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Substituent Effects in Heterogeneous Catalysis. III. Competitive Hydrogenation of Cyclohexanone and 2-Alkylcyclohexanones over Platinum Group Metals

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Cyclohexanone (**1**) and one of its 2-alkyl (methyl, ethyl, or propyl) derivatives (**2**) were hydrogenated competitively at 30 °C in cyclohexane over platinum group metals. The alkyl derivatives **2** were all less reactive than **1** on all the catalysts used. The relative reactivity R_2/R_1 was given by $\log_{10}(R_2/R_1) = \sigma^{**} + \kappa$, with σ^{**} depending only upon the substituent and κ upon the catalyst. The greater the substituent size, the more negative was the substituent constant σ^{**}. The catalyst-dependent constant κ was in general more negative for a catalyst metal having a smaller atomic radius. The above empirical rate expression has been interpreted based on the absolute reaction rate theory. The σ^{**} values calculated on this theoretical ground were in excellent agreement with the observed values.

Substituent effects in homogeneous reactions have been extensively studied, but relatively little work on heterogeneous catalysis has been reported. Especially, the influence of catalyst properties on the substituent effects is still to be explored. Although the application of Hammett-type equations to heterogeneous catalysis was attempted by Kraus,¹⁾ it was successful for only half of the data tested. Besides, it is not always clear why the relative hydrogenation rate should correlate with σ or σ^*. Thus it seems desirable to seek a new approach to the substituent effects in heterogeneous catalysis. The present series of studies has this primary aim. In the first paper²⁾ of this series, methyl substituent effects in cyclohexanone (**1**) hydrogenation were investigated by means of competitive reactions of cyclohexanone and one of its methyl derivatives over platinum group metals. The relative rates observed were discussed in relation to the reaction mechanism and the atomic radius of the catalyst metal.

The present work extends this comparative study to include 2-ethyl- and 2-propylcyclohexanone (**2e** and **2p**). The main purpose of this extension is to see how the substituent size affects the hydrogenation rate. The experiments with 2-methylcyclohexanone (**2m**) were repeated to make a comparison with **2e** and **2p** under strictly identical conditions including catalyst preparaion and preservation.

Experimental

Materials. Cyclohexane (Wako Pure Chemical Ind., "special grade") was used without further purification after determining its purity to be 99.96% by GLPC on an Apiezon Grease L column. **1** and **2m** were also commercial products and distilled before use. **2e** was prepared by hydrogenation of 2-acetylphenol over Raney-Ni³⁾ followed by chromic acid oxidation.⁴⁾ Distillation under reduced pressure gave **2e** as a liquid: bp 71.0 °C/17 mmHg. **2p** was prepared in a similar manner using 2-allylphenol as the starting material. Distillation under reduced pressure gave **2p** as a liquid: 86.7 °C/17.5 mmHg. The purity of these ketones was greater than 99% by gas chromatography.

All the catalysts used were unsupported metal powders, and prepared by reduction of the corresponding metal oxides or hydroxides. The procedure for the preparation was described previously²⁾ except for Pt. The Pt catalyst was prepared using $PtCl_2$ (Mitsuwa Yakuhin Kagaku KK) as a starting material. To a hot suspension of $PtCl_2$ (1 g) in dilute HCl (2000 ml) was added 5—10% aqueous NaOH in small portions until the pH reached 8. The resulting black hydroxide suspension was simmered for 30 min and then filtered off. The hydroxide was washed repeatedly with water until the washings were neutral, transferred into a 100 ml autoclave, and about 20 ml of water was added. The hydroxide was reduced with stirring for 20 min at temperatures up to 30 °C and an initial hydrogen pressure of 80 atm. The resulting metal black was filtered off, washed with water until the washings were neutral, dried under reduced pressure, and stored over silica gel.

Kinetic Procedures. Competitive hydrogenations were conducted at 30 °C and in hydrogen of atmospheric pressure using an equimolar mixture of **1** and **2** in cyclohexane (0.5 mol/l of each ketone). Reaction mixtures were analyzed by gas chromatography on a column of 10 wt% bis(2,3-dihydroxypropyl) ether on 60—80 mesh C-22 SK. Of the two peaks due to the isomer mixture of any *cis*- and *trans*-2-alkylcyclohexanols, the one having the shorter retention time was assigned to the cis isomer and the other to the trans.⁵⁾ Details on the experimental procedure and the design of the glass reaction vessel have been given before.²⁾

Data Treatments. In dealing with competitive reactions on solid catalysts it is usual to assume (i) that the reaction rate is proportional to the surface concentration of the adsorbed substrate, and (ii) that the substrate adsorption during reaction obeys the Langmuir isotherm. Applying these assumptions to our reaction systems leads to the following two rate expressions:

$$-\mathrm{d}C_1/\mathrm{d}t = k_1K_1C_1/(1+K_1C_1+K_2C_2), \qquad (1)$$

$$-\mathrm{d}C_2/\mathrm{d}t = k_2K_2C_2/(1+K_1C_1+K_2C_2), \qquad (2)$$

where C is the concentration, t is the time, k is the rate constant, and K is the adsorption equilibrium constant. Combining Eqs. 1 and 2 and defining R by

$$R_1 \equiv -\mathrm{d}C_1/C_1\mathrm{d}t, \qquad (3)$$

$$R_2 \equiv -\mathrm{d}C_2/C_2\mathrm{d}t, \qquad (4)$$

we obtain a relative rate expression such as

$$\frac{R_2}{R_1} = \frac{k_2K_2}{k_1K_1} = \log\left(\frac{C_{2\,(\mathrm{i})}}{C_2}\right)\Big/\log\left(\frac{C_{1\,(\mathrm{i})}}{C_1}\right), \qquad (5)$$

where subscript (i) refers to the initial state at $t=0$. Equation 5 serves to calculate relative rates from competitive hydrogenation data.

For more rigor, the role of hydrogen should be taken into account in Eqs. 1 and 2. However, we can ignore this because whatever the involved hydrogen kinetics, we are always led to Eq. 5 by cancellation.

Results

Reaction Products. With respect to the cis/trans ratio for the product alcohol, Pd was rather cis selective (cis%; 85 for **2m**, 73 for **2e**, and 77 for **2p**). The other metals were less selective, and the observed cis% fell in the rather narrow range 58—73 for all the substrates **2m**, **2e**, and **2p**.

In the hydrogenation of **1** and **2** over Pt, more hydrogen was consumed than expected from stoichiometry for complete hydrogenation to the corresponding alcohols. This is probably due to accompanying hydrogenolysis. However, the extent of hydrogenolysis did not exceed 5% of the total conversion of the ketone. In the case of Pd, two unidentified gas chromatographic peaks (one from **1** and one from **2**) developed as the hydrogenation proceeded, but each of the by-products was always less than 2% of the corresponding alcohol. For the rest of the catalysts, there were no indications of any side reactions. Thus it is reasonable to evaluate R_2/R_1 based on Eq. 5 which ignores side reactions.

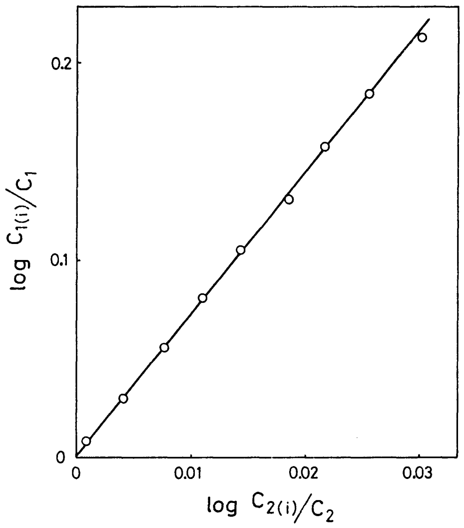

Fig. 1. A typical linear plot according to Eq. 5, observed for **1** and **2e** in competitive hydrogenation on Ir.

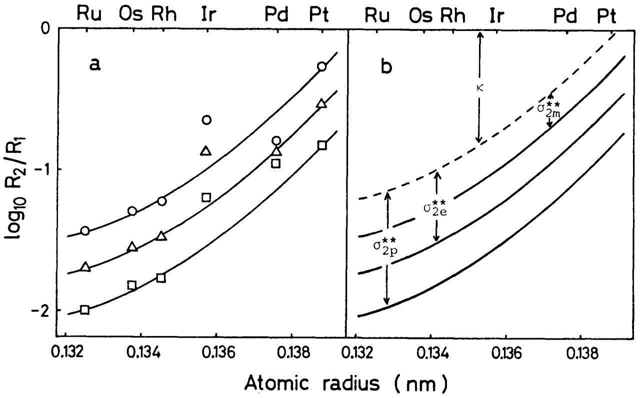

Fig. 2. Alkyl substituent effects in cyclohexanone hydrogenation.
○: **2m**, △: **2e**, □: **2p**.
κ: catalyst-dependent constant, σ^{**}: substituent constant.

Substituent Effects. The log-log plots drawn according to Eq. 5 were linear, with the exception of that for Pt catalyst, which exhibited a slight curvature. Figure 1 shows a typical linear log-log plot observed on Ir. The values for relative reactivity R_2/R_1 were determined from the slope of the straight lines or from the tangent to the curved line at zero conversion. In repeated runs using the same reaction mixture and catalyst, the R_2/R_1 values observed were usually reproducible to within 5%. All the R_2/R_1 values for the same catalyst were averaged, and $\log(R_2/R_1)$ was plotted in Fig. 2a against the atomic radius of the catalyst metal. Here the atomic radius is one-half the internuclear distance between nearest neighbors in the metal crystal which is stable under room conditions. In regard to the **2m**/**1** system, the general trend observed earlier (Fig. 2, Ref. 2) was reproduced here: the greater the atomic radius the greater the relative reactivity. In general the agreement on the R_{2m}/R_1 value itself is fairly good between the present and earlier experiments.

Of particular interest in Fig. 2a is the parallelism of the three correlation lines for the **2m**/**1**, **2e**/**1**, and **2p**/**1** systems with almost identical spacings. The distances between the adjacent data points for Ir also resemble these spacings. In what follows we are mainly concerned with explaining these apparent identities.

Discussion

Empirical Formulations. Figure 2b is a reproduction of Fig. 2a with omission of the data points. In order to derive an empirical expression for the observed relative rates, let us draw a reference line, shown as a dotted line in Fig. 2b: although the location and physical meaning of this reference line is defined later by our reaction model, at this point suffices it to say that the reference line lies between the horizontal line at $\log_{10}(R_2/R_1)=0$ and the correlation line for the **2m**/**1** system. We refer to the distance between the horizontal and reference lines as κ (catalyst-dependent constant) and the distances between the reference and correlation lines as σ^{**} (substituent constant): the subscript to σ^{**} indicates the substituted ketone. Obviously, the relative reactivity can be written as

$$\log_{10}(R_2/R_1) = \sigma^{**} + \kappa. \qquad (6)$$

One may speculate that σ^{**} is related to the substrate size and κ to the catalyst property. It will be demonstrated below that such speculation may indeed be justified on the basis of the absolute reaction rate theory.

Theoretical Treatment. Now we aim at deriving Eq. 6. The argument developed herein is not intended to be very rigorous. Since we are dealing with heterogeneous catalysis in the liquid phase, we will be forced to be rather speculative and to employ a few ad hoc approximations. One of the basic assumptions we make is that when converted to the activated complex, ketones **1** and **2** are adsorbed on the catalyst and are "immobile" with complete loss of translational and rotational freedom.

In deriving Eq. 5 we have assumed that both **1** and **2** are in adsorption equilibrium during reaction. Then, the overall hydrogenation rate must be controlled by one of the following steps: (i) the reaction of adsorbed ketone with adsorbed hydrogen to form a half-hydrogenated intermediate, (ii) the reaction of this intermediate with adsorbed hydrogen to form adsorbed alcohol, or (iii) the desorption of the adsorbed alcohol. If step (i) is rate-determining, the overall rate will be given by[6]

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t} = C_{\mathrm{H_2}}^{1/2}C_1C_\mathrm{s}\frac{kT}{h}\,\frac{f_1^{\neq}}{F_{\mathrm{H_2}}^{1/2}F_{1(l)}f_\mathrm{s}}\exp\left(\frac{-\varepsilon_1}{kT}\right), \tag{7}$$

$$-\frac{\mathrm{d}C_2}{\mathrm{d}t} = C_{\mathrm{H_2}}^{1/2}C_2C_\mathrm{s}\frac{kT}{h}\,\frac{f_2^{\neq}}{F_{\mathrm{H_2}}^{1/2}F_{2(l)}f_\mathrm{s}}\exp\left(\frac{-\varepsilon_2}{kT}\right), \tag{8}$$

where factor kT/h has its usual meaning, f is the complete partition function, F is the partition function per unit volume, ε is the apparent activation energy, *i.e.*, the true activation energy subtracted by the heat of adsorption, subscript s indicates a vacant dual site that can accommodate both an adsorbed ketone molecule and a hydrogen atom, subscript l refers to the liquid state, and superscript $\neq$ indicates the activated complex. It is to be noted that we are dealing with competitive reactions and that **1** and **2** are not very much different in molecular size. This permits us to make an approximation that the adsorption site s is common to reactions of both **1** and **2**. Hence we can regard quantities C_s and f_s as identical for Eqs. 7 and 8. Combining Eqs. 7 and 8 and referring to Eqs. 3 and 4 we have

$$R_2/R_1 = (F_{1(l)}f_2^{\neq}/F_{2(l)}f_1^{\neq})\exp\{-(\varepsilon_2-\varepsilon_1)/kT\}. \tag{9}$$

Even if we consider step (ii) or (iii) as the rate-determining, we will still be led to Eq. 9 by cancellation. Thus, Eq. 9 can be regarded as a general expression which is applicable to different kinetics or different rate-determining steps.

Since the activated complex has been assumed to possess no translational and rotational freedom, we need to consider merely its vibration. Thus

$$f^{\neq} = f_{\mathrm{vib}}^{\neq}. \tag{10}$$

We are not aware of any theories of liquids which permit us to formulate F_l exactly. However, what is needed herein is merely the ratio $F_{1(l)}/F_{2(l)}$, not the F_l formulation itself. The ratio can be estimated by an extension of Keii's idea.[7] As a rough approximation, let us suppose that Henry's law holds for the dissolution of **1** and **2** in cyclohexane and also that the Henry's-law constant is the same for these two ketones. Then

$$F_{1(l)}/F_{2(l)} = F_{1(\mathrm{g})}/F_{2(\mathrm{g})}, \tag{11}$$

where subscript g refers to the gas phase. The substitution of F_g for F_l underlies the conventional theoretical treatments of isotope effect problems in liquid phase reactions. A fair success in such treatments[8,9] gives indirect further support to Eq. 11. The F_g is usually expressed by

$$F_\mathrm{g} = \frac{(2\pi mkT)^{3/2}}{h^3}\,\frac{8\pi^2(8\pi^3I)^{1/2}(kT)^{3/2}}{\sigma h^3}f_{\mathrm{vib}}, \tag{12}$$

where m is the mass, I is the product of the three principal moments of inertia, and σ is the symmetry number. Applying Eq. 12 to both ketones **1** and **2**, taking Eqs. 9, 10, and 11 into account, and omitting the symmetry number[10] we obtain

$$\frac{R_2}{R_1} = \left(\frac{m_1}{m_2}\right)^{3/2}\left(\frac{I_1}{I_2}\right)^{1/2}\left[\frac{f_{2.\mathrm{vib}}^{\neq}f_{1.\mathrm{vib}}}{f_{1.\mathrm{vib}}^{\neq}f_{2.\mathrm{vib}}}\right]\exp\left\{\frac{-(\varepsilon_2-\varepsilon_1)}{kT}\right\}. \tag{13}$$

Let us consider the magnitude of the quantity in the square brackets. Most stretching and bending molecular vibrations related to the C–C, C–H, and C=O bonds absorb at frequencies higher than 1000 cm^{-1}, and hence their contributions to the partition function are negligible. Some skeletal and adsorption-bond vibrations probably absorb at lower frequencies, thus contributing somewhat to the partition function. However, these contributions are expected to cancel out almost completely in the square brackets. Therefore, it might not be a serious error to set the quantity in the square brackets equal to unity. Based on this approximation Eq. 13 can be reduced to

$$\log_{10}(R_2/R_1) = \frac{3}{2}\log_{10}(m_1/m_2) + \frac{1}{2}\log_{10}(I_1/I_2) - \frac{\varepsilon_2-\varepsilon_1}{2.303kT}. \tag{14}$$

The first and second terms of the right side of Eq. 14 depend only upon the substrates, while the third term probably reflects the catalyst property. Our empirical expression 6 becomes identical to the theoretical Eq. 14, if we put

$$\sigma^{**} = \frac{3}{2}\log_{10}(m_1/m_2) + \frac{1}{2}\log_{10}(I_1/I_2), \tag{15}$$

and

$$\kappa = -(\varepsilon_2-\varepsilon_1)/2.303kT. \tag{16}$$

Substituent Constants. As evident from Eq. 15, σ^{**} depends only upon the m and I values of the substrates under comparison. In order to calculate I exactly, all the probable conformations of the cyclohexanone ring and the substituted alkyl group should be considered with the appropriate statistical weight. However, owing to a lack of necessary data for such a rigorous treatment, we had to be content with an approximation in which only the most likely conformation is considered. The actually assumed conformation was the chair form with the alkyl substituent in the equatorial position. For the sake of convenience, all the carbon atoms of the substituent were set so as to lie in the C(2)–C(1)=0 plane. The bond lengths and bond angles used were: r(C=C)=0.124 nm, r(C–C)=0.154 nm, r(C–H)=0.109 nm; ϕ\{C(2)–C(1)–C(6)\}=117°, ϕ\{C(1)–C(2)–C(7)\}=113.25°, any other ϕ (C–C–C)=109.5°, ϕ(H–C–H)=

Table 1. Theoretical values for σ^{**}

Paired substrates	$\frac{3}{2}\log_{10}\frac{m_1}{m_2}$	$\frac{1}{2}\log_{10}\frac{I_1}{I_2}$	σ^{**}	
2m/1	−0.087	−0.20	−0.29	($\sigma_{\mathrm{2m}}^{**}$)
2e/1	−0.16	−0.41	−0.57	($\sigma_{\mathrm{2e}}^{**}$)
2p/1	−0.23	−0.61	−0.84	($\sigma_{\mathrm{2p}}^{**}$)

109.5°. The details of I calculations based on these data will be published elsewhere, and the σ^{**} values and related data are summarized in Table 1.

Turning back to Fig. 2b, it is seen that one can calculate $\Delta\sigma^{**}$ values ($\sigma^{**}_{2e}-\sigma^{**}_{2m}$ and $\sigma^{**}_{2p}-\sigma^{**}_{2m}$) from the experimental data. In Table 2 the experimental and theoretical $\Delta\sigma^{**}$ values are compared. The agreement between theory and experiment is remarkable except for Pd. The exceptional result with Pd is not unexpected since the reaction mechanism is complex for this metal.[11–13)]

TABLE 2. COMPARISON OF EXPERIMENTAL AND THEORETICAL $\Delta\sigma^{**}$

Catalyst		$\Delta\sigma^{**}$	
		$\sigma^{**}_{2e}-\sigma^{**}_{2m}$	$\sigma^{**}_{2p}-\sigma^{**}_{2m}$
Observed	Ru	−0.27	−0.54
	Rh	−0.25	−0.54
	Pd	(−0.074)	(−0.153)
	Os	−0.27	−0.53
	Ir	−0.28	−0.55
	Pt	−0.27	−0.56
	Average[a)]	−0.27	−0.54
Calcd from Eq. 15		−0.28	−0.55

a) Averaged over all the metals except Pd.

Catalyst-Dependent Constant. We are now brought to the question why κ is invariant among the three reaction systems: **2m/1**, **2e/1**, and **2p/1**. This constancy means that ε is the same for the three **2**'s. The constancy of ε is explained by assuming a particular model for the activated complex of **2** that is adsorbed on the catalyst. Figure 3 illustrates the assumed model.

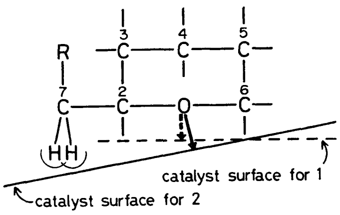

Fig. 3. Adsorption model for substituted (**2**) and unsubstituted cyclohexanone (**1**). R=H, methyl, or ethyl.

Important in this assumption is that in the case of **2m** one hydrogen at the C(7) position points away from the catalyst surface while the other two hydrogens point toward it. It must be this "pointing away" hydrogen that is replaced by a methyl or ethyl group upon going from **2m** to **2e** or **2p**. In this situation, no significant difference is expected among these **2**'s either in the heat of adsorption or in activation energy. As for **1**, however, it lacks the excess repulsive interaction between the substituent and the catalyst surface. Consequently, as shown in Fig. 3, the adsorption bond for **1** is probably shorter and hence stronger compared with that for **2**.

For both **1** and **2**, there must be two different forms of adsorption depending upon which face of the six-membered ring is directed toward the catalyst surface. By cis-addition of two hydrogen atoms from the catalyst side, one form is converted to the cis alcohol, and the other to the trans alcohol. In general both forms must be quite different from each other in adsorption strength. Thus, in principle, one should treat the rates of cis- and trans-alcohol formation separately in a theoretical consideration such as the one we made above. Nevertheless, we have been quantitatively successful in $\Delta\sigma^{**}$ correlation without such a separation. This is presumably aided by the observed fortuitous practical constancy of cis/trans ratio for different substrate ketones.

Concluding Remarks. Looking back at Eq. 14, let us remember that relative reactivity R_2/R_1 in a competitive reaction depends only upon the masses and the moments of inertia provided that $\varepsilon_1=\varepsilon_2$. Such conditions would be brought about if the substituent neither affects the functional group nor interacts with the catalyst surface. In other words, these conditions will be realized when the polar, steric, and "anchor" effects of the substituent are absent or negligible. The requirement for such substituent inertness may be fulfilled by an inactive substituent like alkyls unless they interact with the catalyst surface upon adsorption. Thus, the theoretical treatment presented in this paper would be expected to find a wider use even beyond ketone hydrogenation.

Measuring R_2/R_1 at various temperatures would provide a means to test the validity of our reaction model and its theoretical treatment: in Eq. 14 $\log(R_2/R_1)$ should vary linearly with the reciprocal of absolute temperature if $\varepsilon_1\neq\varepsilon_2$, and be temperature independent if $\varepsilon_1=\varepsilon_2$.

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