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Substituent Effects in Heterogeneous Catalysis. V. Steric Hindrance of Bulky Alkyl Substituents in Cyclohexanone Hydrogenation

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Synopsis. The reactivities of 2-isopropyl- and 2-*t*-butylcyclohexanone were measured relative to cyclohexanone in both individual and competitive hydrogenation over Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3. The results obtained suggest that alkyl substitution sterically hinders much more significantly the ketone adsorption than the following surface reaction. A molecular model is presented for adsorption of each ketone.

In the preceding two reports[1,2] of this series, we studied the effect of alkyl substitution in cyclohexanone hydrogenation using 2-methyl-, 2-ethyl-, and 2-propylcyclohexanone (**2m**, **2e**, and **2p**), along with cyclohexanone (**1**) itself. Since ethyl and propyl substituents are rather flexible, little or no additional steric hindrance to adsorption is expected when going from **2m** to **2e** or **2p**. In support of this speculation, our previous work indicated that **2m**, **2e**, and **2p** exhibit almost the same reactivity in their individual hydrogenations. However, increasing the branching degree of the alkyl substituent might cause a marked increase in steric hindrance to adsorption and reactions. The main purpose of the present work is to test this anticipation by conducting individual and competitive hydrogenations of 2-isopropyl- and 2-*t*-butylcyclohexanone (**2ip** and **2tb**).

Interest in enzymatic and related reactions is growing. Although it is acknowledged that steric factors play an important role in these reactions, little is known concerning the correlation of steric factors with complexation and catalysis.[3] In heterogeneous catalysis as well, there seem to be many cases where steric factors play a part. Especially, a rigid bulky group in close proximity to the functional group in general ought to exert steric hindrance to adsorption and reactions. However, few studies have been reported about the extent of such steric hindrance. This paper describes our first attempt to study this problem.

Experimental

Compound **2ip** was prepared by hydrogenation of *o*-isopropylphenol over Raney-Ni,[4] followed by chromic acid oxidation.[5] Distillation under reduced pressure gave **2ip** as a liquid: bp 82.0 °C/20 mmHg. **2tb** was similarly prepared from *o*-*t*-butylphenol: bp 89.0 °C/19 mmHg. The catalysts used were the same commercial products that were employed in the previous work:[2] they were pelletized Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3, each containing 0.5 wt % of the metal. Hydrogenation runs, either individual using a single ketone substrate or competitive using two ketone substrates, were conducted in cyclohexane at 30 °C and in hydrogen of atmospheric pressure. The procedure has been detailed previously.[2]

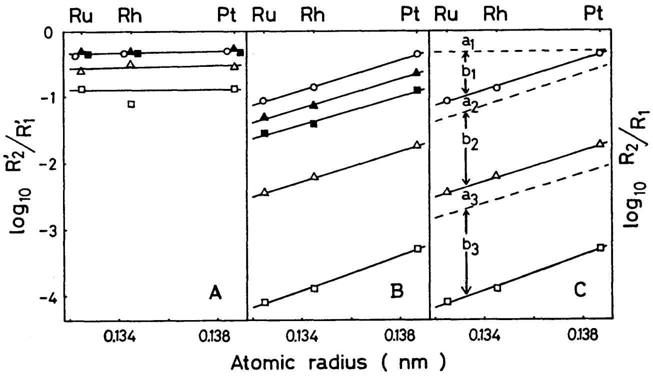

Fig. 1. Comparative data in hydrogenation of **1** and **2**. (A) Rates of **2** relative to **1** in individual reactions; (B) Rates of **2** relative to **1** in competitive reactions; (C) Substituent effects in adsorption and in surface reaction.

○: **2m**, ▲: **2e**, ■: **2p**, △: **2ip**, □: **2tb**.

$a_1 \equiv \log_{10}(k_{2m}/k_1)$, $b_1 \equiv \log_{10}(K_{2m}/K_1)$

$a_2 \equiv \log_{10}(k_{2ip}/k_{2m})$, $b_2 \equiv \log_{10}(K_{2ip}/K_{2m})$

$a_3 \equiv \log_{10}(k_{2tb}/k_{2ip})$, $b_3 \equiv \log_{10}(K_{2tb}/K_{2ip})$

Results and Discussion

Individual Reactions. Preliminary experiments confirmed that in individual hydrogenation the reaction rate is zero order in ketone over a wide concentration range down to or even lower than 0.5 mol/l. The rate measurements were all made in this zero-order region, and the rates of **2** relative to **1** are plotted in Fig. 1A against the atomic radius of the catalyst metal. For comparison, the data on **2e** and **2p** obtained previously[2] are also given in Fig. 1A. It is seen that in general the relative rate R_2'/R_1' in individual reaction is not very different from metal to metal, and depends only upon the substituent itself. Another characteristic feature is that R_2'/R_1' decreases in the order **2m**=**2e**=**2p**>**2ip** >**2tb**.

In considering this activity sequence it should be noted that R_2'/R_1' is related to the reactivity of the adsorbed species by

$$R_2'/R_1' = k_2/k_1, \tag{1}$$

where k is the rate constant referred to the unit fraction of the surface covered. The observed identity **2m**=**2e** =**2p** has already[1,2] been explained by assuming for these ketones a particular adsorption model in which no additional steric hindrance is brought about when going from **2m** to **2e** and to **2p**.

Now let us consider why R_2'/R_1' decreases in the order **2m**>**2ip**>**2tb**. For these ketones we assume those adsorption models that are illustrated in Fig. 2 which represents the projection of the alkyl substituents on a

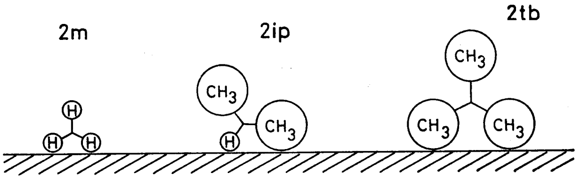

Fig. 2. The orientation of a C(7)–H or C(7)–CH_3 bond in the alkyl substituent relative to the catalyst surface for adsorbed **2m**, **2ip**, and **2tb**.

plane perpendicular to the catalyst surface. It seems very likely that the steric hindrance to adsorption due to the alkyl substituents is minimized in the assumed model A comparison of the three ketones indicates that the bulkier the substituent, the greater the steric hindrance to adsorption that would be exerted; by bringing a C(7)–H bond more perpendicular to the catalyst surface plane when going from **2m** to **2ip**, and by directing two methyl groups toward the catalyst when going from **2ip** to **2tb**. In antiparallel with this increasing steric hindrance the adsorption strength of ketones is expected to decrease in the order **2m**>**2ip**>**2tb**. The observed order of decreasing R_2'/R_1' probably reflects this order of decreasing adsorption strength and, in turn, decreasing reactivity.

TABLE 1. DIRECT AND INDIRECT MEASUREMENTS OF RELATIVE RATE $\log_{10}(R_{2tb}/R_{2m})$

Catalyst	$\log_{10}$ (R_{2ip}/R_{2m})	$\log_{10}$ (R_{2tb}/R_{2ip})	$\log_{10}(R_{2tb}/R_{2m})$	
			Indirect	Direct
Pt/Al_2O_3	−1.36	−1.59	−2.95	−2.89
Rh/Al_2O_3	−1.35	−1.64	−2.99	−3.04
Ru/Al_2O_3	−1.38	−1.64	−3.02	−2.88

Competitive Reactions. The observed relative rate R_2/R_1 in competitive reaction is plotted in Fig. 1B against the atomic radius of the catalyst metal. The data for **2m**, **2e**, and **2p** were obtained directly by competitive hydrogenation with **1**, but the data for **2ip** and **2tb** were determined indirectly by hydrogenating each competitively with **2m** and then by allowing for the relative rate R_{2m}/R_1 measured by a separate experiment. The validity of this indirect procedure for determining R_2/R_1 is confirmed by the data of Table 1 which compare the directly and indirectly determined R_{2tb}/R_{2m} values. It is seen that for all the catalysts the agreement is satisfactory. Fig. 1B shows that the magnitude of the substituent effect based on **1**, *i.e.*, $\log(R_2/R_1)$, depends upon the catalyst metal whereas those for any **2** based on another, such as $\log(R_{2ip}/R_{2m})$ and $\log(R_{2tb}/R_{2ip})$, are independent of the catalyst.

As previously shown,[6] the relative rate in competitive reaction may be given by

$$R_2/R_1 = (K_2/K_1)(R_2'/R_1'), \tag{2}$$

where K is the adsorption coefficient in Langmuir's adsorption isotherm. Combining Eqs. 1 and 2 we obtain

$$\log(R_2/R_1) = \log(K_2/K_1) + \log(k_2/k_1). \tag{3}$$

Equation 3 means that the substituent effect in competitive reaction is divided into two terms; the substituent effect in adsorption and that in surface reaction. Such a division is also feasible in a comparison between different **2**'s. The extents of the two terms worked out for a few ketone pairs are given in Fig. 1C. It is seen that only b_1 varies with the catalyst. This indicates that an increase in adsorption hindrance due to methyl substitution leading **1** to **2m** varies with the catalyst, whereas that caused by further methyl substitution leading **2m** to **2ip** or leading **2ip** to **2tb** is independent of the catalyst. The reason for this unique behavior of the methyl substituent on **2m** is obscure at present although it must be related to the close proximity of that substituent to the carbonyl group. Figure 1C also shows that bulky alkyl groups hinder the adsorption markedly but the following surface reaction to a much smaller extent. Interestingly, the same trend has been observed in olefin hydrogenation by Hussey *et al.* (Table 3 or 4 in Ref. 7).

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