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Active Centers in Cyclohexene Disproportionation on Supported Palladium

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The disproportionation of cyclohexene to cyclohexane and benzene has been kinetically studied between 30° and 50°C by feeding streams of cyclohexene in helium over different catalysts beds. Each catalyst sample consisted of highly dispersed palladium supported on alumina. The activity of the catalyst samples present maxima in correspondence to particular values of the percentage of palladium on the support.

A statistical analysis of the distribution of palladium atoms on the surface of the support has shown that the activity maxima can be related to the probability of formation of particular atomic clusters (active centers).

INTRODUCTION

In a previous paper the results of a kinetic study of the disproportionation of cyclohexene to benzene and cyclohexane on palladium catalyst have been reported (*1*). In that research the kinetic runs were performed in tetrahydrofuran solution on black palladium and it was found that the reaction goes through cyclohexadiene as intermediate.

A surface bimolecular kinetic scheme was proposed and by means of its application it was possible to give a satisfactory interpretation of a large set of experimental results.

In order to improve the knowledge of the reaction mechanism it seemed of interest to us to extend the research by working with supported palladium catalysts. The reactions were performed with a large set of catalysts obtained by precipitation of palladium on aluminum oxide. The amount of palladium in each catalyst was always less than 6% of the necessary quantity for the formation of a complete coverage of the surface. This quantity was evaluated on the basis of the surface area of alumina and of the area covered by a palladium atom (radius 1.278 Å). The reaction runs were made by feeding a stream of cyclohexene in an inert gas (helium) over a catalyst bed.

The aim of the work was to verify whether activity could be related to the probability of formation of particular atomic clusters (active centers) evaluated by the study of the statistical distribution of palladium atoms on the surface of the support at different palladium percentages.

A preliminary communication of some results has already been presented (*2*).

EXPERIMENTAL

Materials. The cyclohexene was a BDH product, purified by fractional distillation. The support was alumina, Alcoa Chemicals F-110, (surface area about 200 m^2/g), ground and classified (40–60 mesh).

The alumina was heated 2 hr at 330°; after cooling it was immersed in a solution of $PdCl_2$. Different solutions of $PdCl_2$ were employed which had been obtained from a neutral saturated solution, diluted after acidification by hydrogen chloride. After 24 hr the alumina was filtered and dried. The catalyst was reduced in a hydrogen

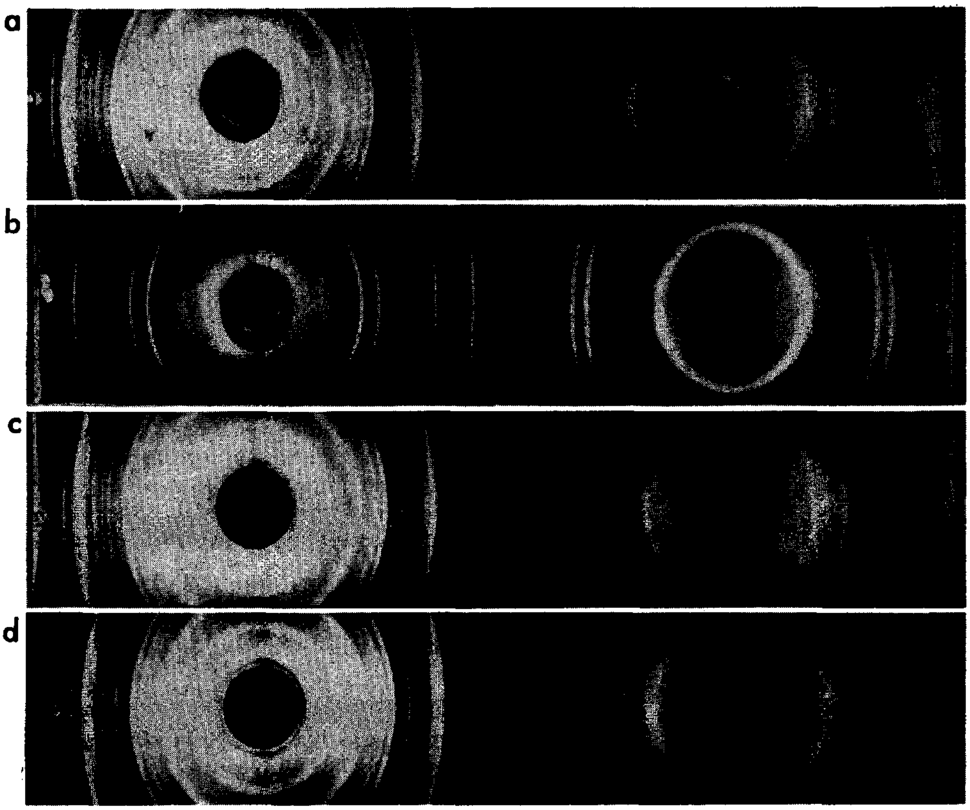

FIG. 1. X-Ray powder diffraction patterns: (a) γ alumina Alcoa F-110; (b) palladium black; (c) catalyst at 2.985% of palladium; (d) catalyst No. 1 (see Table 1).

stream during 2 hr at 330°. The catalyst was washed exhaustively with hot distilled water till elimination of chloride ions was complete; after drying, another reduction in the hydrogen stream was made under the previous conditions.

A standard procedure was rigorously followed in the preparation of catalysts.

Catalyst analysis. Nineteen samples of catalysts with different percentages of palladium were prepared. The analysis of the amount of palladium in each sample was made by a Philips X-ray Fluorescence Spectrograph, after a calibration with samples at known content of palladium.

X-Ray powder diffraction patterns of black palladium, alumina, and some catalyst samples were obtained using the Debye-Scherrer method. The results, shown in Fig. 1, reveal that in the catalyst samples there were no palladium crystallites of a size detectable by X-ray diffraction. In fact the characteristic lines of palladium crystals (see Fig. 1b), are not present in the diffraction patterns (c) and (d) . In a mechanical mixture of alumina and black palladium, in the same amount of catalyst samples, such lines were easily detectable.

Apparatus. In Fig. 2 a scheme of the apparatus is given. The stream of helium, coming from the cylinder B, was dried (E) and then split in two streams (G). One of the streams was saturated (S) with cyclohexene at 20°C, (±0.1°), that is, a temperature lower than room temperature, and then mixed in M with the other stream of helium. The gas mixture fed the reactor, where it was preheated to reaction temperature (±0.1°) and contacted the catalyst. The catalytic bed was supported by glass wool in a tubular reactor 177 mm high and with an 8 mm diameter. The stream outgoing from the reactor at different times

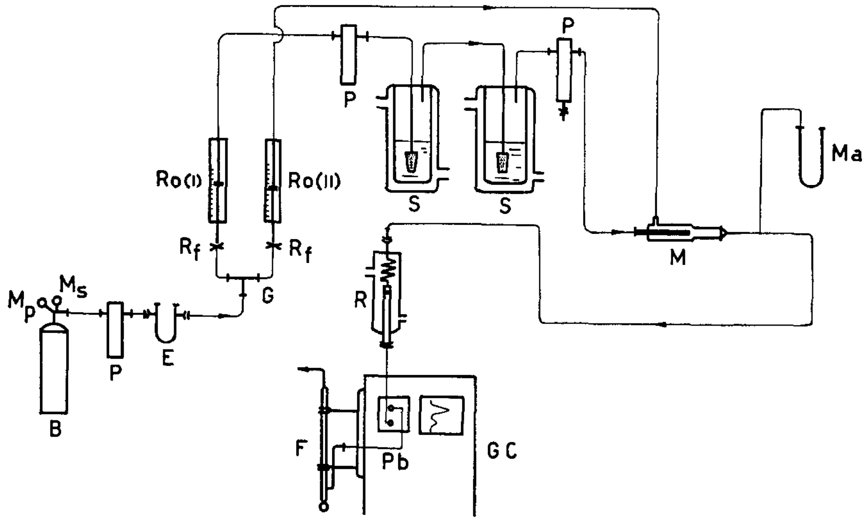

FIG. 2. Scheme of the apparatus used for experimental runs: B, cylinder; M_p, M_s, M_a, manometers; P, pressure-stabilizing chambers; E, drier; G, T-joint; R_f, valves; R_o, rotameters; S, saturators; R, reactor; M, mixer; F, bubble flow meter; GC, gas chromatograph; Pb, injector to GC.

was directly injected in a gas chromatograph for analysis.

Procedure and analysis. Every kinetic experiment was made at different concentrations and flow rates obtained by varying the stream of gas $R_0(I)$. The time for obtaining the stationary conditions was about 30 min.

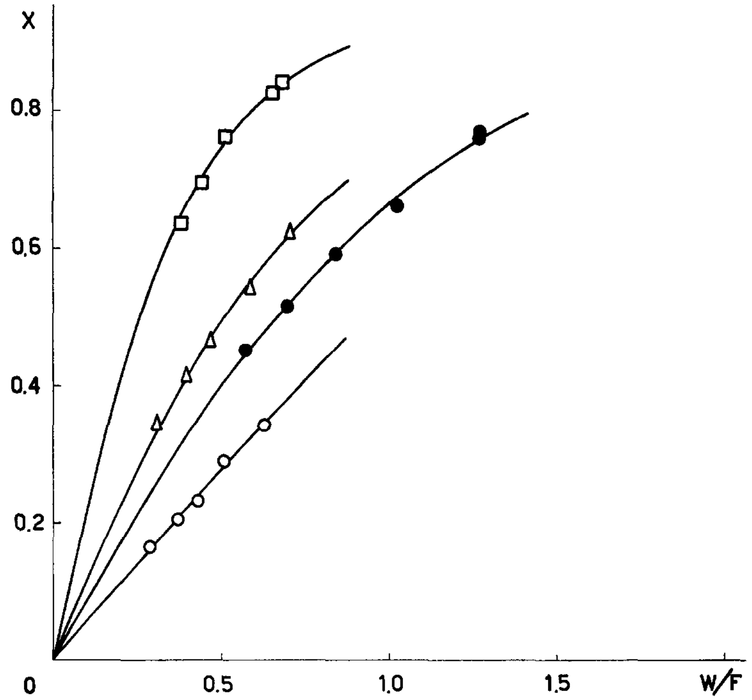

FIG. 3. Examples of kinetic runs: conversion degree (X) vs. contact time (W/F); solid lines from Eq. (6); □, catalyst No. 10 at 50°; △, catalyst No. 10 at 40°; ○, catalyst No. 10 at 30°; ●, catalyst No. 17 at 40°.

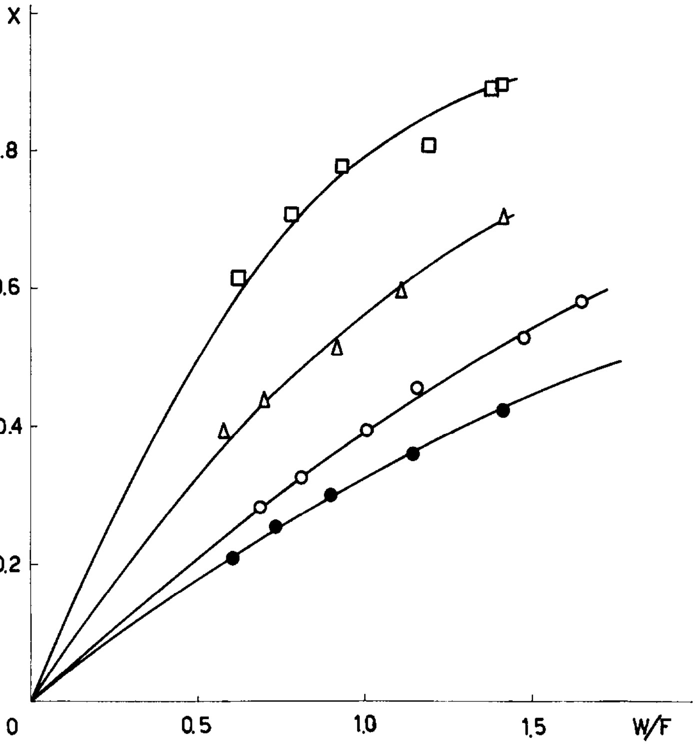

FIG. 4. Examples of kinetic runs; conversion degree (X) vs. contact time (W/F); solid lines from Eq. (6); □, catalyst No. 18 at 50°; △, catalyst No. 18 at 40°; ●, catalyst No. 18 at 30°; ○, catalyst No. 4 at 30°.

Gas chromatographic analysis was performed on a Fractovap B/f (C.Erba) using a 3-m stainless steel column of 20% Carbowax-400 on 30–60 mesh Celite at 70°. Hydrogen was used as carrier gas.

The relative amounts of the compounds involved in the reaction were evaluated from peak areas. The conversion degree of cyclohexene was easily determined from such peak areas because the reaction proceeds without change of total molar concentration.

The concentrations of the different compounds in the stream going to the reactor were evaluated by the known values of the flow rates and from the amount of cyclohexene vaporized in S, calculated by its vapor pressure at 20°. The range of variation of cyclohexene concentrations in all our experiments was between 5×10^{-3} and 15×10^{-3} mole/liter. Nineteen kinetic runs have been performed at 40°, each one with a different sample of catalyst. Each run consisted of five kinetic experiments at different concentrations of cyclohexene in the feeding stream to the reactor. Some examples of the runs are graphically reported in Figs. 3 and 4. Four kinetic runs were performed at 30° and at 50°. Some experiments were performed with alumina without palladium: no reaction takes place.

KINETIC INTERPRETATION

Two kinetic models were employed for the interpretation of the experiences. In both cases it was assumed that the rate-limiting step is the surface reaction, taken as monomolecular or bimolecular, respectively.

Due to its saturation cyclohexane should be more weakly adsorbed on the catalyst surface than cyclohexene and benzene (*1*). Therefore in the first case, in the Langmuir-Hinshelwood scheme, the reaction rate can be written as follows:

$$r = \frac{dX}{d(W/F)} = k\frac{b_E C_E}{1 + b_E C_E + b_B C_B} \quad (1)$$

where X is the conversion degree of cyclohexene; W, the weight of catalyst; F, the flow rate of cyclohexene; k, the rate constant; b_i, the absorption constant; and C_i, the molar concentration. The subscripts E and B stand, respectively for cyclohexene and benzene. Neglecting the unit at the denominator, Eq. (1) becomes

$$\frac{dX}{d(W/F)} = k\,\frac{1-X}{(1-X)+(1/3)Z_BX} = k\,\frac{1-X}{1+\beta X} \qquad (2)$$

where Z_B is the relative adsorption constant b_B/b_E, and $\beta = (1/3)\ Z_B - 1$.

It is important to point out that if the previous approximation is well observed, the value of β cannot be less than -1, otherwise Z_B should assume a physically meaningless negative value. By integration such an equation gives

$$\frac{W}{F} = \frac{1}{k}\left\{\ln\left[\frac{1}{(1-X_f)}\right] - \beta[X_f + \ln(1-X_f)]\right\} = \frac{I}{k} \qquad (3)$$

X_f being the final conversion degree of cyclohexene.

For a bimolecular surface reaction the reaction rate can be written as follows:

$$r = \frac{dX}{d(W/F)} = k\,\frac{b_E{}^2C_E{}^2}{(1+b_EC_E+b_BC_B)^2} \qquad (4)$$

where the symbols have the previously indicated meaning. Also in this case, neglecting the unit at the denominator we obtain:

$$\frac{dX}{d(W/F)} = k\,\frac{(1-X)^2}{[(1-X)+(1/3)Z_BX]^2} = k\,\frac{(1-X)^2}{(1+\beta X)^2} \qquad (5)$$

By integration there derives the equation

$$\frac{W}{F} = \frac{1}{k}\left\{\left[\frac{X_f}{(1-X_f)}\right] - \beta^2\left[\frac{X_f(X_f-2)}{(1-X_f)} + 2\ln\left(\frac{1}{(1-X_f)}\right)\right] + 2\beta\left[\ln(1-X_f) + \frac{X_f}{(1-X_f)}\right]\right\} = \frac{I}{k} \qquad (6)$$

In spite of the rather crude approximation Eqs. (2) and (5) offer flexible kinetic models for the correlation of experimental data. In fact, for instance, Eq. (5) for β equal to zero corresponds to a homogeneous second order rate equation; for $\beta = -1$ it corresponds to a zero order rate equation. Furthermore by such approximation the kinetic experiences are interpreted avoiding the use of concentrations, but taking into account only the conversion degree of cyclohexene.

In both Eqs. (3) and (6) there are two parameters, k and β, that can be evaluated minimizing the function

$$F(k, \beta) = \sum_i [(W/F)_{i,\mathrm{exptl}} - I_i(\beta)/k]^2 \qquad (7)$$

where $(W/F)_{i,\mathrm{exptl}}$ is the experimental value of contact time for the ith point, i and $I_i(\beta)/k$ is the calculated contact time applying Eqs. (3) or (6). The summation is extended over all the experimental points of the run under consideration. The condition $[\partial F/\partial k] = 0$ gives directly

$$k = \sum_i [I_i(\beta)]^2 \bigg/ \sum_i \left[\left(\frac{W}{F}\right)_{i,\mathrm{exptl}} I_i(\beta)\right] \qquad (8)$$

and therefore the evaluation of β and k has been performed by minimizing the function F with respect to β, taking into account the preceding relation.

Such analysis applied to the monomolecular surface reaction model, that is employing Eq. (3), gave no satisfactory results. In fact for several runs it was not possible to get a well-defined minimum value of the function F. The resulting values of β were scattered in a wide range and a few of them were less than -1.

Such difficulties did not arise with the bimolecular surface reaction model; the latter gave a complete satisfactory agreement between experimental and calculated conversion by means of Eq. (6); the function F had well-defined minima for physically significant values of β. The results of this analysis are collected in Tables 1 and 2.

It is interesting to note that for all the runs at 40° (Table 1) the parameter β has

TABLE 1

KINETIC DATA AND ACTIVITIES AT 40°

Catalyst No.	% Pd	β	k $\left(\frac{\text{moles}}{\text{liter g cat}}\right)$	$A \times 10^2$ $\left(\frac{\text{moles}}{\text{hr g cat}}\right)$	a $\left(\frac{\text{moles}}{\text{hr g Pd}}\right)$
1	0.213	−0.75	0.683	0.241	1.132
2	0.413	−0.75	0.843	0.577	1.397
3	0.433	−0.95	0.994	0.828	1.912
4	0.484	−0.75	1.075	0.863	1.783
5	0.730	−0.75	0.768	0.929	1.272
6	0.774	−0.55	1.001	1.112	1.437
7	0.874	−0.75	0.658	0.954	1.091
8	0.898	−0.75	0.317	0.471	0.524
9	1.107	−0.57	1.109	1.799	1.626
10	1.416	−0.65	1.286	2.810	1.981
11	1.615	−0.75	1.135	3.036	1.880
12	1.656	−0.90	0.860	2.641	1.595
13	1.687	−0.75	0.978	2.735	1.621
14	1.736	−0.75	1.075	3.095	1.783
15	1.890	−0.85	0.556	1.877	0.993
16	2.190	−0.90	0.498	2.019	0.922
17	2.487	−0.75	0.914	3.768	1.515
18	2.599	−0.70	0.746	3.101	1.193
19	2.692	−0.90	0.516	2.571	0.955

TABLE 2

KINETIC DATA AND ACTIVITIES AT 30° AND 50°

Catalyst No.	% Pd	β	k $\left(\frac{\text{moles}}{\text{liter g cat}}\right)$	$A \times 10^2$ $\left(\frac{\text{moles}}{\text{hr g cat}}\right)$	a $\left(\frac{\text{moles}}{\text{hr g cat}}\right)$	T (°C)
4	0.484	−0.75	0.448	0.360	0.743	30
4	0.484	−0.40	1.519	0.951	1.965	50
10	1.416	−0.90	0.579	1.519	1.073	30
10	1.416	−0.70	2.418	4.735	3.344	50
17	2.487	−0.65	0.515	1.972	0.793	30
17	2.487	−0.90	1.802	8.317	3.344	50
18	2.599	−0.55	0.389	1.405	0.558	30
18	2.599	−0.80	1.165	5.208	2.004	50

a mean value of —0.76 [±0.07 mean deviation] corresponding to an almost constant value of Z_B (0.72 ± 0.2). This fact seems to justify the approximation introduced for obtaining Eqs. (2) and (5).

For the catalyst samples for which kinetic data were available at three temperatures the linear plot of $\log k$ vs. $1/T$ is reported in Fig. 5.

From the slope of the lines the energies of activation were evaluated through the Arrhenius equation

$$k = A \exp\left(-\Delta E_a/RT\right)$$

The values obtained are collected in Table 3.

Some examples of comparision of ex-

TABLE 3

KINETIC PARAMETERS FROM RATE CONSTANTS IN TABLES 1 AND 2

Catalyst No.	Pd %	$-\Delta E_a$ (kcal/mole)	$\log A$
4	0.484	11.94 ± 1.36	8.2892 ± 0.0608
10	1.416	13.92 ± 0.33	9.8088 ± 0.0149
17	2.487	12.17 ± 0.40	8.4779 ± 0.0181

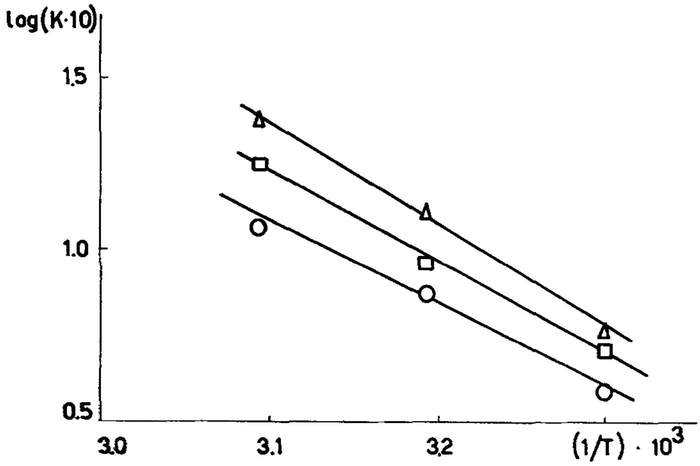

FIG. 5. Log *k* [from Eq. (6)] vs. $1/T$: ○, catalyst No. 4; △, catalyst No. 10; □, catalyst No. 17.

perimental kinetic data with the calculated curves are illustrated in Figs. 3 and 4.

ACTIVE CENTERS IN CATALYST SAMPLES

The catalyst activity has been defined as the inverse of the half-life of cyclohexene in contact with that catalyst. Two different expressions have been used. The former, which is called total activity, A, is referred to 1 g of all catalyst; the latter, called specific activity, a, is referred to 1 g of palladium. Obviously the two activities are related by the following simple relation:

$$ap = A100 \qquad (9)$$

where p is the percentage of palladium in the catalyst.

The values of both activities are collected in Tables 1 and 2. The behavior of the experimental activities as a function of palladium percentage is illustrated in Figs. 6 and 7.

A peculiarity of the diagrams reported in Figs. 6 and 7 is the presence of three well-defined maxima. The percentage of palladium on the Al_2O_3 surface is fairly small with respect to the amount necessary for a full coverage of the surface. In fact, since the specific surface of Al_2O_3 is about 200 m^2/g, with a percentage of palladium

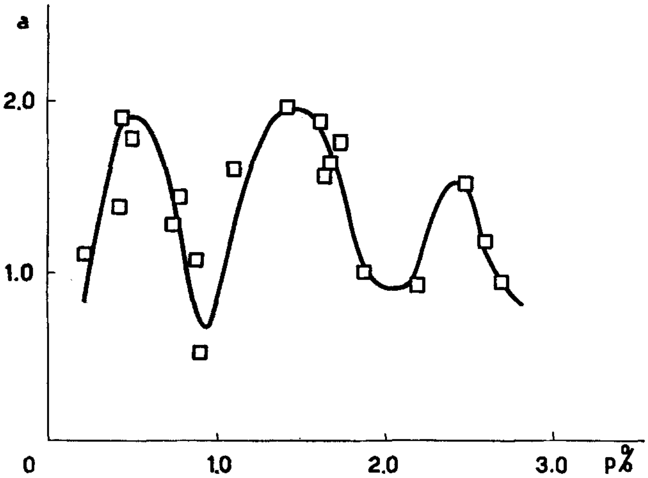

FIG. 6. Specific activity (a) vs. palladium percentage.

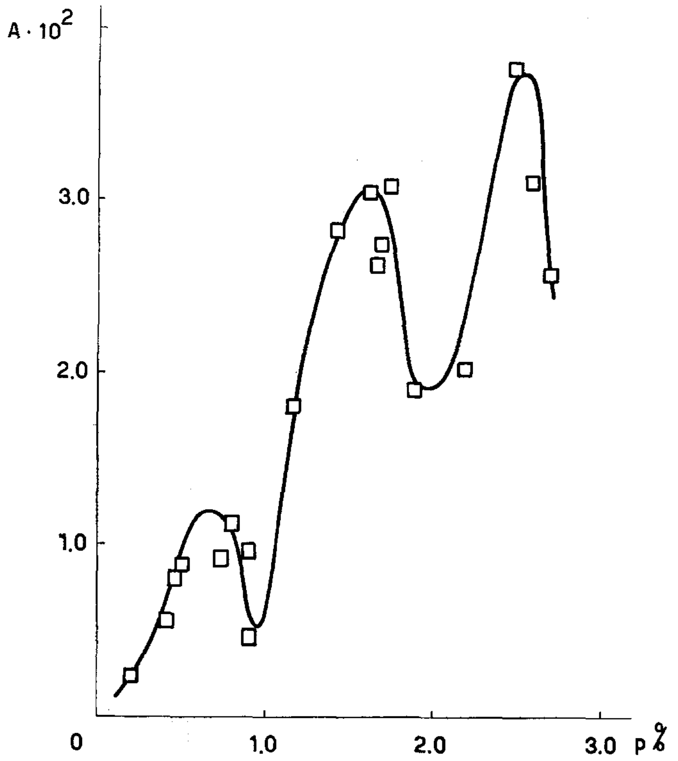

FIG. 7. Total activity (*A*) vs. palladium percentage.

of 3% it is possible to calculate a rough value of 6% of surface coverage.

The interpretation of the activity of such a catalyst can be given on the basis of the theory of "active ensembles" of Kobozev (*3*a). In this theory it is assumed that the carrier of catalytic activity is a phase present in high dilution on the support. This phase, which is in the precrystalline state, consists of a number of ensembles of metallic atoms clustered together in potential holes due to the heterogeneity of adsorption forces binding the catalyst atoms to the support. The presence of three maxima seems to indicate the activity of several forms of ensembles.

In a first approximation the activity of a catalyst sample is independent of the nature of the support, but it depends essentially upon the number of metallic atoms in each ensemble.

The X-ray diffractometric analysis performed on our catalyst samples gave direct information on the highly dispersed state of palladium on the carrier surface. In fact using this method it is possible to determine the dimension of elementary crystallites above 50 Å. When the dimensions of crystallites are less than 10 Å, the condition of the material is considered to be X-ray amorphous (*4*).

It is interesting to remember that the presence of crystalline networks depends on the concentration of the metal on the carrier, and on the method of preparation. For instance, it was shown that the employment of high temperature in the reduction of a supported metallic catalyst allows the growing of the crystallite size (*5*). The relatively low temperature at which we prepared the catalyst samples seems to be unsuitable for the formation of large size crystallites.

If we indicate with Z_0 the number of potential holes on the support and N is the number of metallic atoms on the support surface, the probability of formation of a center of n atoms is given by

$$W_n = [N!/n!(N-n)!](1/Z_0)^n(1-1/Z_0)^{N-n} \quad (10)$$

On the right-hand side the second factor is the probability that in a random precipitation n atoms fall into a potential hole, the third term is the probability that the $(N - n)$ other atoms fall outside. The first term is a configurational statistical factor due to the indistinguishability of atoms. N being very much higher than n, Eq. (10) becomes

$$W_n = (N/Z_0)^n(1/n!) \exp(-N/Z_0) \quad (11)$$

Assuming that the activity of each center depends on the number n, the total activity of the catalyst can be written as follows:

$$A = \sum_n f_n Z_0 W_n = \sum_n f_n Z_0 (N/Z_0)^n (1/n!) \exp(-N/Z_0) \quad (12)$$

where f_n is the coefficient that characterizes the activity of each center.

Because the number of atoms on the catalyst surface is proportional to the percentage p, and remembering the relation (9), the specific activity can be written as follows:

$$a = 100\chi \exp(-\gamma p) \sum_n f_n[\gamma^{n-1}/n!]p^{n-1} \quad (13)$$

where $\chi = 5.64 \times 10^{21}$ (number of metallic atoms in 1 g of metal) and $\gamma = \chi/(Z_0 100)$.

It can be shown (*6*) that the values of n can be obtained by the relation (*3*a)

$$n = \frac{(N/Z_0)^{(A)}_{\max}}{(N/Z_0)^{(A)}_{\max} - (N/Z_0)^{(a)}_{\max}} = \frac{p^{(A)}_{\max}}{p^{(A)}_{\max} - p^{(a)}_{\max}} \quad (14)$$

where the superscript refers to the total or specific activity, and the subscript indicates that the values are taken at the maximum points of the activity curves.

Applying the preceding equation to the values of p of the curves of Figs. 6 and 7 it is possible to obtain the following values of n:4, 10–11, 20–21.

Of course the accuracy of the previous numbers decreases by increasing n. On the basis of such values it is possible to write the equation (13) for our experiments as follows:

$$a = (\alpha_4 p^3 + \alpha_{11} p^{10} + \alpha_{21} p^{20}) \exp(-\gamma p) \quad (15)$$

A set of trials was performed with the aim of reproducing the behavior of experimentally found values of specific activity as a function of p. Figure 8 gives the theoretical specific activity curves corresponding to different chosen values of α.

The parameters of Eq. (15) that give the curves of Fig. 8 are gathered in Table 4.

It is noteworthy that the behavior of the

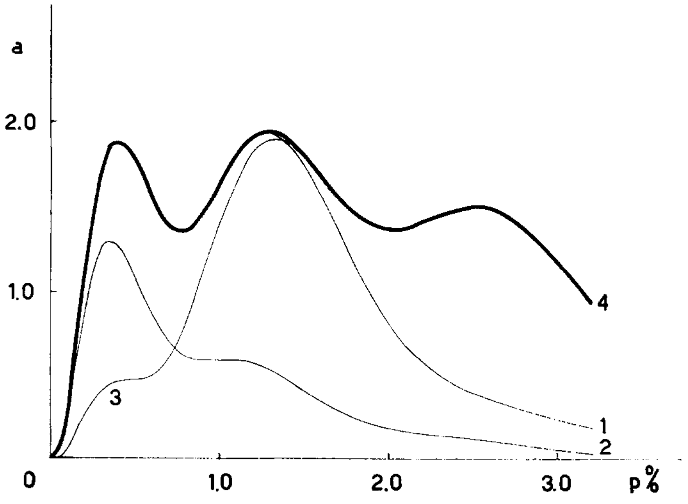

FIG. 8. Theoretical specific activity (a) from Eq. (15) vs. palladium percentage. The parameters of the four curves are collected in Table 4.

curves is quite sensitive to the values of the parameters, particularly to γ. In fact the variation of the parameters produces a great change in the form of the curve up to the disappearance of one or two maxima (thin lines in Fig. 8). The first and second maxima of curve 4 in Fig. 8 are in satisfactory accordance with the experiments, while the third is less pronounced, but in this region it is difficult to guarantee theoretical results close to experiments.

TABLE 4
PARAMETERS OF THE CURVES DRAWN IN FIG. 8

	Curve No.			
	1	2	3	4
α_4	613	613	150	613
α_{11}	2620	2620	2620	2620
α_{21}	0.5	2.669	2.669	2.669
γ	7.6	8.6	7.6	7.6

DISCUSSION

The previous analysis seems to show that the disproportionation of cyclohexene on supported palladium proceeds through a bimolecular surface mechanism. This can be connected with the fact that the minimum number of palladium atoms necessary for accomplishing the reaction is four. On this basis it can be suggested that the rate-limiting step of cyclohexene disproportionation is the direct hydrogen transfer between two absorbed molecules, as shown in the scheme of Fig. 9.

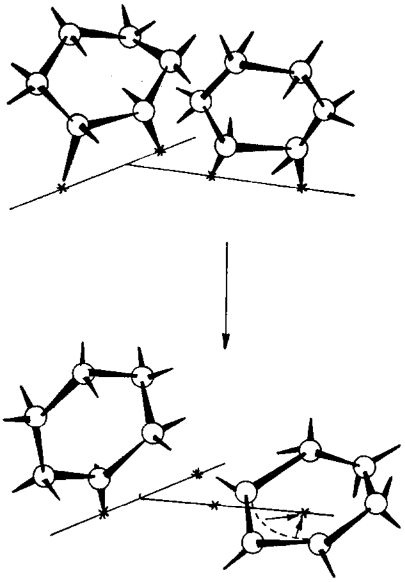

FIG. 9. Scheme of hydrogen transfer reaction between two adsorbed molecules of cyclohexene. The stars indicate palladium atoms.

Two molecules of cyclohexene are associatively adsorbed on a four-atom center. One hydrogen exchange can produce a π-allyl palladium complex which is an intermediate for the formation of 1,3-cyclohexadiene and benzene. Molecular models suggest that the strain corresponding to chemisorption depicted in Fig. 9 (top) is quite small and that the molecules have the right orientation for hydrogen exchange.

It is interesting to note that the value of parameter Z_B is almost constant (0.72 ± 0.2) for all the catalyst samples. Besides, the values of activation energies, collected in Table 3, are very close. Both these facts indicate that the reaction mechanism is the same on the different centers and in spite of the amount of palladium on the carrier.

Curve 4 drawn in Fig. 8 corresponds to a value of parameter γ equal to 7.6; as the number Z_0 of centers is given by $Z_0 = \chi/100\gamma)$, being $\chi = 5.64 \times 10^{21}$, we obtain $Z_0 = 0.74 \times 10^{19}$. It is noteworthy that this value is close to those found by Kobozev and co-workers (*5*) in the study of the decomposition of hydrogen peroxide ($Z_0 = 1.56 \times 10^{19}$) and the synthesis of water ($Z_0 = 1.43 \times 10^{19}$) employing platinum supported on alumina with a specific surface equal to 250 m^2/g. This fact seems to confirm that the carrier is quite inert.

The fluctuation of activity of catalyst samples with the amount of palladium on the carrier is due to a different activity of the centers with a different number of metallic atoms. This is a rather puzzling question. Two interpretations can be offered. In the former we can assume that some kind of centers are particularly apt to retain the energy of the chemical process that is then employed for a further act of activation (*7*). In the latter the minimum of activity corresponding to ensembles of five to eight palladium atoms might be due to an irreversible adsorption of benzene that subtracts the four-atom system necessary for the accomplishment of the reaction as shown in Fig. 9.

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