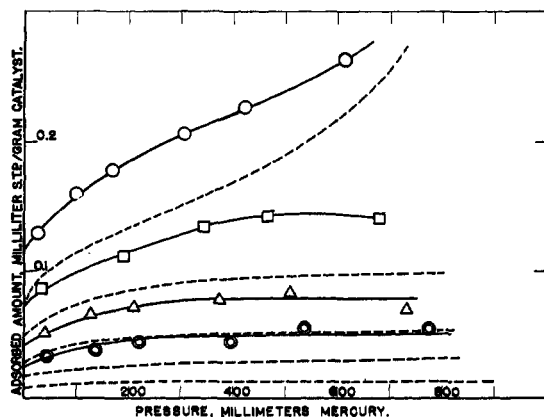


Fig. 1.—Adsorption isotherms of hydrogen on nickel-silica-alumina: full lines, catalyst reduced at 530°; O, 0°; □, 100°; △, 200°; ⊙, 300°; dotted lines: catalyst reduced at 600°.

The adsorption of hydrogen increased very slightly with increasing pressure except at 0°, where the isotherm was more or less concave upwards. The exponents of the pressure from the Freundlich equation, which approximately expressed all the isotherms, are given in Table I for the catalyst reduced at 530°, together with the cor-

responding exponents for reduced nickel⁴ and for nickel-silica.⁵

The difference in adsorption activity for hydrogen between nickel-silica and nickel-silica-alumina would indicate a marked difference in these catalysts. Schuit and deBoer report that, at 100 mm. and -78°, nickel-silica adsorbs 27.5 cc. of hydrogen per gram of nickel, a value assumed to be near saturation. This corresponds to a Ni:H ratio of 7:1. On nickel-silica-alumina, saturation by hydrogen was not attained under the experimental conditions; however, for convenience the adsorbed amount at 760 mm. and 0° will be taken as the adsorption activity. This was only 7.5 cc. of hydrogen per gram of nickel, or a Ni:H ratio of 25:1. The large difference in adsorption activity indicates a poor dispersion of nickel in the nickel-silica-alumina catalyst.

It was difficult to obtain isosteric heat data over the entire range of coverage because of the flatness of the adsorption isotherms. However, a few numerical data are given in Table II. While the heat values do not differ from the current heat data for hydrogen adsorption on nickel, the decline of the heat of adsorption with adsorbed amounts seems more pronounced.

TABLE I

EXPONENTS FROM THE FREUNDLICH EQUATION (FOR HYDROGEN ADSORPTION)

Catalyst Equil. pressures, mm. Temp., °C.	Nickel-silica-alumina 2-800	Nickel ⁴ ~1	Nickel-silica* (29.4% Ni-CLA 8281) 10 ⁻¹ -100
0	0.22	..	0.02
100	.15	0.07	..
200	.16	.12	.13
300	.18	.24	...
40024

TABLE II

ISOSTERIC HEAT DATA

	Adsorbed amounts, cc. S.T.P./g. catalyst	Heat of adsorption, kcal./mole
530° Reduction	0.056	16
	.089	11
	.15	6
600° Reduction	.022	27
	.056	16
	.071	7

Adsorption of hydrogen presumably occurs on the silica-alumina support also, since Guenther⁶ found that activated adsorption of hydrogen occurs on silica-alumina between 300 and 500° and since the carbonyl formation experiment indicates the nickel is not in chemical combination with the support (see later section).

Adsorption of Cyclopropane.—A 3-g. sample of the catalyst used for the hydrogen adsorption was oxidized in air and re-reduced under the standard activation technique. No static reduction was performed. Cyclopropane adsorption was measured at 0 and 32.3°. At these temperatures the

(4) T. Kwan, *J. Research Inst. Catalysis, Hokkaido Univ.*, **1**, 81 (1948).

(5) G. C. A. Schuit and N. H. deBoer, *Rec. trav. chim.*, **72**, 909 (1953).

(6) H. W. Guenther, Ph.D. Thesis, Princeton University, 1946.

adsorption was quick and practically complete in 10 minutes, after which an extremely slow process occurred that was barely detectable after 30 minutes. At 100° this slow process occurred at an appreciable rate with the formation of no uncondensable gas at liquid nitrogen temperature. Mass spectrometric analysis of the gaseous products resulting from the adsorption of cyclopropane at 74° on a 2.3-g. sample of the silica-alumina support showed the presence of ethylene, propylene and benzene. Between 150 and 200° decomposition of cyclopropane set in.

Consequently, adsorption isotherms were determined at 0 and 32.3°. The pressure in the adsorption vessel after 10 minutes was taken as the equilibrium pressure. The data are given in Table III. Log-log plots of these data gave fairly good straight lines with the slopes given in Table IV. The slope at 75°, which will be used in the discussion, was obtained by assuming a linear relationship between the slope and $1/T$, a procedure generally accepted as valid.⁷ The isosteric heat of adsorption ranged from 8.8 to 7.0 kcal./mole under the conditions investigated.

TABLE III
CYCLOPROPANE ADSORPTION DATA

Pressure, mm.	Adsorbed amounts, cc. S.T.P./g. catalyst	Pressure, mm.	Adsorbed amounts, cc. S.T.P./g. catalyst
Temp., 0°		Temp., 32.3°	
5	1.24	13.8	0.8
22	3.06	73.0	2.47
58	5.82	145	4.12
230	13.0	263	5.23
		413	7.8

TABLE IV
EXPONENTS FROM THE FREUNDLICH EQUATION (FOR CYCLOPROPANE ADSORPTION)

Temp., °C.	0	32.3	(75)
Slope	0.64	0.67	(0.70)

Hydrogenation of Cyclopropane.—Preliminary experiments indicated a slow poisoning of the catalyst during the hydrogenation experiments, and a reactivation technique, which consisted of cleaning the catalyst surface with hydrogen at 350° for one hour followed by pumping for one-half hour at the reaction temperature, was worked out. This schedule of pre-treatment was used between each run.

Propane was shown to be the only product of the reaction by a mass spectrometric analysis of the products from a run made at 74° in which the reaction was allowed to go to completion. A 2.3-g. sample of the silica-alumina support showed negligible hydrogenation activity at 74°.

The initially measured rates were complicated by the superposition of the rate of hydrogenation and of a secondary process. This is shown clearly in Fig. 2, an example of the type of data obtained. This secondary process was undoubtedly the same as the slow process observed after the initially very rapid adsorption of cyclopropane at 100° (see

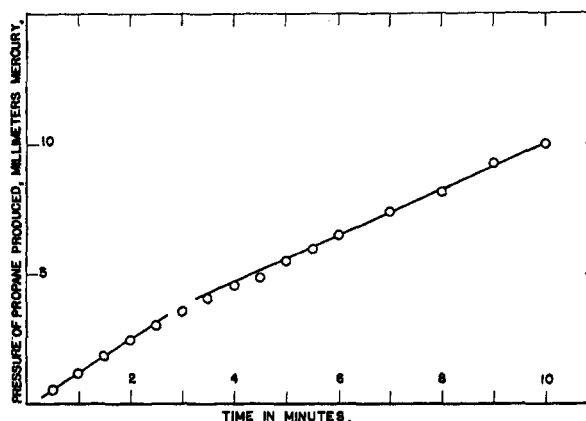


Fig. 2.—Typical rate of hydrogenation of cyclopropane on nickel-silica-alumina; temp., 75°.

above) and involved adsorption of cyclopropane on the support. From plots similar to Fig. 2, however, it was shown that the effect of this process extended over only the first three or four minutes of a run, after which it could no longer be detected. The activation energy and kinetics were thus determined from slopes of pressure-time plots taken at 10 and 25% apparent reaction, respectively.

For the determination of the activation energy of the hydrogenation reaction equimolar mixtures of the reactants at about 200 mm. total pressure were used. The data, listed in Table V, gave an activation energy of 15.2 kcal./mole.

TABLE V
VARIATION OF REACTION VELOCITY, v , WITH TEMPERATURE

Total pressure, mm.	Temp., °C.	Log v (10%)
197.5	73.3	-0.155
207.1	56.0	- .682
236.7	100.0	+ .528
182.0	81.0	+ .053
200.0	73.5	- .167
199.8	64.8	- .398
196.4	91.5	+ .352
207.7	64.8	- .342

In Table VI are given the data for the determination of the kinetics. The small variation in the temperature was shown by calculation not to affect the reaction rates to a measurable extent. The rate equation

$$v = kp_C p_H$$

where the subscripts C and H refer to cyclopropane and hydrogen, respectively, was used to write a set of simultaneous equations

$$0 = \log k + f \log p_C + g \log p_H - \log v$$

that were then solved by the method of least squares⁸ for the specific rate constant k and the exponents f and g . The resulting kinetic expression was

$$v = 0.327 p_C^{0.8} p_H^{-0.1} \quad (1)$$

The sum of the residuals and the sum of the squares of the residuals were 0.000 and 0.004, respectively. Although the initial rates were difficult to analyze, a similar mathematical treatment

(7) See, for example, E. Cremer, *Z. Elektrochem.*, **56**, 439 (1952), and T. Kwan, *This Journal*, **59**, 285 (1955).

(8) See, for example, J. B. Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins Press, Baltimore, 1930, p. 363.

indicated that f and g had values of 0.4 and -0.1 , respectively. This tends to confirm the idea of initial cyclopropane adsorption expressed above.

Propane was found not to affect the rate of reaction by three experiments performed after the catalyst had been reactivated by the standard technique. Table VII shows the experimental conditions and the results of the experiments. The reaction rates were determined at 25% conversion.

Reaction of the Catalyst with Carbon Monoxide.—Two analyses of the catalyst gave results of 3.67 and 3.72% of nickel in the unreduced catalyst. The 1.90-g. sample of unreduced catalyst that reacted with carbon monoxide thus contained 0.070 g. of nickel. The nickel resulting from the decomposition of the carbonyl weighed 0.070 g. An analysis of the support after the carbon monoxide treatment showed no nickel remaining.

TABLE VI
DATA FOR THE DETERMINATION OF THE KINETICS

Initial pressure, mm., of Cyclopropane	Hydrogen Temperature = 73.3–75.5°	Rate (at 25% reaction), mm./min.
106.6	106.7	0.711
157.4	157.7	.748
45.2	45.2	.604
94.9	194.0	.626
57.0	116.4	.576
99.0	300.6	.622
51.1	155.2	.560
283.5	98.3	1.00
146.3	50.7	0.942
99.6	34.6	.900
199.8	199.8	.798
101.9	101.9	.666
134.9	134.9	.700
51.6	51.6	.597
299.1	147.0	.993
196.8	96.7	.929
100.8	49.5	.845

TABLE VII
DEPENDENCE OF REACTION RATE ON PROPANE PRESSURE

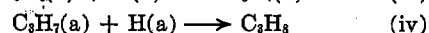
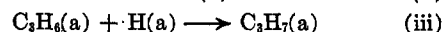
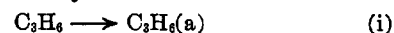
Initial pressure, mm., of Cyclopropane	Hydrogen Temperature = 74.5–75.0°	Propane	Rate (at 25% reaction), mm./min.
49.3	49.4	26.8	0.975
49.3	49.4	64.9	.988
49.1	49.1	116.0	.938

Because of the completeness of the removal of the nickel in the catalyst, we conclude that the nickel has a high accessibility to carbon monoxide, a fact found by Schuit and deBoer⁸ to be characteristic of metallic impregnation catalysts. Furthermore, the complete removal of the nickel at the low temperature of 50°, that is, under conditions commonly used for the production of carbonyls from dispersed metals, suggests that the constitution of the catalyst does not involve any extensive amount of chemical bonding between the nickel and the support, as was suggested by Ciapetta and Hunter.^{3a} This conclusion is supported by the

isosteric heat data given above and by magnetic susceptibility measurements made by Selwood, who reports results characteristic of nickel metal.¹⁰

Discussion

We shall now investigate what mechanism of the hydrogenation of cyclopropane, consistent with the observed adsorption data, most suitably accounts for the observed kinetic law (eq. 1). We assume that the hydrogenation proceeds by the following consecutive elementary reactions



where the suffix (a) refers to the adsorbed state and $\text{C}_3\text{H}_7(\text{a})$ to the half-hydrogenated state of cyclopropane or to the n -propyl radical.

In view of the very fast adsorption rates of the reactants, steps (i) and (ii) may be excluded as the slowest step. The surface reaction of the adsorbed species thus seems to be rate-controlling. On the basis of the Langmuir-Hinshelwood scheme, the reaction rate is given by

$$v = k\theta_{\text{C}}\theta_{\text{H}} = k \frac{b_{\text{C}}p_{\text{C}}\sqrt{b_{\text{H}}p_{\text{H}}}}{(1 + b_{\text{C}}p_{\text{C}} + \sqrt{b_{\text{H}}p_{\text{H}}})^2} \quad (2)$$

if (iii) is assumed to be the slowest step in the overall reaction. From the adsorption data reported in this paper the values for b_{C} and b_{H} may be estimated from the Langmuir isotherm. At 75°, the temperature at which the kinetics were determined, $b_{\text{C}} \cong 0.002 \text{ mm.}^{-1}$ and $b_{\text{H}} \cong 0.01 \text{ mm.}^{-1}$. From these b values and the pressures given in Table VI it may be shown that the cross term, $b_{\text{C}}p_{\text{C}}\sqrt{b_{\text{H}}p_{\text{H}}}$, introduced in writing the approximation

$$\frac{1}{1 + b_{\text{C}}p_{\text{C}} + \sqrt{b_{\text{H}}p_{\text{H}}}} \cong \frac{1}{1 + b_{\text{C}}p_{\text{C}}} \cdot \frac{1}{1 + \sqrt{b_{\text{H}}p_{\text{H}}}} \quad (3)$$

averages 10% and is small enough not to introduce any significant error.

Most adsorption isotherms are approximately expressed by either the Langmuir or the Freundlich equation when the range of pressure is not large. This situation holds sufficiently for the present adsorption data that we may write

$$\frac{b_{\text{C}}p_{\text{C}}}{1 + b_{\text{C}}p_{\text{C}}} \cong (b_{\text{C}}p_{\text{C}})^m \quad (4 \text{ m})$$

$$\frac{\sqrt{b_{\text{H}}p_{\text{H}}}}{1 + \sqrt{b_{\text{H}}p_{\text{H}}}} \cong (b_{\text{H}}p_{\text{H}})^n \quad (4 \text{ n})$$

where $0 < m < 1$ and $0 < n < 1$. The values of m and n have already been given in Tables I and IV. At a temperature of 75°, where the kinetic law was obtained, m is 0.70 and n would be between 0.22 (0°) and 0.15 (100°). Consequently, we obtain the relations

$$\frac{1}{1 + b_{\text{C}}p_{\text{C}}} = (b_{\text{C}}p_{\text{C}})^{m-1} = (b_{\text{C}}p_{\text{C}})^{-0.3} \quad (5)$$

$$\frac{1}{1 + \sqrt{b_{\text{H}}p_{\text{H}}}} = (b_{\text{H}}p_{\text{H}})^{n-0.5} = (b_{\text{H}}p_{\text{H}})^{(-0.35) \sim (-0.3)} \quad (6)$$

From equations 2, 3, 5 and 6 it follows immediately that

(9) G. C. A. Schuit and N. H. deBoer, *J. chim. phys.*, **51**, 482 (1954).

(10) P. W. Selwood, private communication to Hugh Taylor.

$$\nu = k(b_0 p_C)^{0.4} (b_H p_H)^{(-0.1) \sim (-0.2)} = k' \frac{p_C^{0.4}}{p_H^{0.1 \sim 0.2}} \quad (7)$$

Eq. 7 is very close to the observed kinetic law. A similar investigation of the kinetics with the assumption that (iv) is the slowest step results in a kinetic expression where the rate is proportional to $p_C^{0.4} p_H^{0.4}$, entirely different from eq. 1.

In studying the hydrocracking of ethane on fused iron catalysts Cimino, Boudart and Taylor¹¹ found a variety of reaction orders, depending on the amounts of potash added. It was shown, however, that these reaction orders could satisfactorily be summarized by the expression

$$\nu = k p^{n_{C_2H_6}} p_H^x \left(1 - \frac{6-x}{2}\right) \quad (8)$$

Equation 8 was obtained by assuming the slowest step to be the breaking of a C-C bond in an adsorbed dehydrogenated radical through an attack by molecular hydrogen, thus



It is evident that the hydrogen exponent of eq. 8 depends on the variable parameter x and also on the form of the attacking hydrogen.

The application of eq. 8 to our system gives the observed kinetic law if x is taken as 2 or 3 and if atomic hydrogen is assumed to be the agent for breaking the C-C bond. Thus we have

$$\nu = k p_C^{0.5} p_H^{(0.5 - 0.3 \frac{6 - (2 \sim 3)}{2})} = k p_C^{0.5} p_H^{+0.05 \sim -0.1} \quad (9)$$

The present mechanism is consistent with that proposed by Bond and Turkevich¹² and by Bond and Sheridan,¹³ who studied the same reaction with deuterium over pumice-supported Ni, Pd and Pt catalysts and suggested that a gaseous cyclopropane molecule in collision with an adsorbed deuterium atom may react to form either an adsorbed *n*-propyl radical or an adsorbed cyclopropyl radical and a molecule of HD. It should be noted, however, that the kinetic law on nickel-silica-alumina is different from that on the pumice-supported metals studied by Bond, *et al.*, in that the latter is first order with respect to cyclopropane and zero order with respect to hydrogen. This difference again might suggest that, in contrast with pumice-supported nickel, nickel-silica-alumina is a poor catalyst for adsorbing hydrogen. High pressures would be required to cover the entire active surface of the nickel-silica-alumina with hydrogen, and it is under these conditions that Ciapetta and Hunter^{3a} find that hydrocarbons undergo isomerization rather than cracking.

It is interesting to note that the non-catalyzed isomerization of cyclopropane to form propylene,

(11) A. Cimino, M. Boudart and H. S. Taylor, *THIS JOURNAL*, **58**, 796 (1954).

(12) G. C. Bond and J. Turkevich, *Trans. Faraday Soc.*, **50**, 1335 (1954).

(13) G. C. Bond and J. Sheridan, *ibid.*, **48**, 713 (1952).

according to Slater,¹⁴ is initiated when the vibrations of the molecule carry any hydrogen atom too near a carbon atom of another methylene group, followed by C-C bond rupture. We found that on the catalyzing surface the interaction of an adsorbed hydrogen atom with an adsorbed cyclopropane molecule is the most difficult step in the overall hydrogenation reaction. The readily occurring hydrogenation of propylene compared with cyclopropane on a nickel catalyst, as reported by Willstätter and Bruce¹⁵ and also by Corner and Pease,¹⁶ is thus readily understandable.

According to the absolute rate theory, the rate expression for a surface bimolecular reaction such as eq. 2 is given by¹⁷

$$\nu = \frac{kT}{h} G \frac{q^*}{q_C q_H} \frac{q_C \frac{N_C}{Q_C} q_H \sqrt{\frac{N_H}{Q_H}}}{\left(1 + q_C \frac{N_C}{Q_C} + q_H \sqrt{\frac{N_H}{Q_H}}\right)^2} \quad (1)$$

where G is the number of active sites per cm.², q_C and q_H the partition functions of the adsorbed species, q^* the partition function of the activated complex, Q_C and Q_H the partition functions of the gaseous molecules in unit volume, and N_C and N_H the concentrations of the gaseous molecules.

The conventional transformation of eq. 10 into power form, as has been performed by the Langmuir kinetics, yields

$$\nu = \frac{kT}{h} G e^{-E/RT} \frac{(N_C/Q_C)^{0.4}}{(N_H/Q_H)^{0.1}} \quad (11)$$

where E is the activation energy for the reaction, 15.2 kcal./mole, and Q_C and Q_H the parts of the partition functions other than exponential terms, obtainable from the spectroscopic data.¹⁸

The observed rate is of the order of 10^{12} molecules/sec. cm.² at 75° and at a total pressure of 200 mm. for an equimolar mixture. The surface area value of 280 m.²/g., determined by the B.E.T. method for the similar catalyst SA-5N-VII,^{3(a)} was used. The rate calculated from eq. 11 was found to be roughly 10^3 times larger than the observed one if we take $G = 10^{16}$. In the calculation, the entropy difference between the adsorbed state and the activated state was, as is usual, neglected. Since an adsorbed *n*-propyl radical is presumably adsorbed more tightly than adsorbed cyclopropane, it is to be expected that the activated state would be strongly adsorbed on the surface to a considerable extent. Thus a loss in entropy due to the formation of the activated complex would be anticipated. The discrepancy between the observed and calculated values should be ascribed to both G and the entropy factor.

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(14) N. B. Slater, *Proc. Roy. Soc. (London)*, **A218**, 224 (1953).

(15) R. Willstätter and J. Bruce, *Ber.*, **40**, 4456 (1907).

(16) E. S. Corner and R. N. Pease, *Ind. Eng. Chem., Anal. Ed.*, **17**, 564 (1945).

(17) See, for example, Horiuti, "Catalytic Chemistry," Asakura Book Co., Tokyo, 1953.

(18) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, pp. 352, 437.

HYDROGEN SORPTION AND THE PARAHYDROGEN CONVERSION ON EVAPORATED NICKEL FILMS¹

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The changes in electrical resistance of an evaporated nickel film, due to the adsorption and absorption of hydrogen, have been studied at -78° . Three processes have been distinguished. Initially, hydrogen is irreversibly adsorbed causing a drop in resistance. This is followed by reversible adsorption over a pressure range from 10^{-6} to at least 600 mm., causing an increase in resistance; this adsorbed hydrogen is responsible for the parahydrogen conversion. A third type of sorption occurs rapidly at room temperature and to an appreciable extent at -78° , decreasing the resistance of the film and poisoning the catalyst with respect to the parahydrogen conversion. The limitations involved in obtaining evaporated metal films of reproducible properties are discussed.

Introduction

Despite the increasing trend toward studies of simpler heterogeneous catalytic processes no satisfactory, complete theory of any reaction has been achieved. The parahydrogen conversion is possibly the simplest reaction available for study and a large number of papers have been published on this subject.³ The adsorption of hydrogen has similarly been widely investigated on wires and evaporated films.^{3,4} Despite this concentration of effort it is still impossible to progress very far in any theoretical interpretation of the results. A basic reason for this difficulty is that one cannot apply results from, say, hydrogen adsorption on a tungsten film to the kinetics on a tungsten wire, without relative surface area measurements and the knowledge that both surfaces expose identical lattice spacings.

In this work it was originally hoped to carry out parallel investigations of adsorption and reaction kinetics on clean, evaporated metal films of known relative area, prepared under identical conditions. To this end nickel was selected as a catalyst since it was readily obtainable in very pure form and had previously been extensively studied.^{3,4} Evaporated films were used because the temperature control is easier than for a wire and the larger area is much less sensitive to contamination.

Experimental

A conventional high vacuum system was employed. Precautions were taken to avoid contamination by air, mercury and stopcock grease. Parahydrogen was prepared immediately before each series of experiments. Nickel wire, 0.2 mm. diameter, was obtained from Johnson, Matthey & Company, England. It was stated to contain less than 0.01% impurity.

The Measurement of the Electrical Resistance of Nickel Films.—Nickel films were prepared by evaporation, from an electrically heated filament, on to the inside wall of a 20 mm. diameter Pyrex tube. This produced a uniform film across two platinum foil electrodes, sealed in the glass wall. The resistance of the film between these electrodes was measured on a sensitive Wheatstone bridge using a galvanometer for highest accuracy, or a millivoltmeter for rapid measurements. A d.c. potential of 1.5 volts was satisfactory for most films; the current flow was reversed to check for contact resistance and thermal e.m.f. errors, but no difficulties of this nature were detected. The limit of measurement of resistance was 0.001 ohms and the bridge was self-consistent down to this limit.

The cell was connected to a sensitive Pirani gage, for low pressure measurements, and also to the mercury manometer. The lower limit of pressure sensitivity of the Pirani gage was approximately 2×10^{-6} mm. for hydrogen. The nickel film was protected from mercury vapor and grease by a U-trap, packed with glass wool and cooled in liquid nitrogen.

Evaporation Procedure.—The system was carefully outgassed before preparation of a film. Evaporation was controlled by the heating current and took from 0.5–6 minutes. The walls of the cell were cooled to 0° during the evaporation. Films from 5 to 1000 ohms resistance were readily obtained. The resistance decreased rapidly after evaporation as the film annealed. This process was accelerated by warming to 80 – 90° for 10–20 minutes, followed by cycling between 80 and -195° . Annealing was assumed to be complete when the resistance remained constant, at 0° .

Pressure Dependence of Resistance.—The effect of hydrogen on film resistance was studied at -78° . Doses of gas, at known volume, temperature and pressure, were admitted to the film and the resistance changes recorded up to a pressure of approximately 10^{-4} mm. At higher pressures the variation of film resistance was observed without measurement of the volume of gas adsorbed.

The Kinetics of Parahydrogen Conversion.—Catalysts were prepared by the method described above. The reaction vessel was connected by 10 mm. bore tubing to an all-glass circulating pump of the type previously described.⁵ The tubes immediately adjacent to the catalyst vessels were cooled to -195° and plugs of glass wool ensured thorough mixing of the gas stream and condensation of all traces of mercury and stopcock grease vapors. The gas stream was cooled to the reaction temperature by a long glass spiral before passing over the catalyst. The rate of circulation was shown to have no effect on the kinetics of the conversion. Three or four small gas samples were removed during each run and analyzed for p-hydrogen content in a thermal conductivity gage. The data were plotted using a first-order rate equation and gave good, straight lines.

Results

Adsorption of Hydrogen at Very Low Pressures.—The initial rate of adsorption of hydrogen, at -78° , was very rapid, with a residual pressure below 2×10^{-6} mm. of mercury. Successive additions of hydrogen produced a well-defined saturation point, at which a small pressure of hydrogen was detected. The volume of hydrogen adsorbed to this point, per milligram of catalyst, will be referred to as the "saturation" volume of the catalyst. When considerable care was exercised in reproducing the conditions of catalyst preparation, the "saturation" volume was constant to $\pm 5\%$. Changing these conditions gave a variation up to $\pm 10\%$. For example, seven films, between 10 and 24 mg., gave an average "saturation" volume, at -78° , of $(4.5 \pm 0.9) \times 10^{-3}$ ml. mg.⁻¹ at S.T.P. The subsequent experiments, on the changes of

(1) This research was supported by Contract No. AF 18 (600)-987 of the Air Research and Development Command, Baltimore.

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