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Attractive Steric Effects of Alkyl Substituents in Cyclohexanone Hydrogenation Catalyzed by Palladium

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In the Pd-catalyzed competitive hydrogenation of cyclohexanone (A) and its 4-alkyl derivatives (B), most of the bulkier B's have unexpectedly reacted faster, and this unusual result is indicative of an "Attractive steric effect", i.e., attractive interaction of the alkyl substituents with the Pd metal surface.

Introduction

The concept of "attractive steric effect" has been advanced to explain the unusual preferential existence of certain conformers and isomers where bulky groups are in closer proximity[1]. We report here that a similar effect may be seen in the adsorption of organic compounds onto metal catalysts and it may manifest itself as unusual alkyl-substituent effects in metal-catalyzed reactions.

In the hydrogenation of organic compounds catalyzed by transition metals, the reaction rate is usually lowered by substitution of a bulky alkyl group for a hydrogen. For example, this is seen by comparing hydrogenation rates between cyclohexanone and its alkyl-substituted derivatives[2], acetone and alkyl methyl ketones[3], benzene and mono-alkylbenzenes[4], benzene and polymethylbenzenes[5,6], and between ethylene and its alkyl-substituted derivatives[7]. However, our previous work[2] has revealed that in the competitive hydrogenation of cyclohexanone and its 4-methyl derivative on Pd, the bulkier ketone unexpectedly reacts a little faster. We now report our further work on this unusual behavior of Pd.

Experimental

Hydrogenations of A and B were conducted in a glass reaction vessel at 30°C and 1 atm of H_2 using Pd powder as the catalyst and cyclohexane as the solvent, both individually and competitively in pairs (A and B). The Pd powder was prepared by adding aqueous NaOH to aqueous palladium chloride and reducing the resulting precipi-

tate by hydrogen to yield Pd black, which was then washed with water and dried.

Results and Discussion

The results are summarized in Table 1. All the $(R_B/R_A)_{comp}$ and $(R_B/R_A)_{ind}$ values were reproducible to ±1.5% and ±5% on repeated runs, respectively. It is seen that except for 4-t-butylcyclohexanone all of the $(R_B/R_A)_{comp}$ values are a little greater than unity in confirmation of the earlier result that bulkier B is more reactive in competitive hydrogenation. However, in individual hydrogenation, B is less reactive as is seen from the $(R_B/R_A)_{ind}$ data although 4,4-dimethylcyclohexanone is rather exceptional.

Table 1. Relative rates and related data in Pd-catalyzed hydrogenation of cyclohexanone (A) and its 4-alkyl-substituted derivatives (B).

Cyclohexanone (Symbol)		Relative rate		α_B/α_A
		$(R_B/R_A)_{comp}$ [a]	$(R_B/R_A)_{ind}$ [b]	
Unsubstituted	(A)	1	1	1
4-methyl	(B)	1.02	0.76	1.3
4-ethyl	(B)	1.08	0.65	1.7
4-n-propyl	(B)	1.12	0.53	2.1
4-i-propyl	(B)	1.12	0.32	3.5
4-t-butyl	(B)	0.85	0.32	2.6
4,4-dimethyl	(B)	1.35	1.01	1.3

a) Relative rate in competitive reaction, which was conducted using an equimolar mixture of A and B (1 mol/l of each).

b) Relative rate in individual reaction, which was conducted using A solutions at concentrations of ≥2 mol/l or B solutions at concentrations of ≥1 mol/l.

Most of these results are rationalized in terms of attractive steric effects of the alkyl substituents: this is understandable if we consider the physical meanings of $(R_B/R_A)_{comp}$ and $(R_B/R_A)_{ind}$. Let us assume that the rate of hydrogenation of A (or B) is proportional to the amount of adsorbed A (or B) and also that the adsorption of these ketones obeys the Langmuir isotherm. On these assumptions, when A and B are individually hydrogenated, their reaction rates may be given by

$$(R_A)_{ind} \equiv \frac{dC_A}{dt} = \frac{k_A\beta_A\alpha_A C_A}{1 + \alpha_A C_A} \quad (1A)$$

$$(R_B)_{ind} = \frac{k_B\beta_B\alpha_B C_B}{1 + \alpha_B C_B} \quad (1B)$$

where k is the rate constant referring to the unit surface concentration of the adsorbed ketone, α is the adsorption coefficient, and β is the saturated adsorption amount. At high concentrations where $1 \ll \alpha C$, Eqs. (1A) and (1B) produce the relation.

$$(R_B/R_A)_{ind} = (k_B/k_A)(\beta_B/\beta_A). \quad (2)$$

On the other hand, for competitive hydrogenation

$$(R_A)_{comp} \equiv (1/C_A)(dC_A/dt) = \frac{k_A\beta_A\alpha_A}{1 + \alpha_A C_A + \alpha_B C_B} \quad (3A)$$

$$(R_B)_{comp} = \frac{k_B\beta_B\alpha_B}{1 + \alpha_A C_A + \alpha_B C_B}. \quad (3B)$$

Dividing Eq. (3B) by Eq. (3A)

$$(R_B/R_A)_{comp} = (k_B/k_A)(\alpha_B/\alpha_A)(\beta_B/\beta_A). \quad (4)$$

Combining Eqs. (2) and (4)

$$\alpha_B/\alpha_A = (R_B/R_A)_{comp}/(R_B/R_A)_{ind}. \quad (5)$$

Two of the prerequisites for Eq. (5) have been checked by subsidiary experiments. (i) Measuring $(R_A)_{ind}$ and $(R_B)_{ind}$ at various C_A and C_B, we found that individual hydrogenation is zero order in A or B under the experimental conditions of Table 1 ($C_A \geq 2$ mol/l and $C_B \geq 1$ mol/l). This conforms to the assumption $1 \ll \alpha C$ used for obtaining Eq. (2). (ii) Eq. (4) implies that $(R_B/R_A)_{comp}$ is unaffected by C_A and C_B. In order to test this, 4-t-butylcyclohexanone was chosen for B and $(R_B/R_A)_{comp}$ was measured at various C_B/C_A ratios. The $(R_B/R_A)_{comp}$ values were constant to about 1% over a C_B/C_A range of 0.5 to 2 (C_A = 1 mol/l).

The α_B/β_A values estimated from Eq. (5) are listed in Table 1. Obviously, they are all greater than unity, thus suggesting an attractive interaction of the alkyl substituents with the catalyst surface. The $(R_B/R_A)_{comp}$ values of >1 are now attributed to this attractive steric effect.

A comparison of the $(R_B/R_A)_{ind}$ values for the three n-alkyl substituted derivatives indicates that the longer the substituent chain the smaller its value. This

is interpreted to mean that the longer the substituent chain the greater the cross-sectional area of the adsorbed molecule which is inversely proportional to β. The dependence of β on the chain length, in turn, can be regarded as presenting additional evidence for an attractive interaction of the alkyl substituents with the catalyst surface. If this attractive steric effect were absent, the substituents would be conformationally flexible apart from the catalyst surface, and hence all the B's having a n-alkyl substituent would be nearly identical with A in the value of β. A detailed discussion of the last three cyclohexanones in Table 1 (i-propyl, t-butyl, and dimethyl derivatives) will be given in a subsequent report.

Although it may appear strange at first glance, the attractive interaction of the alkyl groups with Pd is not unexpected from the nature of this metal. Pd is among the most active transition metals for exchange of saturated hydrocarbons with deuterium[8]. Whatever the reaction mechanism, this suggests a strong interaction of Pd with the methyl or methylene hydrogens. Interestingly, the attractive interaction of alkyl groups with a solid surface may not be confined to Pd alone. Indeed, Moro-oka and Ozaki[9] have presented evidence to indicate that in olefin adsorption on nickel oxide alkyl groups of the olefin as well as the double bond interact attractively with the oxide surface.

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