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Attractive Interactions of Alkyl Substituents with Palladium Catalyst in the Hydrogenation of Cyclohexanones

Cyclohexanone and its 4-alkyl-substituted derivatives were hydrogenated over Pd catalyst in cyclohexane solvent both individually and competitively in pairs (cyclohexanone and one of the derivatives). Most of the derivatives were less reactive than cyclohexanone individually, but more reactive competitively. These findings were explained in terms of attractive interactions between Pd and the alkyl substituents. Similar results were obtained on 2- and 3-alkyl-substituted cyclohexanones. The rate of cyclohexanone hydrogenation was different in five different hexane isomers used individually as solvents. This solvent effect was also explicably based on the concept of Pd–alkyl interactions.

INTRODUCTION

Heterogeneous catalysis is characterized by an adsorption process. The competitive reaction method, in which two or more compounds react simultaneously, provides one means for the investigation of adsorption in progress (*1–3*). Only one compound is usually allowed to react for the investigation of catalysis under various reaction conditions in the individual reaction method. Though the competitive reaction method provides little or no information about surface reaction, amount of adsorbed species or absolute strength of adsorption, relative strength of adsorption is sometimes determined by the method because of the ease of the operation and the excellent reproducibility of the data. Some factors affecting the reactivity are cancelled out under the conditions of competitive reaction because they affect both substrates equally. Then the method is suitable for the investigation of a weak interaction between a substrate and a catalyst.

In the previous paper we showed that 4-methylcyclohexanone (**1**) was a little more reactive than unsubstituted cyclohexanone (**2**) in the competitive hydrogenation on Pd catalyst; whereas **1** was less reactive on all other catalysts examined (*4*). These findings suggested the presence of an attractive interaction between the methyl group and the Pd catalyst. Since attractive interactions of alkyl groups with nickel oxide were reported (*5*), attractive interactions of alkyl substituents with Pd were examined by the method.

EXPERIMENTAL

Materials. 3-Ethylcyclohexanone (bp 81.6°C/120.0 mmHg) (*6*), 4-*n*-propylcyclohexanone (**3**, bp 92.0°C/20.0 mmHg) (*6*), 4-ethylcyclohexanone (**4**, bp 193°C) (*6*), 4-isopropylcyclohexanone (**5**, bp 89.0°C/19 mmHg) (*6*), 4-*tert*-butylcyclohexanone (**6**, bp 89°C/19 mmHg, mp 49°C) (*6*), 3-*n*-propylcyclohexanone (bp 74°C/12 mmHg) (*7*), and 4,4-dimethylcyclohexanone (bp 74°C/21 mmHg, mp 40.5°C) (*8*) were prepared according to the literatures. The preparation of the other ketones was described previously (*9*).

Cyclohexane (**7**) was a special grade commercial product. For the estimation of substituent effects this **7** was used as received, but for the measurement of solvent effects, it was subjected to further purification. The procedure for purification consisted of drying **7** over sodium and then passing it through a rectifying column. The other solvents were purified by the same procedure.

Unsupported Pd-black catalyst was prepared by hydrogenation of the palladium(II) hydroxide which had been obtained as a

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dark-brown precipitate by addition of alkali solution to an aqueous solution of palladium(II) chloride (*4*).

Apparatus and operating procedures. A shaking-type reaction vessel having a capacity of about 10 ml was used for the hydrogenation at atmospheric pressure (*4*).

A weighed catalyst sample (5–20 mg) was placed in the reaction vessel together with 5 ml of **7** as a solvent. The vessel was flushed with hydrogen and agitated for 30 min at 30°C to activate the catalyst. Then a reactant was introduced to the vessel by a microsyringe, and in competitive reactions a pair of **2** and one of the substituted cyclohexanones was introduced. The concentration was usually 1.0 mol/liter with respect to each ketone. Aliquots of the reaction mixture were sampled at appropriate time intervals, and analyzed by GLC.

Catalyst activities remained unchanged for at least 2 h. The reaction rates were proportional to the catalyst weight. For all the experiments, the rates measured were reproducible to ±5%. The relative rates measured in competitive reactions were reproducible to ±1.5%.

RESULTS AND DISCUSSION

Side reactions. The hydrogenation of **2** was accompanied by two side reactions, hydrogenolysis to 1-hexanol (<0.5% of total conversion) and formation of 2-cyclohexylcyclohexanone (<2%) (*10*). In hydrogenations of the other ketones, the corresponding by-products were formed in similar percentages or in negligible amounts. Thus the side reactions were negligible.

Data analysis. As previously shown (*11*), the relative rate of individual reaction (R_B/R_A) and the relative rate of competitive reaction (R'_B/R'_A) may be given by the equations

$$R_B/R_A = (k_B/k_A)(\beta_B/\beta_A) \quad (1)$$

$$R'_B/R'_A = (k_B/k_A)(K_B/K_A)(\beta_B/\beta_A), \quad (2)$$

where k is the rate constant referred to the unit surface concentration of the adsorbed molecule, β is the adsorption amount at monolayer saturation, and K is the adsorption equilibrium constant. Combining Eqs. (1) and (2) yields

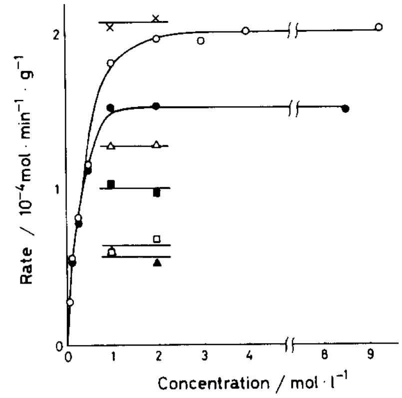

FIG. 1. Concentration dependence of hydrogenation rates of 4-substituted cyclohexanones; (○) **2**, (●) **1**, (△) **4**, (■) **3**, (▲) **5**, (□) **6**, (×) 4,4-dimethylcyclohexanone.

$$K_B/K_A = (R'_B/R'_A)(R_B/R_A). \quad (3)$$

Rate R was estimated from the slope of the appropriate pseudo-zero-order plot in a high ketone concentration region where the saturation rate was attained. Relative rate R'_B/R'_A was determined on the basis of the linear first-order log–log plot of ketone concentrations (*9*).

Hydrogenations of 4-alkylcyclohexanones. The reaction rates are shown in Fig. 1 as a function of the ketone concentrations. At low ketone concentrations the rates of **1** and **2** were proportional to their concentrations. The rate curves were asymptotic to constant values at high ketone concentrations. These findings indicate that the ketones had saturated the catalysts at the higher concentration regions. The same results were obtained for the other 4-alkylcyclohexanones.

The alkyl substituents of the 4-alkylcyclohexanones are remote from their carbonyl groups, therefore it is reasonable to assume that the alkyl substituents did not affect the reactivity of the carbonyl groups inductively or mesomerically (*12*), and

TABLE 1

Substituent Effects in Alkyl-Substituted Cyclohexanone Hydrogenation on Pd Catalyst

Substrate	Reactivity		Adsorption constant K_B/K_A
	Individual reaction R_B/R_A	Competitive reaction R'_B/R'_A	
2	1	1	1
1	0.76	1.02	1.3
4	0.65	1.08	1.7
3	0.53	1.12	2.1
5	0.32	1.12	3.5
6	0.32	0.85	2.6
4,4-Dimethylcyclohexanone	1.01	1.35	1.3
3-Methylcyclohexanone	0.62	0.87	1.4
3-Ethylcyclohexanone	0.74	0.82	1.1
3-*n*-Propylcyclohexanone	0.54	0.89	1.6
8	0.431	0.160	0.37
9	0.118	0.135	1.14
10	0.043	0.113	2.63

hence that the k values of the 4-alkylcyclohexanones are equal to that of **2**. Then the values of R_B/R_A in Eq. (1) are determined mainly by β's, and R is proportional to β. Table 1 lists the R_B/R_A values. This table shows that the larger the substituent became, the less reactive the ketone bearing that substituent in comparison of **2**, **1**, **4**, and **3** became. This substituent effect shows that a ketone with a larger substituent has a smaller β value, and hence occupies a larger surface area of Pd surface on adsorption. This suggests the presence of interactions between the alkyl substituents and the Pd catalyst.

*Competitive reactions of 4-alkylcyclohexanones with **2**.* The K_B/K_A values calculated from Eq. (3) are listed in Table 1 together with the R'_B/R'_A values. In contrast to the individual reactions, the 4-alkylcyclohexanones except **6** had higher reactivities than **2** in the competitive runs, and the ketones with larger substituents had higher reactivities. This tendency could be elucidated in terms of adsorption constants. It can be seen from Table 1 that the larger the substituent became, the stronger the adsorption of the 4-alkylcyclohexanone bearing that substituent became. Therefore the 4-alkylcyclohexanones were considered to be adsorbed on the Pd surface not only at their carbonyl groups but also at the alkyl substituents during the course of the carbonyl hydrogenation. This consideration of the interactions agreed with the results obtained from the individual reactions.

*Substituent effect of **6**.* It is very likely that alkyl substituents of **5** and **6** were adsorbed in such orientations as shown in Fig. 2. In these models the attractive interactions between the methyl groups and Pd surface were taken into account. Of particular importance is that one of the three methyl groups of **6** cannot be adsorbed at the same time when its carbonyl group is adsorbed. Thus it seems reasonable to assume that there is no difference between these two ketones in k and β values. Actu-

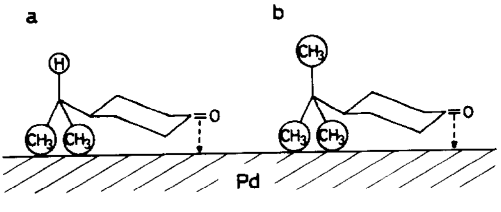

FIG. 2. Adsorbed states of **5** (a) and **6** (b).

ally they showed equal reactivity in individual reactions.

In such a case, the K_B/K_A value can be calculated on the basis of the ponderal effect pointed out by Ingold *et al.* (*13*). First the ponderal effect for adsorption is explained briefly. If a substituent of an adsorbed molecule is allowed to interact with the adsorbent without causing any change in the main adsorptive bond, K of this molecule will be larger than that of the parent molecule. Figure 3a illustrates this situation, and a typical example is seen in the adsorption of a series of *n*-alkane molecules on graphite (*14*). On the other hand, as shown in Fig. 3b, if an introduced substituent is sterically prohibited to interact with the adsorbent directly without any change of the main adsorptive bonds, K decreases according to the ponderal effect. The entropy loss of adsorption of the substituted molecule is greater than that of the parent molecule because the mass and the moment of inertia of the former are greater than those of the latter. The change in the K values can be calculated by statistics (*15*):

$$K_B/K_A = (m_A/m_B)^{3/2}(I_A/I_B)^{1/2}, \quad (4)$$

where m is the mass of the molecule and I is the product of the three principal moments of inertia of the molecule. Table 2 lists the calculated values together with the experimental values, and reasonably good agreement between these values was obtained. Consequently, exceptionally low reactivity of **6** in competitive reaction is attributed to the ponderal effect of the methyl group.

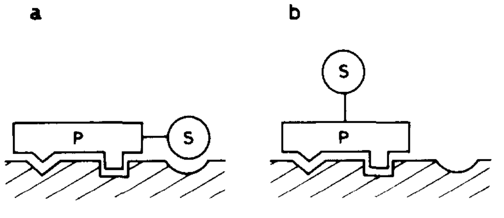

FIG. 3. Two assumed adsorbed states of substituents; (a) in the presence of an additional interaction, (b) in the absence of an additional interaction; P, parent molecule; S, substituent.

TABLE 2

Calculated and Observed Relative Adsorption Coefficients for **6**

Substrate	Molecular weight	Moment of inertia (10^{-112} $g^3 \cdot cm^6$)	$(K_B/K_A)_{calc.}$	$(K_B/K_A)_{obs.}$
5	140	4.25	1	1
6	154	6.76	0.69	0.75

The ponderal effect is present in the other ketones, however it is not discussed for them. The presence of the attractive interactions is not affected qualitatively, though the ponderal effect is taken into account.

Substituent effects of 2- and 3-alkylcyclohexanones. As can be seen from Table 1, R_B/R_A values decreased when alkyl substituents were introduced to the 3-position of **2**, and their K values were greater than that of **2**. These findings indicated that the attractive interaction was also present in the reaction system of the 3-alkylcyclohexanones.

The R_B/R_A values decreased in increasing order of alkyl substituent **2** > 2-methylcyclohexanone (**8**) > 2-ethylcyclohexanone (**9**) > 2-*n*-propylcyclohexanone (**10**) as Table 1 presents. The K values increased in the same order except for **8**. The small adsorption constant of **8** in comparison with **2** is explained in terms of a steric hindrance to adsorption caused by the methyl substituent which is fixed to the cyclohexanone ring (*9*). In contrast, the terminal methyl group of **9** and the ethyl group of **10** are able to occupy suitable positions for adsorption based on their flexibility. Larger K values for **9** and **10** than that of **2** indicate that the attractive interactions of their alkyl substituents with the Pd catalyst overcame the repulsive interactions between their methylene groups and Pd. Consequently, the attractive interactions were present in this series except for **8**.

Solvent effects. Compound **2** was hydrogenated in some hexane isomers at a low concentration (1/16 mol/l). Table 3 shows

TABLE 3

Solvent Effect in Hydrogenation of **2** on Pd Catalyst[a]

Solvent	Rate (10^{-4} mol · min^{-1} · g-cat^{-1})	Relative rate
7	4.82	1
2,3-Dimethylbutane	4.66	0.97
12	3.78	0.78
Methylcyclopentane	3.57	0.74
11	2.14	0.44

[a] Concentration of **2**, 1/16 mol/liter; at 30.0°C.

the results. In *n*-hexane (**11**), which is capable of having the largest number of methyl or methylene groups accessible to the catalyst plane because of the flexible normal chain structure, **2** was hydrogenated most slowly. This finding indicates that **11** was strongly adsorbed on the Pd surface. In contrast, in 2,2-dimethylbutane (**12**), whose methyl or methylene groups cannot interact with the Pd surface simultaneously because of the branched molecular structure, **2** was hydrogenated rather fast. This indicates that **12** was weakly adsorbed on the Pd surface. These results suggest that hydrocarbons were adsorbed on the Pd catalyst competitively with **2**, and that the extent of the interaction was dependent on their molecular structure.

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