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Determination of the Mechanism of Cyclohexane Dehydrogenation over Pt- and Pt–Pd-Supported Catalysts through Theoretical and Experimental Studies

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Cyclohexane dehydrogenation by highly dispersed Pt–Pd bimetallic catalysts is analyzed on the basis of experimental and theoretical data. Experimentally it is established that no alloy formation exists and that the activation occurs over Pt sites only. A single center mechanism implying a series of Π–σ shifts is proposed. To justify this, a molecular orbital self-consistent field study of the molecular structure and electronic charge distribution of the Pt-active site and the chemisorbed cyclohexane molecule as they change during the process is presented. This permits elucidation of the crucial steps of the corresponding reaction coordinate.

INTRODUCTION

In a previous paper (*1*) a study of the catalytic activity of bimetallic Pt–Pd/Al_2O_3 for the dehydrogenation of cyclohexane was presented. The results reported in Ref. (*1*) are here supported by the proposal of a mechanism for the dehydrogenation process.

This mechanism is presented based both on experimental results and on theoretical arguments. Among the first are hydrogen adsorption data. The theoretical studies are essentially based on molecular orbital calculations of the cyclohexane molecule adsorbed over a six Pt-atom group.

In the following section we present the experimental methods and data. Then a section presenting the theoretical method and results and their bearing on the mechanism follows. Finally, in the last section a discussion of the main conclusions derived from the previously presented data and of the proposed mechanism is given.

EXPERIMENTAL METHODS AND DATA

Catalyst Preparation

The starting material was alumina Pechiney SCS-350, 230–270 mesh, with a BET area of 350 m²/g. The impregnation solutions were prepared with chloroplatinic acid and palladium chloride, analytical quality grade (Merck). Separate solutions were employed to impregnate the support by the ion-exchange method (*2*); bimetallic catalysts were prepared by coimpregnating both metals. After drying for 12 hr at 120°C in air, catalysts were stored until reduction.

Dispersion Measurements

Adsorption measurements were made by the gravimetric method in a Cahn RG

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TABLE 1

Characterization and Cyclohexane Dehydrogenation Activity at 190°C of Pt, Pd, and Pt/Pd Bimetallic Catalysts

Metal content		Hydrogen adsorption (μg/g of catalyst)	% Dispersion	Crystallite size (Å)		Activation energy (kcal/mole °C)	Molecules converted/surface Pt atom/sec $\times 10^3$
%Pt	%Pd			Chemical adsorption	Electron microscopy		
0.2		15	48	21		14.3	740
0.4		30	50	20		15.7	560
0.6		48	52	19	19	16.0	730
0.8		60	49	21		—	—
1.0		79	51	20		17.1	570
	0.2	19	33	31		14.0	24[a]
	0.6	70	41	25		—	—
	0.8	85	37	27	32	15.7	6
	1.0	106	37	27		16.9	8
Bimetallic catalysts			Mean dispersion	Mean crystallite			
0.2	0.8	103	42	24		14.9	184
0.4	0.6	99	42	23	27	15.3	116
0.8	0.2	87	43	25		15.3	134

[a] Molecules/surface Pd/sec.

UHV Electrobalance. Catalysts were reduced *in situ* at 400°C under hydrogen flow (1.8 liters/hr) for 6 hr and then evacuated at 10^{-5} Torr for 12 hr at the temperature of reduction. Matheson UHP oxygen and hydrogen were utilized and adsorbed at 24°C at pressures of 100 and 10 Torr, respectively, in order to obtain the 1:1 Pt–H and Pd–H stoichiometry relation (*3–5*).

The dispersion values for the monometallic catalysts and the mean dispersion values for the bimetallic catalysts were calculated from the hydrogen adsorption, employing the following titration reaction:

$$\text{Pt–O} + \tfrac{3}{2}H_2 \rightarrow \text{Pt–H} + H_2O \text{ (support).}$$

Details for mean dispersion values of bimetallic catalysts were reported in a previous publication (*6*).

The values obtained by chemisorption of hydrogen (Table 1) were corroborated by electron microscopy using a replica technique and the particle sizes obtained by means of a volume/surface ratio $\bar{d} = ndi^3/ndi^2$.

X-ray diffraction spectra, as reported earlier (*6*), were obtained with a Phillips PW-1380 horizontal goniometer with a copper tube and graphite monochromator. The diffraction pattern definitively shows that no alloy formation takes place for the coimpregnated bimetallic system.

Catalytic Activity

The catalyst samples (25–50 mg) used for the dispersion measurements were reactivated at 400°C in hydrogen. Initial rates of cyclohexane dehydrogenation were obtained in a conventional flow reactor at low conversion (<1%), under experimental conditions of 50 Torr for cyclohexane and 90 and 440 Torr for hydrogen and nitrogen, respectively. The catalytic apparatus was coupled to a gas chromatograph; the products of the reaction were benzene and hydrogen. No other products, such as cyclohexene and cyclohexadiene, could be detected by chromatographic analysis. Activity measurements for all runs were performed between 150 and 220°C.

For each of the supported catalysts, values corresponding to the number of molecules converted per surface metallic atom per second are reported (Table 1).

For bimetallic catalysts, the calculations of activities were made on the basis of

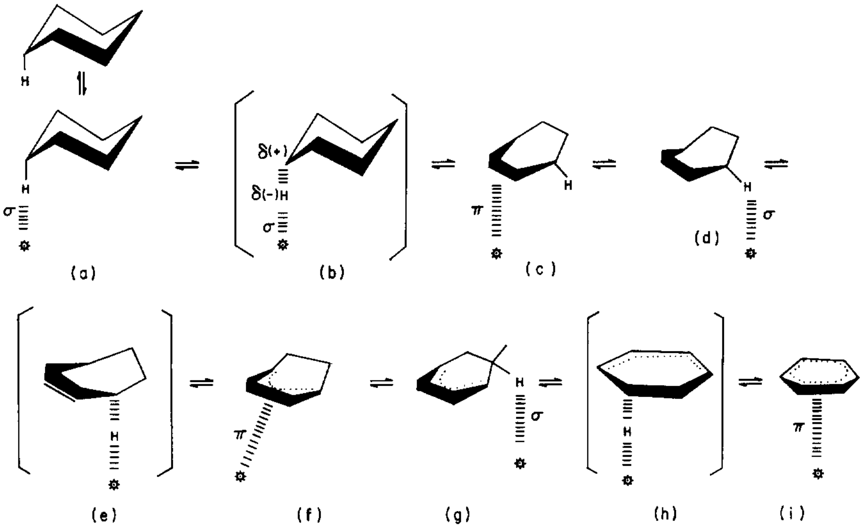

FIG. 1. Mechanism of dehydrogenation of cyclohexane on a Pt cluster.

surface platinum atom concentrations, assuming (Table 1) that the adsorptive properties and the dispersion values of the monometallic catalysts do not change in the bimetallic systems. Palladium adsorption values were not considered because palladium has a negligible catalytic activity under the experimental conditions used. It should be noted that we did not consider any spillover effects. For palladium catalysts, activities are given as a reference value, in terms of molecules converted by the surface palladium atoms.

Hydrogen Chemisorption

In Table 1 the individual adsorption of hydrogen on Pt and Pd catalysts is given. We also observe in Table 1 that the total chemisorption of hydrogen over the bimetallic Pt–Pd catalysts is the sum of the individual metal's chemisorption. This permits us to relate these results of hydrogen chemisorption with the chemisorption of cyclohexane over Pt sites (as Table 1 also shows, Pd has no dehydrogenation activity to speak of). We note that if the dehydrogenation mechanism involves abstraction of hydrogen atoms, we should expect the total rate of the reaction to increase by the addition of palladium at the least, and not to decrease, as was observed (see Table 1). Also it would depend on the atomic ratio Pt/Pd; we do not detect any change when the atomic ratio changes from 2.1 to 0.13.

Mechanism of Dehydrogenation

In view of the above, we propose the mechanism shown in Fig. 1, which implies that the chemisorption of cyclohexane over the active site depends on the capacity of the metal to coordinate not a hydrogen atom but a "hydride." The degree of this coordination to the metal will give the driving force for the elimination of a H_2 molecule, and will determine the velocity of the first step in Fig. 1. The degree of coordination of a hydride with the metal will in fact play an important role in all steps of the reaction.

THEORETICAL STUDY OF THE MECHANISM

Method

All calculations reported henceforth were carried out using an all-valence electron self-consistent field program previously tested and applied in the study of several catalytic processes (*7, 8*). The program uses the CNDO approximation and all the necessary parameters are reported in Refs. (*7, 8*).

We used this program to study the charge distribution of the chemisorbed system [step (a) in Fig. 1], i.e., a system consisting of a cyclohexane molecule and a six-atom Pt site. The structure of the site was chosen based on recent studies by Somorjai and co-workers (*9, 10*).

Hydride Formation

In Table 2, we present the bond orders and net charges during chemisorption. Notice that the changes in the Pt_1–H_1, Pt_1–C_1, and C_1–H_1 bond orders are given as the adsorptive bond distance is shortened in a series of decrements of 0.2 from 3.5 to 1.6 Å. It is quite evident that the coordination of the atom H_1 to the Pt group initially increases the positive charge on H_1 (in the isolated cyclohexane the H atoms are always slightly positive, the carbons carrying a small negative charge), but this trend is reversed gradually and the hydrogen acquires a net negative charge. The interaction between the carbon atom C_1 and the Pt site is surprisingly large, as Table 2 shows. C_1 loses its negative charge rather soon and becomes positive. The fact that the Pt_1–C_1 bond order is not negligible compared with Pt_1–H_1 implies a capacity of the Pt atom to interact with the carbon and the hydrogen atoms simultaneously. This supports the single-center hypothesis of the mechanism in Fig. 1. It should be recalled that Somorjai (*10*) has definitively shown that two center mechanisms can be ruled out experimentally in Pt surfaces. We further see in Table 2 the weakening of the C_1–H_1 bond and, from the net charges on the C_1–H_1 atoms, the reversal of the charge polarization, i.e., the concentration of electronic charge on the H_1. This is the theoretical justification of the hydride hypothesis of our mechanism.

TABLE 2

Changes in the Adsorption Bond Orders Pt_1–H_1 and Pt_1–C_1 and in the H_1 and C_1 Net Charges as the Cyclohexane Molecule Approaches (in 10 Successive Steps) the Adsorption Site of the Platinum Cluster

Step	Bond order			Net charge	
	Pt_1–C_1	Pt_1–H_1	C_1–H_1	C_1	H_1
1	0.009	0.014	0.951	−0.044	+0.041
2	0.044	0.069	0.888	−0.035	+0.056
3	0.091	0.138	0.793	−0.022	+0.079
4	0.117	0.164	0.757	−0.018	+0.092
5	0.141	0.180	0.729	−0.016	+0.105
6	0.148	0.155	0.816	+0.003	+0.054
7	0.221	0.270	0.698	+0.041	+0.052
8	0.285	0.462	0.496	+0.094	+0.004
9	0.300	0.776	0.174	+0.145	−0.124
10	0.465	0.915	0.062	+0.127	−0.083

Π–σ *Shifts*

The next aspect studied was related to the platinum–cyclohexane bond that is formed after the elimination of a hydrogen molecule. In Fig. 2 three different positions of the cyclohexane molecule over the platinum cluster are shown. In (a) the substrate has its double bond above the Pt_1 atom and consequently a Π-type adsorptive bond is formed. This is verified in Table 3, where the dominant contributions to the molecular orbital associated to the coordination bond in the shift mechanism are given. Notice the formation of hydrides pointing in the xz direction both at the doubly bonded carbons and at the Pt_1 site (whose d-orbitals are crucial for the adsorption, as usual). Position (c) in Fig. 2 is the assumed final situation of the shift, i.e., a σ-type adsorption bond between Pt_1 and H_2, which is bonded to the α-carbon. The second position (b) corresponds to an intermediate situation between the two extreme cases just described. The reversible shift between the Π- and σ-bonded complexes in Fig. 1 is related to the relative stabilities of the structures in Fig. 2. The σ-bonded structure has an energy only slightly higher than the Π-bonded one, by merely 4 kcal/mole. Our molecular orbital results also predict the

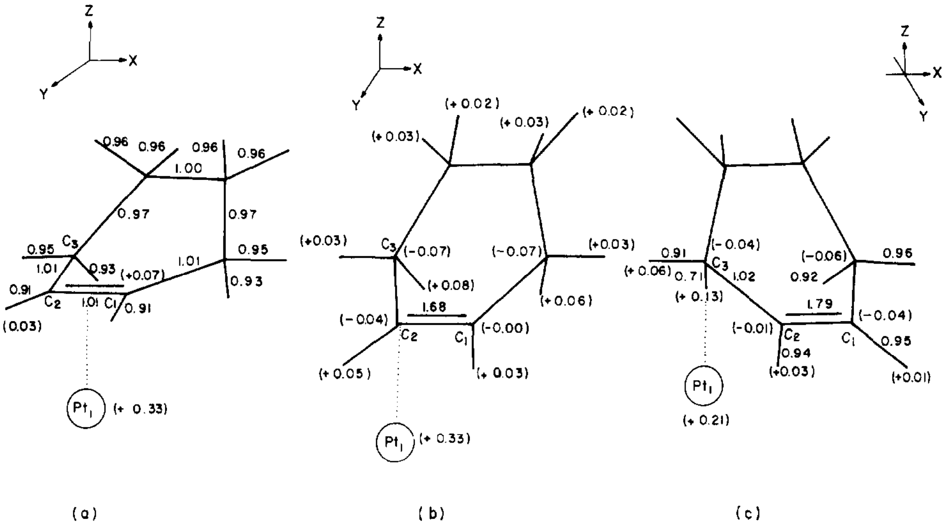

FIG. 2. Bond orders and net charges (in parentheses) of the cyclohexane coordinated over the Pt$_1$ atom in the platinum cluster.

activation barrier of the shift as being 12 kcal/mole. This barrier is not, by any means, prohibitively high and this fact points out the feasibility of going from one configuration to the other. We can conclude that the successive dehydrogenation steps consist of a σ-adsorption followed by an H_2 elimination by the hydride mechanism, leaving a Π-adsorption which then shifts to a σ-bond, again followed by another H_2 elimination through a similar hydride formation, etc.

One should note, however, that the barrier for the hexene Π–σ shift is not negligible, and its 12 kcal/mole activation energy is quite close to the experimental value (Table 1) for the total activation energy for the process, 14 to 17 kcal/mole (*1*). The second dehydrogenation leaves a Π-adsorbed cyclohexadiene molecule that must again make a Π–σ shift to permit the last dehydrogenation [this is step (g) in Fig. 1]. From the above, one must assume that this Π–σ shift for cyclohexadiene is much more favored energetically than that for cyclohexene discussed above. This has been established experimentally by Somorjai and co-workers (9). Calculations on this shift were nonetheless carried out. This Π–σ shift for cyclohexadiene is depicted in Fig. 3, where the following structures are given: first Pt$_1$ under the center of the

TABLE 3

Dominant Contributions to the Highest Occupied Molecular Orbital (i.e., the One Most Closely Associated with the Adsorptive Pt–olefin Bond) for the Two Configurations of the Cyclohexene Molecule over the Platinum Cluster[a]

	Adsorbed configuration									
	Π-Type bond							σ-Type bond		
Atom		Pt$_1$		C$_1$		C$_2$		Pt$_1$	C$_3$	C$_1$
Atomic orbital	S	d_{z^2}	d_{xz}	P_x	P_z	P_x	P_z	d_{yz}	P_y	P_z
Coefficient	0.383	−0.472	−0.291	−0.22	−0.29	0.22	−0.29	0.456	−0.22	0.27

[a] See text and Fig. 3.

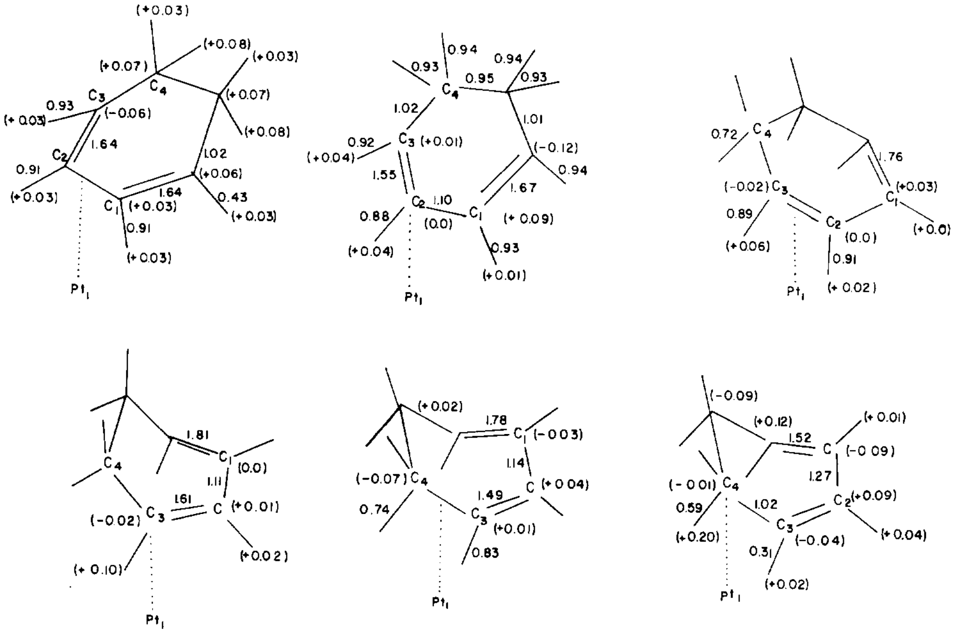

FIG. 3. Bond orders and net charges of cyclohexadiene over the Pt cluster.

delocalized Π-bond, then under carbon atom C_2, then under the bond between C_2 and C_3, then under the carbon atom C_3, then under the bond between C_3 and C_4, and finally forming a σ-bonded structure with a hydrogen of C_4. This last structure is the most stable energetically and no barriers have to be surmounted, implying that step (d) is much more hindered than step (g) and is consequently the rate-determining step.

DISCUSSION

We summarize here the most important experimental and theoretical results concerning the proposed mechanism (Fig. 1). They concern two main questions, namely, the similarities and differences between the monometallic and bimetallic systems and the justification of the proposed reaction mechanism.

Concerning the first point, the most relevant results (see Table 1) are the following:

(1) The total chemisorption of H_2 on the bimetallic system is the sum of the chemisorption on the individual metals.

(2) The total rate of conversion of cyclohexane decreases as palladium is added on coimpregnated catalysts.

(3) The dehydrogenation activity of bimetallic catalysts is not influenced by changing the atom ratio Pt/Pd within the range of 2.1 to 0.13.

As concerns the second point, the main experimental and theoretical results are:

(4) No alloy formation exists, as previous X-ray studies have demonstrated (*6*), implying that the dispersed Pt and Pd form separated clusters.

(5) The dehydrogenation takes place exclusively at Pt-cluster sites, Pd being effectively inert. The total velocity of reaction on Pt catalysts is 100 times faster than on Pd (*1*).

(6) Our theoretical results show that in the interaction of C–H with a Pt cluster, the hydrogen aquires a net negative charge while the carbon is positively charged, thus supporting the hydride mechanism (see Table 2).

(7) The molecular orbital results predict the barrier of the reversible shift between the Π- and σ-bonded hydrocarbon to be of

the order of 12 kcal/mole, which would make it the rate-determining step. This value for the barrier is in accordance (Table 1) with the experimental estimations (*1*).

A mechanism previously accepted (*11*) for the dehydrogenation of cyclohexane consisted of the reversal of the steps in benzene hydrogenation and went through α-, $\alpha\beta$- and Π-adsorbed olefins, followed by stepwise removal of neutral H atoms and subsequent enlargement of the Π systems. As practically no olefin or diene is detectable in the gas phase, it would be necessary to assume that these steps are quite fast, the rate-determining step being the α- and $\alpha\beta$-chemisorption of the molecule (*11*). This mechanism cannot be assumed to interpret the present results, and on their bases the mechanism in Fig. 1 is here suggested. The corresponding steps have been theoretically analyzed in this paper, finding a reasonable correspondence between the theoretical and experimental results. It should be mentioned that the latest experiments of Somorjai (*10*) seem to definitively discard the $\alpha\beta$-adsorption and support the Π–σ shift here advocated.

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