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Substituent Effects in Heterogeneous Catalysis. IV. Adsorption Estimations during Competitive Hydrogenation of Cyclohexanone and Its 2-Alkyl Derivatives

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Cyclohexanone (**1**) and its 2-alkyl derivatives (2-methyl-, 2-ethyl-, and 2-propylcyclohexanone (**2m**, **2e**, and **2p**)) were hydrogenated both individually and competitively in pairs (**1**+**2**) in cyclohexane using Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3 as catalysts. For all the catalysts, the reaction rates in competitive reaction decreased in the sequence, **1**$\gg$**2m**$>$**2e**$>$**2p**, while those in individual reaction were in the relation, **1**$>$**2m**$\approx$**2e**$\approx$**2p**. By the analysis of these kinetic data, the relative values of adsorption equilibrium constants have been estimated for **2m**, **2e**, and **2p**. These experimental values are in good agreement with the theoretical ones which have been derived on the basis of statistical mechanics using an adsorption model characterized by immobile adsorption of the substrate ketones.

The first[1)] and third papers[2)] of this series dealt with alkyl substituent effects in cyclohexanone (**1**) hydrogenation catalyzed by platinum group metals. The substituent effects were studied by means of competitive hydrogenation of **1** and its alkyl derivatives (2-methyl-, 2-ethyl-, and 2-propylcyclohexanone abbreviated subsequently to **2m**, **2e**, and **2p**). The logarithm of the observed relative rates was expressed as the sum of substituent constant σ^{**} and catalyst-dependent constant κ;

$$\log_{10}(R_2/R_1) = \sigma^{**} + \kappa. \tag{1}$$

A theoretical relative-rate expression corresponding to this empirical one (1) was derived on the basis of Eyring's rate equation using a simple reaction model in which the substrate ketones lose the translational and rotational freedom at the transition state. Comparing the empirical and theoretical relative-rate expressions, σ^{**} was quantitatively correlated as a function of the mass and the moment of inertia of the two substrate ketones under comparison. On the other hand, it is generally accepted in heterogeneous catalysis that the relative rate R_2/R_1 in competitive reaction can be expressed as

$$R_2/R_1 = (k_2/k_1)(K_2/K_1), \tag{2}$$

where k is the rate constant referred to the unit fraction of the surface covered and K is the adsorption equilibrium constant.

Thus we can now question whether k_2/k_1 or K_2/K_1 makes the chief contribution to σ^{**}. The main purpose of the present work is to resolve this question by estimating these relative values. The results are considered in the light of a statistical-mechanical treatment of adsorption equilibrium.

It is more or less conventional to compare the adsorption of the two reaction substrates by subjecting them to both individual and competitive reactions and by analyzing the obtained comparative data. This conventional technique was used in the present work. The catalysts chosen were Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3, all in the form of pellets. At the beginning, adsorption estimations on the same powder metal catalysts that were used in the previous work were attempted but failed owing to the difficulty in obtaining a good reproducibility in catalytic activity.

Experimental

Materials and Apparatus. Commercial cyclohexane (Wako Pure Chemical Ind., "Special grade") was used as received. Compounds **1** and **2m** were also commercial products and distilled before use. The preparation of **2e** and **2p** has been described previously.[2)] The catalysts chosen were Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3, each containing 0.5 wt % of the metal. They were all purchased from Engelhard Industries in the form of pellets (1/8 inch diameter). The glass reaction vessel has already been illustrated in detail.[1)]

Kinetic Procedure. In order to obtain reliable kinetic data from a series of individual reaction runs using the same kind but different batches of catalyst, the catalytic activity must be very similar for all the runs. Such a requisite was realized by pretreating the catalyst in the following fashion. One to ten catalyst pellets were weighed into a small glass test tube, and about 10 ml of cyclohexane was added. The test tube was placed in a 100-ml autoclave. The autoclave was charged with hydrogen to about 80 atm, heated to 80 °C, and allowed to stand at that temperature for 20 min with occasional gentle swirling by hand. No significant hydrogen consumption was observed during this pretreatment.

Then, the catalyst pellets were transferred to the glass reaction vessel pre-charged with cyclohexane that had already been made air-free by hydrogen flushing, care being taken to minimize the time of exposure of the catalyst to air. The reaction vessel was connected to a hydrogen reservoir and flushed repeatedly with hydrogen. Freshly distilled **1** and/or **2** were introduced into the reaction vessel by a syringe. The volume of the reaction solution thus prepared was made to be exactly 5 ml by adjusting the volume of the cyclohexane precharge and by standardizing the flushing procedure. The reaction was allowed to start by shaking the reaction vessel at 30 °C and in hydrogen of atmospheric pressure, and the reaction mixture was sampled at appropriate time intervals for the following 2 h (up to a conversion of *ca.* 5%). The activity of all the catalysts remained constant during this initial period of reaction. The reaction mixtures sampled were analyzed using a gas chromatograph.

Results

Relative Rates. Under our reaction conditions the rate of individual hydrogenations of **1** or **2** was proportional to the catalyst weight but unaffected by the fre-

Table 1. The observed rates

Catalyst	Competitive reaction		Individual reaction					
	Ketone pair	R_2/R_1	Ketone	$10^8R_1'$ mol/s g-cat		$10^8R_2'$ mol/s g-cat		R_2'/R_1'
				0.5[a]	1[a]	0.5[a]	1[a]	
Ru/Al_2O_3			**1**	3.63	3.27			
	1+2m	0.086	**2m**			1.40	1.40	0.41
	1+2e	0.051	**2e**			1.57	1.55	0.45
	1+2p	0.029	**2p**			1.38	1.38	0.40
Rh/Al_2O_3			**1**	21.7	18.2			
	1+2m	0.134	**2m**			9.2	8.0	0.43
	1+2e	0.072	**2e**			9.7	10.0	0.49
	1+2p	0.040	**2p**			7.8	9.2	0.43
Pt/Al_2O_3			**1**	60	58			
	1+2m	0.45	**2m**			30	30	0.51
	1+2e	0.23	**2e**			33	32	0.55
	1+2p	0.13	**2p**			30	27	0.48

a) Initial concentration of substrate ketone in mol/l.

quency at which the reaction vessel was shaken. It has also been observed that the hydrogenation rate is practically independent of ketone concentrations down to 0.5 mol/l or less for all the catalysts. The data on individual hydrogenations in Table 1 were all obtained in this concentration-independent region. Let us assume that R_1', the rate of individual hydrogenation of **1**, may be expressed by

$$R_1' = k_1K_1C_1/(1+K_1C_1), \tag{3}$$

where k is the rate constant. From the above-mentioned zero order kinetics in C_1, it follows that $K_1C_1 \gg 1$ in Eq. 3. Thus we have

$$R_1' = k_1. \tag{4}$$

Since the same argument holds for ketone **2**, we are led to

$$R_2'/R_1' = k_2/k_1. \tag{5}$$

Numerical values for R' were all estimated from the linear plot of product alcohol concentrations against reaction time. It is to be noted that R_2' represents the sum of the rates of cis- and trans-alcohol formation. The observed cis/trans ratio of product alcohols did not significantly differ for the three substrate ketones on a certain catalyst.

The observed values for R_1' and R_2' are given in Table 1. Interestingly enough, on each catalyst the R_2' values for **2m**, **2e**, and **2p** agree to within experimental error. In contrast R_1' is twice as great as R_2'.

Also included in Table 1 are the R_2/R_1 values, the relative rates in competitive reaction. The two characteristic features observed previously for unsupported metal catalysts were reproduced here with the Al_2O_3-supported catalysts. One of them is that, for all the catalysts, R_2/R_1 decreases in the sequence **2m**>**2e**>**2p**, *i.e.*, as the substituent size becomes larger. The other is that the R_2/R_1 value for a particular **2** decreases in the sequence Pt/Al_2O_3, Rh/Al_2O_3, Ru/Al_2O_3, *i.e.*, in the order of decreasing atomic radius of the catalyst metals. This indicates that the alkyl substituent effect in cyclohexanone hydrogenation is more pronounced for a metal having a shorter atomic radius.

Relative Adsorption. Let us derive equations which will serve to obtain some relative adsorption data. Applying Eqs. 2 and 5 to the **1-2m** pair system and combining the resulting equations yields

$$\log (K_{2m}/K_1) = \log (R_{2m}/R_1) - \log (R'_{2m}/R_1'). \tag{6}$$

Similarly for the **1-2e** pair system we have

$$\log (K_{2e}/K_1) = \log (R_{2e}/R_1) - \log (R'_{2e}/R_1'). \tag{7}$$

In these two equations we can equate the last terms to each other, as the fair agreement was obtained between R'_{2m} and R'_{2e}. Then, from Eqs. 6 and 7,

$$\log (K_{2e}/K_{2m}) = \log (R_{2e}/R_1) - \log (R_{2m}/R_1). \tag{8}$$

Analogous considerations with respect to the **1-2m** and **1-2p** pairs lead to

$$\log (K_{2p}/K_{2m}) = \log (R_{2p}/R_1) - \log (R_{2m}/R_1). \tag{9}$$

Equations 8 and 9 indicate that the relative adsorption equilibrium constants can be estimated experimentally using the relative rate data listed in Table 1. The results of actual calculations are given in Table 2 under the heading "Observed."

Table 2. Observed and calculated relative adsorption equilibrium constants

Catalyst		Obsd	Calcd
Ru/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.24	−0.28
	$\log_{10}(K_{2p}/K_{2m})$	−0.46	−0.55
Rh/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.27	−0.28
	$\log_{10}(K_{2p}/K_{2m})$	−0.53	−0.55
Pt/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.28	−0.28
	$\log_{10}(K_{2p}/K_{2m})$	−0.54	−0.55

Discussion

We intend herein to derive theoretical expressions corresponding to Eqs. 8 and 9, based on statistical mechanics employing a simple model for competitive ketone adsorption during hydrogenation. Let us recall that our reaction systems consist of a solid catalyst and a cyclohexane solution of **1** and **2** under hydrogen of atmospheric pressure. We assume that during reaction both **1** and **2** are in adsorption equilibrium competing for the same adsorption sites. We also assume that the adsorption of the solvent and the product alcohols is negligible. The latter assumption seems reasonable in view of the use of nonpolar cyclohexane as the solvent and of our concern about only the initial stage of reactions up to a conversion of 5%.

Employing the Langmuir adsorption model, the partition function Q_a for the adsorbed phase is given by

$$Q_a = \{L!/M_1!M_2!(L-M_1-M_2)!\}q_{1(a)}^{M_1}q_{2(a)}^{M_2}, \tag{10}$$

where L is the number of adsorption sites, M is the number of adsorbed molecules, q is the molecular partition function, and subscript a refers to the adsorbed state. The chemical potential of adsorbed molecules **1** is expressed as

$$\begin{aligned}\mu_{1(a)} &= (-\partial kT\ln Q_a/\partial M_1)_{L,M_2,T,V}\\ &= -kT\{-\ln M_1+\ln(L-M_1-M_2)+\ln q_{1(a)}\}.\end{aligned} \tag{11}$$

Similarly for adsorbed molecules **2**,

$$\mu_{2(a)} = -kT\{-\ln M_2+\ln(L-M_1-M_2)+\ln q_{2(a)}\}. \tag{12}$$

On the other hand, the partition function Q_l for a ternary solution containing N_1, N_2, and $N_{s(olvent)}$ molecules of the indicated constituents is approximately described by[3,4]

$$Q_l = \frac{(N_1+N_2+N_s)!}{N_1!N_2!N_s!}q_{1(l)}^{N_1}q_{2(l)}^{N_2}q_{s(l)}^{N_s}, \tag{13}$$

where the subscript l refers to the liquid state. Based on Eq. 13 the chemical potentials of **1** and **2** in the solution are given by

$$\mu_{1(l)} = -kT\{\ln(N_1+N_2+N_s)-\ln N_1+\ln q_{1(l)}\} \tag{14}$$

and

$$\mu_{2(l)} = -kT\{\ln(N_1+N_2+N_s)-\ln N_2+\ln q_{2(l)}\}. \tag{15}$$

Since at adsorption equilibrium the relations

$$\mu_{1(l)} = \mu_{1(a)},\quad \mu_{2(l)} = \mu_{2(a)} \tag{16}$$

hold, Eqs. 11, 12, 14, and 15 yield

$$\frac{M_2/N_2}{M_1/N_1} = \frac{K_2}{K_1} = \frac{q_{1(l)}q_{2(a)}}{q_{2(l)}q_{1(a)}}. \tag{17}$$

We now come to the problem of how to express the molecular partition functions in Eq. 17. If the adsorbed **1** and **2** are immobile with loss of translational and rotational freedom, only $q_{\mathrm{vib(ration)}}$ should be considered. Thus

$$q_{2(a)}/q_{1(a)} = (q_{2,\mathrm{vib}(a)}/q_{1,\mathrm{vib}(a)})\exp\{-(w_2-w_1)/kT\}, \tag{18}$$

where w is the heat of adsorption. On the other hand, until now no theories of liquids have been developed which allow one to express exactly the molecular partition function q for a molecule in the liquid phase. As an approximation, however, it is often assumed that the internal molecular motions of a molecule in the liquid phase are identical with those of the same molecule in the gas phase.[5,6] Employing this assumption for our reaction solutions would not be seriously in error, because nonpolar cyclohexane is used as the solvent and we eventually deal with only relative values of like molecules. The problem of seeking a q_l expression now reduces to that of evaluating merely the translational partition function $q_{\mathrm{tr}(l)}$. According to Eyring and Hirschfelder[5] $q_{\mathrm{tr}(l)}$ can be expressed as $q_{\mathrm{tr(gas)}}$ times v_f, where v_f represents the free volume. Then we have

$$q_l = \frac{(2\pi mkT)^{3/2}}{h^3}v_f\frac{8\pi^2(8\pi^3I)^{1/2}(kT)^{3/2}}{\sigma h^3}q_{\mathrm{vib}}, \tag{19}$$

where m is the mass, I is the product of the three principal moments of inertia, and σ is the symmetry number. Applying Eq. 19 to both ketones **1** and **2** we obtain

$$\frac{q_{2(l)}}{q_{1(l)}} = \left(\frac{m_2}{m_1}\right)^{3/2}\left(\frac{I_2}{I_1}\right)^{1/2}\left(\frac{v_{f,2}}{v_{f,1}}\right)\left(\frac{q_{2,\mathrm{vib}}}{q_{1,\mathrm{vib}}}\right), \tag{20}$$

where the symmetry numbers are omitted since we are eventually concerned with rate processes.[7,8] An approximation

$$v_{f,1} = v_{f,2} \tag{21}$$

reduces Eq. 20 to

$$\frac{q_{2(l)}}{q_{1(l)}} = \left(\frac{m_2}{m_1}\right)^{3/2}\left(\frac{I_2}{I_1}\right)^{1/2}\left(\frac{q_{2,\mathrm{vib}}}{q_{1,\mathrm{vib}}}\right). \tag{22}$$

Alternatively, one can derive Eq. 22, as was done in the preceding paper,[2] by assuming Henry's law and the identical Henry's-law constants for the dissolution of **1** and **2** in cyclohexane. Inserting Eqs. 18 and 22 into Eq. 17 yields

$$\begin{aligned}\frac{K_2}{K_1} &= \left(\frac{m_1}{m_2}\right)^{3/2}\left(\frac{I_1}{I_2}\right)^{1/2}\left(\frac{q_{1,\mathrm{vib}}q_{2,\mathrm{vib}(a)}}{q_{2,\mathrm{vib}}q_{1,\mathrm{vib}(a)}}\right)\\ &\quad\times\exp\left\{\frac{-(w_2-w_1)}{kT}\right\}.\end{aligned} \tag{23}$$

Applying Eq. 23 to substrates **2m** and **2e** and combining the resulting equations gives

$$\begin{aligned}\frac{K_{2e}}{K_{2m}} &= \left(\frac{m_{2m}}{m_{2e}}\right)^{3/2}\left(\frac{I_{2m}}{I_{2e}}\right)^{1/2}\left(\frac{q_{2m,\mathrm{vib}}q_{2e,\mathrm{vib}(a)}}{q_{2e,\mathrm{vib}}q_{2m,\mathrm{vib}(a)}}\right)\\ &\quad\times\exp\left\{\frac{-(w_{2e}-w_{2m})}{kT}\right\}.\end{aligned} \tag{24}$$

In Eq. 24 we assume as an approximation that

$$w_{2m} = w_{2e}, \tag{25}$$

$$q_{2m,\mathrm{vib}}q_{2e,\mathrm{vib}(a)}/q_{2e,\mathrm{vib}}q_{2m,\mathrm{vib}(a)} = 1. \tag{26}$$

Approximation 25 is consistent with the observed identity $R'_{2m}=R'_{2e}$ because this identity can be interpreted as indicating that **2m** and **2e** are similar not only in the transition state but also in the adsorbed state. Approximation 26 also seems to be justified based on this resemblance in the adsorbed state although we can hardly develop rigorous arguments based on the concept of normal vibrations. Let us divide each substrate molecule into two parts: the carbonyl group and the rest. The rest part would undergo little or no change when the substrate molecule goes from the dissolved to the adsorbed state. Thus, merely considering the carbonyl group will suffice for estimating the value for the left-hand side of Eq. 26. With this in mind we could equate $q_{2m,\mathrm{vib}}$ to $q_{2e,\mathrm{vib}}$ since there seems to be no significant difference between **2m** and **2e** in the nature of the carbonyl group. Nor can we expect any significant difference between $q_{2m,\mathrm{vib}(a)}$ and $q_{2e,\mathrm{vib}(a)}$ in view of the above-discussed resemblance between the adsorbed **2m** and **2e**. Thus we are led to approximation 26. Approximations 25 and 26 reduce Eq. 24 to

$$\log(K_{2e}/K_{2m}) = \frac{3}{2}\log(m_{2m}/m_{2e}) + \frac{1}{2}\log(I_{2m}/I_{2e}). \quad (27)$$

By applying a similar argument to the **2m-2p** pair system we are led to

$$\log(K_{2p}/K_{2m}) = \frac{3}{2}\log(m_{2m}/m_{2p}) + \frac{1}{2}\log(I_{2m}/I_{2p}). \quad (28)$$

Equations 27 and 28 correspond to Eqs. 8 and 9, respectively. In Table 2, the theoretical values for relative adsorption equilibrium constants predicted by Eqs. 27 and 28 are compared with the observed values based on Eqs. 8 and 9. The agreement between theory and experiment is excellent.

Concluding Remarks. The most important experimental results are summarized in two reactivity sequences: **1**$\gg$**2m**$>$**2e**$>$**2p** in competitive hydrogenation and **1**$>$**2m**$\approx$**2e**$\approx$**2p** in individual hydrogenation. The identity of the three **2**'s in the latter sequence suggests that the reactivity of the carbonyl group itself and the interaction of the substituent with the catalyst surface remain unchanged when the methyl is replaced by the ethyl or propyl group. In other words, these three substituents are very similar in their chemical nature, and can be considered as "pseudo-isotopes." The observed reactivity sequence in competitive reaction is regarded as reflecting the effect of these pseudo-isotopes upon substrate adsorption. Indeed, the results in competitive reaction have been quantitatively accounted for based on this concept by means of a statistical mechanical treatment. As for the immobile adsorption model employed in this theoretical treatment, it was referred to by Glasstone *et al.*[9] as early as 1941 as the "entropy of activation in adsorption."

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