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Kinetic Studies of the Catalytic Ortho-Parahydrogen Conversion and Hydrogen-Deuterium Equilibration on γ-Alumina

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Kinetic studies of the catalytic ortho-parahydrogen conversion and hydrogen-deuterium equilibration on highly purified γ-alumina were conducted in the range of temperature from 77 to 221°K and in the range of pressure from 10 to 120 mmHg. The rate equation obtained can be well explained by a mechanism which involves the reaction between an adsorbed atom and a molecule. The true activation energy, E, and the heat of adsorption of the reactive molecule, Q, were estimated as E=0.51—0.80 and Q=0.51—0.72 kcal/mol for the conversion (77—195°K), and E=4.6 and Q=1.9 kcal/mol for the equilibration (145—221°K). The conversion at temperatures below 90°K was found to proceed mostly *via* the magnetic mechanism. A thermal desorption study of adsorbed ethylene showed that there are three types of adsorption on γ-alumina with different activation energies of desorption, and that these species occupy a total of only a few hundredths of the surface. It was concluded that the most strongly-adsorbed ethylene blocks the reactions *via* the chemical mechanism, while the most weakly-adsorbed one retards the conversion *via* the magnetic mechanism. The nature of active sites for the reactions was discussed by taking the results of the ESR measurement into consideration.

During the past three decades, a number of investigations have been made in an attempt to ascertain the mechanisms of the ortho-parahydrogen conversion and of the hydrogen-deuterium equilibration on various solid surfaces, and several mechanisms have been proposed. Bonhoeffer and Farkas[1] proposed a dissociation-recombination mechanism of hydrogen on the surface. Later, Rideal[2] proposed an alternative mechanism, *i. e.*, the exchange of hydrogen atoms between an adsorbed hydrogen molecule and an atom, in order to account for the fact that the reaction rate is appreciable on some catalysts at which the rate of atomic recombination is extremely slow. Couper and Eley[3] have modified this mechanism by assuming the reaction of an adsorbed atom with a gaseous molecule. Further, Boreskov and Vassilevitch[4] proposed a mechanism in which the molecule, after the exchange, migrates to the site of weakest adsorption and then desorbs. A mechanism of bimolecular reaction between adsorbed molecules was proposed by Schwab and Killmann.[5,6]

Besides the chemical mechanisms expressed above, the interconversion between nuclear spin isomers, para- and orthohydrogen or ortho- and paradeuterium, proceeds physically by means of perturbations due to the inhomogeneous magnetic field of paramagnetic substances.

More detailed and accurate kinetic studies are needed in order to clarify which mechanism is operative and to determine whether adsorbed molecular hydrogen participates in the reactions. Only a few studies, however, have concerned themselves with these problems.

Among a number of active substances for these reactions, it has recently been reported[7,8] that evacuated or irradiated alumina is catalytically active to both the ortho-parahydrogen conversion*1 and the hydrogen-deuterium equilibration.*1 The fact that alumina, originally diamagnetic and a poor adsorbent of hydrogen, accelerates the conversion at such a low temperature as 77°K and the equilibration at higher temperatures suggests the existence of paramagnetic sites and of dissociatively-adsorbed hydrogen on the surface.

1) K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, **12B**, 231 (1931).
2) E. K. Rideal, *Proc. Cambridge Phil. Soc.*, **35**, 130 (1939).
3) A. Couper and D. D. Eley, *Discussions Faraday Soc.*, **8**, 172 (1950).
4) G. K. Boreskov and A. A. Vassilevitch, Actes Congr. Intern. Catalyse, 2e, Paris, 1960, **1**, 1095 (Editions Technip, Paris, 1961).
5) G. M. Schwab and E. Killmann, *ibid.*, 2e, Paris, 1960, **1**, 1047 (Editions Technip, Paris, 1961).
6) G. M. Schwab and E. Killmann, *Z. physik. Chem. (N. F.)*, **24**, 119 (1960).
7) G. J. K. Acres, D. D. Eley and J. M. Trillo, *J. Catalysis*, **4**, 12 (1965).
8) I. Yasumori and S. Ohno, This Bulletin, **39**, 1302 (1966).
*1 Hereafter these will be called simply as conversion and equilibration.

The kinetics of the conversion and of the equilibration on the surface of highly-purified γ-alumina were examined in detail in the present experiment. In addition, studies of the effect of adsorbed ethylene on the reaction rates, on the thermal desorption of ethylene, and on ESR of γ-alumina were carried out in order to obtain some information on the nature of the active sites.

Experimental

Apparatus and Procedure. Kinetic studies of the conversion and of the equilibration on γ-alumina were carried out using an apparatus which consisted of a conventional high-vacuum system with a grease-free reaction vessel of about 950 m*l* combined with a circulation pump and arrangements for the preparation and storage of normal hydrogen, para-rich hydrogen, and deuterium. The reaction system was connected with a low-pressure-type gas chromatograph[8] *via* a greaseless valve and a trap cooled at 77°K.

The temperature of the catalyst vessel was maintained using the following cooling agents: liquid nitrogen (77°K), liquid oxygen (90°K), a mixture of *n*-propanol and methanol (100 : 30) cooled with liquid nitrogen (145°K), *n*-propanol cooled with liquid nitrogen (159°K), methanol cooled with solid carbon dioxide (195°K), and *n*-hexanol cooled with liquid nitrogen (221°K). The effective volume of the reaction vessel at each temperature was measured using hydrogen.

A measured amount of the reactant gas was introduced into the reaction vessel and left in contact with the catalyst for a given time; then about 1% of the gas was sampled for the gas-chromatographic analysis.

In case of the thermal desorption study, alumina was preliminally exposed to 5×10^{-2} mmHg of ethylene, at various temperatures, and then evacuated at the same temperature. The temperature of the alumina was then raised linearly with the time up to 350°C; the pressure change due to the desorption under pumping was simultaneously registered. The details of this apparatus will be reported later.

The amounts of irreversibly-adsorbed ethylene on γ-alumina were estimated as follows. Gamma-alumina in a small vessel was evacuated at 500°C. A known amount of ethylene was then introduced into the vessel at 195 or 298°K and left in contact with the alumina for 0.5 hr. The amount of ethylene remaining in the gas phase was then measured by collecting it into a side tube at the temperature of liquid nitrogen. The difference between the amounts of introduced ethylene and of collected one was equated with that of irreversibly-adsorbed ethylene.

The surface area of γ-alumina was determined by the BET method in a constant-volume system using nitrogen at 77°K.

The ESR spectra were measured at 9194 Mc/s on an X-band spectrometer (Japan Electron Optics Laboratory Co., JES-3B 365) using powdered γ-alumina placed in a quartz tube 4 mm in inside diameter. After calcination at 500°C, the samples were evacuated at various temperatures for 5 hr *via* a cold trap at 77°K and then sealed off prior to ESR measurements.

Materials. Cylinder hydrogen was purified by diffusing it through a heated thimble made of palladium-silver alloy. High-purity deuterium and ethylene from the Takachiho Chemical Co. were used without further purification. Cylinder helium was passed through a liquid-nitrogen trap, filled with Linde molecular sieve 13X, in order to remove the oxygen and other condensables.

Normal hydrogen was used as the reactant of the conversion at temperatures of 77 and 90°K, while para-rich hydrogen prepared by equilibrating it at 77°K was used in the temperature range from 145 to 195°K. In the case of equilibration, an equimolar mixture of hydrogen and deuterium was used as the reactant.

Aluminum oxide was prepared by the hydrolysis of aluminum isopropoxide which had been distilled three times under reduced pressure. The spectroscopic analysis of the oxide showed that the contents, as impurities, of iron, copper, magnesium, and manganese are all less than 1 ppm except for silicon (20 ppm). An X-ray diffraction study showed that the oxide, after having been calcined at 100 and 250°C, has the structure of pseude-böhmite, and that it changes to γ-alumina upon calcination at 500°C.

The γ-alumina catalyst finally adopted was calcined at 500°C for 10 hr in air, and then evacuated at the same temperature for 20 hr *in vacuo* at better than 1×10^{-6} mmHg. Prior to each run of reaction, the catalyst was evacuated at 500°C for 2 hr and cooled down to the reaction temperature by introducing about 10 mmHg of helium into the reaction vessel.

In some runs, the catalyst evacuated at 500°C was preliminarily brought into contact with 10 mmHg of ethylene for 1 hr at 195 or 298°K and then evacuated for 1 hr.

Results and Discussion

Experimental-rate Expression. It was verified that the diffusion through the catalyst pore has no influence on the rate; a calculation of the Thile modulus, by assuming a pore radius of 10 Å showed that the effectiveness factor of the surface was almost unity under the present reaction conditions.

As may be seen from the time course of the reaction under constant pressures (Fig. 1), the experimental-rate constants, k_e, of both conversion and equilibration were expressed as:

$$k_e = \frac{1}{t}\ln\frac{X_0-X_e}{X_t-X_e}\ \text{min}^{-1} \qquad (1)$$

where X_0 is the initial mole fraction of the species which disappears with the progress of the reaction, and where X_t and X_e are those of the same species at the time t and the equilibrium at the experimental temperature, T, respectively. A specific rate, k_m, was calculated by the following equation:

$$k_m = n\frac{k_e}{60S} = \frac{k_ePV}{60SkT}\ \text{molecules}\cdot\text{sec}^{-1}\text{cm}^{-2} \qquad (2)$$

whene n is the number of molecules in the reaction system; P, the total pressure of the reactant; V, the effective volume of the reaction

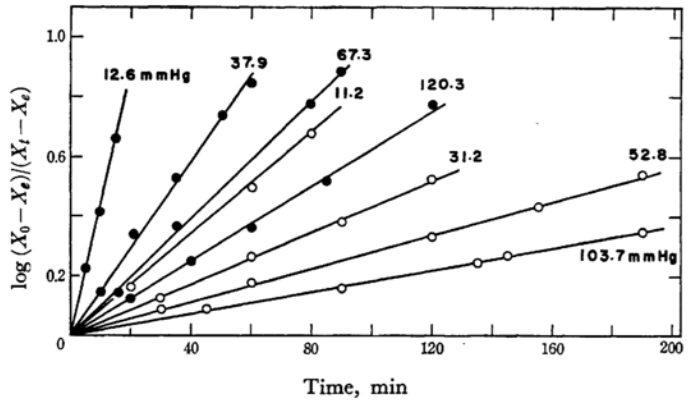


Fig. 1. Time course of the conversion and the equilibration on γ-alumina at various pressures.
●, conversion at 77°K; ○, equilibration at 159°K: catalyst, 33.4 mg

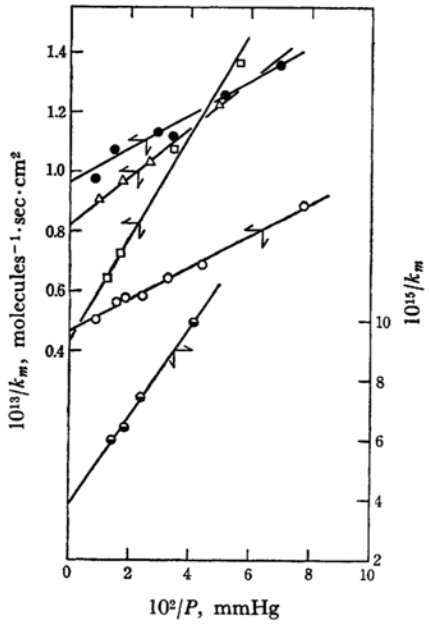


Fig. 2. Dependence of the conversion reaction rate on the total pressure.
●, 77°K; ○, 90°K; ◒, 145°K on unpoisoned γ-alumina: △, 90°K on γ-alumina poisoned by ethylene at 298°K: □, 195°K on γ-alumina poisoned by ethylene at 195°K

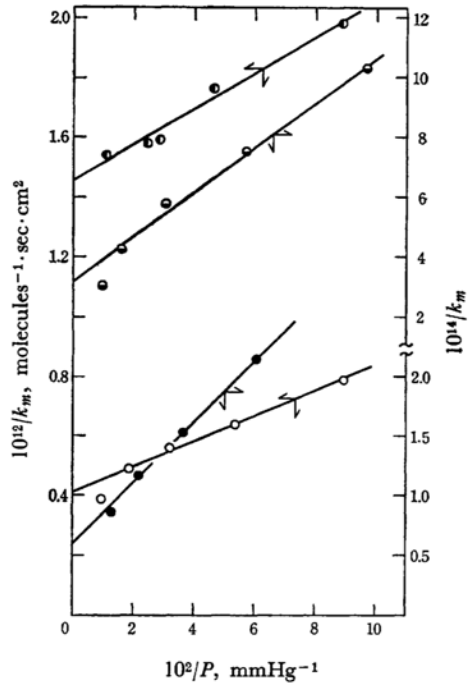


Fig. 3. Dependence of the equilibration reaction rate on the total pressure.
◐, 145°K; ○, 159°K; ◒, 195°K and ●, 221°K

system; S, the surface area of the catalyst, and k, the Boltzmann constant.

Figure 2 shows that the linear relationship holds between $1/k_m$ and $1/P$ for the conversion in the range of temperature from 77 to 195°K and in the range of pressure from 12.8 to 120.3 mmHg. Similar behavior can also be seen in Fig. 3 for the equilibration in the range of temperature from 145 to 221°K and in the range of pressure from 10.3 to 106.5 mmHg.

From these results, a rate expression which fits both the reactions may be given as:

$$-\frac{n}{S}\cdot\frac{dX_t}{dt}=k\frac{aP}{1+aP}(X_t-X_e)$$

molecules·sec^{-1}cm^{-2} (3)

where k corresponds to the value of k_m extrapolated to an infinite pressure. The Arrhenius plots of k shown in Fig. 4, may be expressed as:

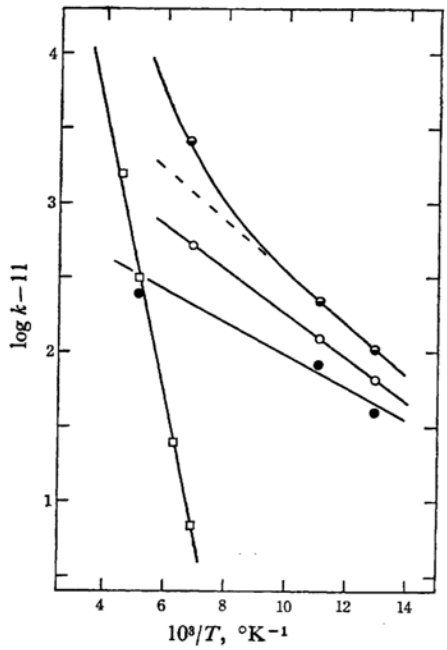


Fig. 4. Arrhenius plots of the extrapolated rate, k, in the conversion and the equilibration. ◒, conversion on unpoisoned γ-alumina; ○, conversion on γ-alumina poisoned by ethylene at 298°K and ●, at 195°K: □, equilibration on unpoisoned γ-alumina

$$k = A\exp(-E/\boldsymbol{R}T) \tag{4}$$

where A and E are constants.

The a parameter in Eq. (3) was determined from the slopes of the plots in Figs. 2 and 3. This parameter, as a function of the temperature, is shown in Fig. 5; it may be expressed as:

$$a = a_0\exp(Q/\boldsymbol{R}T), \tag{5}$$

by taking two constants, a_0 and Q. The estimated values of these constants are shown in Table 1.

It is found that the Arrhenius plot of k for the conversion deviates upward from a straight line with increasing temperatures and that it approaches that for the equilibration. This deviation does not, however, appear when the catalyst is preliminarily

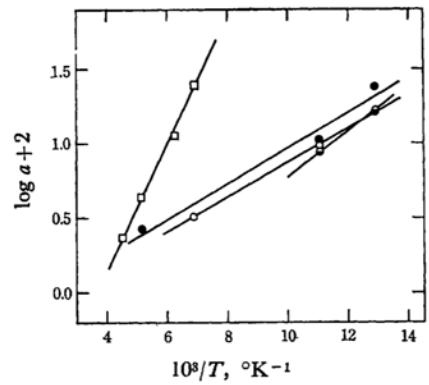


Fig. 5. Relationship between parameter, a, and temperature. Symbols are the same as those in Fig. 4.

treated by ethylene at 195 or 298°K. These results suggest that the reactions *via* a chemical mechanism are mostly retarded by adsorbed ethylene which remains on the surface of the catalyst evacuated at 298°K, while the low-temperature conversion is stopped by ethylene adsorbed at 195°K. It may, therefore, be concluded that the conversion at high temperatures proceeds *via* a mechanism similar to that of the equilibration, but that the reaction *via* another, probably physical, mechanism becomes predominant at low temperatures.

Mechanism of the Conversion. *Derivation of Rate Expression.* By assuming that the conversion takes place magnetically at low temperatures, the reaction may be described by the following scheme:

$$\begin{array}{ccc} o\text{-}H_2(g) & & p\text{-}H_2(g) \\ {\scriptstyle k_1}\downarrow\uparrow{\scriptstyle k_{-1}} & & {\scriptstyle k_2}\downarrow\uparrow{\scriptstyle k_{-2}} \\ o\text{-}H_2(a) & \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} & p\text{-}H_2(a) \\ \vdots & & \vdots \\ S_m & & S_m \end{array} \tag{I}$$

where S_m is a paramagnetic site on the surface. The rate equations for these steps may be written as:

$$\frac{dN_{go}}{dt} = \frac{V}{\boldsymbol{k}T}\cdot\frac{dP_o}{dt} = -k_1P_o(1-\theta)\sigma_1S + k_{-1}\theta_o\sigma_1S \tag{6}$$

TABLE 1. KINETIC CONSTANTS IN THE CONVERSION AND THE EQUILIBRATION

Reaction	Catalyst treatment	E (kcal/mol)	Q (kcal/mol)	a_0 mmHg^{-1}	A molecules·sec^{-1}cm^{-2}
o-H_2=p-H_2	(A); evacuated at 500°C	0.80*	0.72*	1.7×10^{-3}	19×10^{14}
	C_2H_4 adsorbed at 298°K after (A)	0.70	0.50	5.3×10^{-3}	5.8×10^{14}
	C_2H_4 adsorbed at 195°K after (A)	0.51	0.51	6.3×10^{-3}	1.2×10^{14}
H_2+D_2=2HD	evacuated at 500°C	4.6	1.9	2.8×10^{-4}	5.0×10^{18}

* Calculated from rates at 77 and 90°K.

$$\frac{dN_{gp}}{dt} = \frac{V}{kT}\cdot\frac{dP_p}{dt} = -k_2P_p(1-\theta)\sigma_1 S + k_{-2}\theta_p\sigma_1 S \quad (7)$$

$$\frac{d\theta_o}{dt} = k_1P_o(1-\theta) - k_{-1}\theta_o - k_3\theta_o + k_{-3}\theta_p \quad (8)$$

$$\frac{d\theta_p}{dt} = k_2P_p(1-\theta) - k_{-2}\theta_p + k_3\theta_o - k_{-3}\theta_p \quad (9)$$

where:

$$\theta = \theta_o + \theta_p$$

P_o and P_p are the partial pressures of ortho- and parahydrogen; N_{go} and N_{gp}, the numbers of the respective molecules in the gas phase; θ_o and θ_p, the surface coverages of these species, and σ_1, the number of active sites per unit area of the catalyst surface. At a steady state where $d\theta_o/dt = d\theta_p/dt = 0$, the expressions for the surface coverage are obtained as:

$$\theta_o = \frac{1}{D}\{k_1(k_{-2}+k_{-3})P_o + k_2k_{-3}P_p\} \quad (10)$$

$$\theta_p = \frac{1}{D}\{k_1k_3P_o + k_2(k_{-1}+k_3)P_p\} \quad (11)$$

where:

$$D = k_1(k_{-2}+k_3+k_{-3})P_o + k_2(k_{-1}+k_3+k_{-3})P_p + (k_{-1}k_{-2}+k_{-1}k_{-3}+k_{-2}k_{-3}).$$

By substituting these relations into Eqs. (6) and (7), we obtain the equations:

$$\frac{dP_o}{dt} = \frac{\rho}{D}(k_{-1}k_2k_{-3}P_p - k_1k_{-2}k_3P_o) \quad (12)$$

and

$$\frac{dP_p}{dt} = \frac{\rho}{D}(k_1k_{-2}k_3P_o - k_{-1}k_2k_{-3}P_p) \quad (13)$$

where:

$$\rho \equiv \sigma_1 S k T/V.$$

Assuming that there is no difference between the adsorption behavior of these isomers, *i. e.*, that $k_1=k_2$ and that $k_{-1}=k_{-2}$, Eq. (12) can be rewritten in the form:

$$-\frac{d(PX_o)}{dt} = \rho\frac{k_{-1}(k_3+k_{-3})}{k_{-1}+k_3+k_{-3}}\cdot\frac{(k_1/k_{-1})P}{1+(k_1/k_{-1})P} \times\left[X_o - \frac{1}{1+k_3/k_{-3}}\right] \quad (14)$$

where X_o is the mole fraction of orthohydrogen. This equation can easily be reduced to Eq. (3). The E and Q constants in Table 1 can, therefore, be expressed as:

$$E = -R\frac{d\ln\{k_{-1}(k_3+k_{-3})/(k_{-1}+k_3+k_{-3})\}}{d(1/T)} \quad (15)$$

$$Q = R\frac{d\ln(k_1/k_{-1})}{d(1/T)} = R\frac{d\ln a}{d(1/T)} \quad (16)$$

which have physical significance as the activation energy and the heat of adsorption, respectively.

Rate-determining Step of the Conversion. There are two extreme cases which depend on the relative order of the magnitude of rate constants, $k_{-1} \gg k_3$, k_{-3} and *vice versa*, corresponding to the cases where the rate is controlled by the surface conversion or by the desorption, respectively. In the former case, Eq. (14) can be simplified to:

$$-\frac{d(PX_o)}{dt} = \rho(k_3+k_{-3})\frac{(k_1/k_{-1})P}{1+(k_1/k_{-1})P}(X_o - X_e) \quad (17)$$

while in the latter case it can be simplified to the same equation except that k_{-1} replaces (k_3+k_{-3}) in Eq. (17).

The former case is preferable to the latter, as will be dicussed below. If the latter case were operative, the observed rate would correspond to the rate of desorption. On the basis of the activated complex theory, the rate of desorption is given as:

$$v = k_d n_{H_2(a)} = \frac{kT}{h}\exp(-E/RT)\sigma_1\theta_{H_2(a)} \quad \text{molecules}\cdot\text{sec}^{-1}\text{cm}^{-2} \quad (18)$$

The frequency factor, A, is equivalent to the $kT/h\cdot\sigma_1$ in Eq. (18). Hence, the observed value of A, 19×10^{14} molecules·sec^{-1}·cm^{-2}, in Table 1 results in the value of σ_1 of $1—3\times10^3$ sites·cm^{-2} at 77—90°K, a value which is too small to keep the rate of surface conversion faster than that of desorption.

Isotope Effect. As may be seen in Table 1, the activation energy of the conversion at temperatures below 90°K is smaller than that of the equilibration by about 4 kcal/mol. This difference is larger than that in the zero-point energies between gaseous hydrogen and deuterium, 1.8 kcal/mol. The latter should be the maximum difference in activation energy due to the isotope effect, as has been pointed out by Eley *et al.*[7] There ia a difference of 1.2 kcal/mol between the heats of adsorption determined from the kinetics of equilibration and of conversion. Moore and Ward[9] have estimated the heats of the molecular adsorption of para-, orthohydrogen, hydrogen deuteride, ortho-, and paradeuterium on alumina by gas chromatography. The obtained values, ranging from 1.40 (p-H_2) to 1.65 kcal/mol (p-D_2), lead to a maximum difference of 0.25 kcal/mol due to the isotope effect.

The above kinetic results can not be explained by the isotope effect only. The conversion at temperatures below 90°K, therefore, proceeds *via* a mechanism different from that of the equilibration.

9) W. R. Moore and H. R. Ward, *J. Phys. Chem.*, **64**, 832 (1960).

Mechanism of the Equilibration. The equilibration can only occur *via* a chemical mechanism. On the assumption that the Rideal mechanism is operative, the reaction scheme may be expressed as:

$$\begin{array}{ccccc} H_2(g) & & 2HD(g) & & D_2(g) \\ {\scriptstyle k_1'}\uparrow\downarrow{\scriptstyle k'_{-1}} & & {\scriptstyle k_2'}\uparrow\downarrow{\scriptstyle k_{-2}'} & & {\scriptstyle k_1''}\uparrow\downarrow{\scriptstyle k_{-1}''} \\ H_2(a) & & 2HD(a) & & D_2(a) \\ + & \underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}} & + & \underset{k_{-3}''}{\overset{k_3''}{\rightleftharpoons}} & + \\ D(a) & & H(a)\ D(a) & & H(a) \end{array} \qquad \text{(II)}$$

By a treatment similar to the above, when the exchange of atoms is the rate-controlling step a rate equation may be derived as follows:

$$-\frac{d(PX)}{dt} = \rho'\theta_a(k_3'+2k_{-3}')\frac{(k_1'/k'_{-1})P}{1+(k_1'/k'_{-1})P} \times\left[X-\frac{1}{1+k_3'/2k'_{-3}}\right] \qquad (19)$$

with:

$$\rho' \equiv \sigma_2 S\boldsymbol{k}T/V,$$

where X is the sum of the mole fractions of hydrogen and deuterium in the gas phase and σ_2 is the number of active sites per unit area of the catalyst surface. The precise form of σ_2 is given in Eq. (20).

A thermal desorption study of hydrogen adsorbed on the alumina showed that no appreciable desorption occurred up to 250°K. Hence, by assuming that the surface coverage of the adsorbed hydrogen atom, θ_a, remains unaltered throughout the present experiment, it may be seen that Eq. (19) coincides with the experimental results, Eq. (3).

The heat of adsorption, 1.9 kcal/mol, estimated from the kinetic study is quite similar to those obtained by gas chromatography. To judge from these coincidences, it is probable that the equilibration proceeds mainly through a reaction of molecularly-adsorbed hydrogen with the adsorbed hydrogen atom.

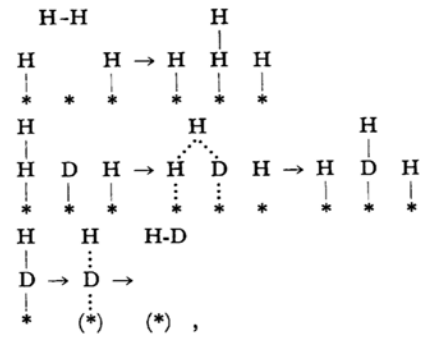
The application of the activated complex theory to this mechanism gives the following expression for the rate of the surface process:

$$v = \sigma_2 k_3'\theta_a\theta_m = \frac{z\sigma_a\sigma_m}{n_0} k_3'\theta_a\theta_m\ . \qquad (20)$$

The rate constant, k_3', has the form $k_3' = \boldsymbol{k}T/\boldsymbol{h}\cdot\exp(-E/\boldsymbol{R}T)$ if the ratio of partition functions, $f(X_{\ddagger})/f(H(a))\cdot f(H_2(a))$, is unity. σ_a and σ_m are the number of sites which hold hydrogen atoms and molecules respectively. z is the number of nearest neighbors around the respective site; θ_m, the fraction of the surface covered by adsorbed hydrogen molecules, and n_0, the total number of active sites, $\sigma_a+\sigma_m$. This equation can be used to evaluate the number of adsorption sites on the present catalyst surface. Assuming that σ_a and σ_m are of the same order of magnitude, that $z=4$, and that $n_0=1\times10^{15}$ cm^{-2}, σ's can be evaluated as 0.5×10^{10} cm^{-2} from the observed value, 5.0×10^{18}, of A shown in Table 1.

A separate study of the poisoning effect of ethylene adsorbed at 298°K showed that the amount of adsorbed ethylene which completely blocks the reaction can be estimated to be 2×10^{12} molecules·cm^{-2} from the initial decrease in the equilibration rate. Dolidze *et al.*[10] have reported that γ-alumina, calcined at 500°C in air and evacuated at 320°C, can adsorb 3×10^{11} hydrogen atoms per unit area at 523°K under pressures below 10^{-2} mmHg. These values seem to be in satisfactory agreement with one another in view of the approximations made.

A rate equation similar to Eq. (19) can be derived on the basis of the Boreskov-Vassilevitch reaction scheme as:



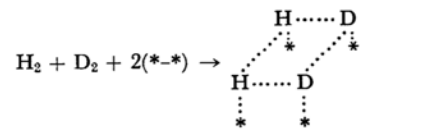
(IIIa)

(IIIb)

(IIIc)

provided that (IIIb) is the rate-controlling step, where * represents an active site and (*), the site for the weakest adsorption.

The Schwab-Killmann mechanism (IV).



(IV)

does not fit the observed kinetic equation. This mechanism results in the rate equation:

$$-\frac{d(PX)}{dt} = \rho''\left(\frac{aP}{1+aP}\right)^2\left[k_4\frac{X^2}{4} - k_{-4}(1-X)^2\right] \qquad (21)$$

where $\rho''\equiv\sigma_3^2 S\boldsymbol{k}T/2V$, where k_4 and k_{-4} are the rate constants of HD formation and its reverse on the surface respectively, and σ_3, the number of dual sites per unit area. This equation does not agree with Eq. (3) in two aspects, *i. e.*, the time-course characteristics and the pressure dependence.

Properties of Active Sites. It may be seen from Fig. 4 that the adsorbed ethylene affects the

10) G. M. Dolidze, Yu. A. Kobanovskii and L. S. Polak, *Kinetika i Kataliz*, **6**, 897 (1965).

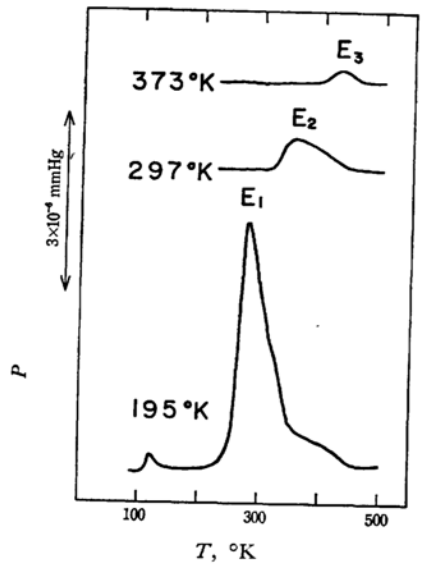


Fig. 6. Desorption spectra of adsorbed ethylene on γ-alumina.
Rate of temperature rise, 2.70°K/min

rate of conversion in different ways depending upon the reaction temperatures. Figure 6 shows the thermal desorption spectra of the adsorbed ethylene on the alumina preliminarily evacuated at 500°C. Irreversibly-adsorbed ethylene at 195°K gave a spectrum consisting of a small peak at 110°K, a large peak, E_1, with a maximum at 280°K, and a shoulder on the high-temperature side of E_1. With an adsorption sample at 297°K, an unsymmetrical peak, E_2, with a maximum at 355°K was obtained, but not the E_1 peak. Finally, a sample of adsorption at 373°K gave only a small, symmetrical peak, E_3. The relative areas of the peaks were estimated to be $16.3(E_1) : 3.3(E_2) : 1.0(E_3)$, and the activation energies of the desorption of the respective peaks were determined[11] to be $19(E_1)$, $25(E_2)$ and $31(E_3)$ kcal/mol on the assumption that the desorption obeys the first-order law. The peak at 110°K was attributed to the desorption of ethylene physically adsorbed on the alumina and/or the wall of the apparatus.

It was found, by a static measurement of the adsorption, that the fraction of the surface occupied by ethylene is quite small; the sum of the fractions of the surface covered by adsorbed ethylene which give the E_1, E_2, and E_3 peaks was 0.024, while that corresponding to E_2 and E_3 was 0.0021. The E_2 and E_3 peaks were found to coincide with those observed by Amenomiya and Cvetanović by a method of inert-gas flow.[11]

The γ-alumina in the present experiment gave a sharp, symmetrical ESR signal 12 oe wide, corresponding to $g=2.004$. The intensity of this signal changed with the evacuation temperatures, as is shown in Table 2. A similar signal with $g=2.003$ has been reported by Berger and Roth.[12]

Table 2. Changes in the intensity of ESR signal ($g=2.004$) of γ-alumina with evacuation

Evacuation	Intensity of ESR signal
30°C—5 hr	1.8×10^{14} spins/g
500°C—5 hr	0.75
550°C—5 hr	0.71
C_2H_4 adsorbed at 30°C after 550°C—5 hr	0.94

Provided that the conversion at low temperatures takes place only on these ESR active sites, its rate at 77°K is estimated to be 1×10^5 molecules·sec^{-1}·$spin^{-1}$ under a total pressure of 12.6 mmHg.

Eley *et al.*[7] have reported that there is a linear relationship between the rate of conversion and the number of unpaired electrons produced on α-alumina by γ-ray irradiation. On the basis of their findings, the rate of conversion at 77°K may be estimated as 2 molecules·sec^{-1}·$spin^{-1}$ under a total pressure of 4 mmHg provided that all these electrons are effective for the reaction. In the present study, the decrease in the conversion rate per ethylene molecule adsorbed at 195°K, which mostly retards the low-temperature conversion, is estimated as 0.5 under similar conditions. This value agrees in order of magnitude with the result reported by Eley *et al.* The ESR active sites do not, therefore, correspond to that for the low-temperature conversion.

This consideration leads to the following conclusions. There are two kinds of paramagnetic centers on or in evacuated γ-alumina; one gives an ESR signal, but has little effect on the low-temperature conversion, while the other gives no ESR signal, but accelerates the conversion. These active sites, including those for the equilibration, exist over only a small percentage of the whole surface. The most strongly-adsorbed ethylene retards the reaction *via* the chemical mechanism, while the most weakly-adsorbed one retards the conversion *via* the physical mechanism.

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