Substituent Effects in Heterogeneous Catalysis. VII. Temperature Independence of the Relative Rates in Metal-catalyzed Hydrogenation of Cyclohexanone and Its 2-Alkyl Derivatives

Teiji CHIHARA and Kazunori TANAKA*

The Institute of Physical and Chemical Research, Wako, Saitama 351

(Received March 8, 1980)

The rates of hydrogenation of cyclohexanone and its 2-alkyl derivatives have been measured using decalin as the solvent in a temperature range of −5 to 68 °C over Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3 catalysts. As predicted previously, 2-methyl-, 2-ethyl-, and 2-propylcyclohexanone have exhibited nearly identical temperature dependencies in adsorption and hydrogenation, while cyclohexanone and 2-isopropylcyclohexanone had quite different dependencies.

This is a continuation of our series of studies concerning the effects of alkyl substitution in cyclohexanone (**1**) hydrogenation catalyzed by platinum metals. Three recent papers[1-3] have dealt with **1** and its 2-alkyl derivatives, *i.e.*, 2-methyl-, 2-ethyl-, 2-propyl-, 2-isopropyl-, and 2-*t*-butylcyclohexanone (abbreviated to **2m**, **2e**, **2p**, **2ip**, **2tb**, respectively). The activity sequence for hydrogenation of each of the individual ketones is

$$\mathbf{1} > \mathbf{2m} = \mathbf{2e} = \mathbf{2p} > \mathbf{2ip} > \mathbf{2tb}, \quad (1)$$

while the activity sequence for competitive hydrogenation of a mixture of different ketones is

$$\mathbf{1} \gg \mathbf{2m} > \mathbf{2e} > \mathbf{2p} \gg \mathbf{2ip} \gg \mathbf{2tb}. \quad (2)$$

As pointed out previously,[3] sequence (1) seems to be inversely related to the steric hindrance of the alkyl substituents. With respect to the identity **2m**=**2e**=**2p** for the triad ketones having a straight side chain, it should be noted that **2e** and **2p** are viewed as being brought from **2m** by alkyl substitution of a hydrogen atom β to the carbonyl group. Thus, it is unlikely that the triad ketones are significantly different from one another in charge density of the functional group. Another important fact is that the side alkyl chains of **2e** and **2p** are flexible. Owing to this flexibility, upon adsorption of **2e** and **2p** the side chains could point away from the catalyst surface and also from the carbonyl group. In different terms, the steric hindrance of the side chain to adsorption and the subsequent surface reaction remain unchanged on going from **2m** to **2e** or **2p**. Thus, it is expected that the adsorption strength as well as the reactivity of the carbonyl group should be the same for the adsorbed triad ketones, thus, giving rise to the observed identity **2m**=**2e**=**2p** in sequence (1).

The adsorbed triad ketones, however, might be different in entropy factor. It is very likely that upon adsorption a ketone loses its translational and rotational freedom.[4] If so, the greater the substituent, the greater would be the entropy loss. As previoulsy demonstrated, the relative magnitudes of the entropy losses for different ketones can be calculated in terms of the molecular weight (m) and product of the three principal moments of inertia (I). Such calculations account quantitatively for the reactivity differences in sequence (2) between **2m**, **2e**, and **2p**.

The purpose of the present work has been to substantiate the above interpretation of the alkyl substituent effects. One of the basic assumptions involved here is that the adsorption and hydrogenation of the triad ketones (**2m**, **2e**, **2p**) are different only in entropy factor. If this assumption is valid, the heat of adsorption as well as the activation energy must be identical for the triad ketones; that is to say, the relative rates of hydrogenation of the triad ketones must be temperature independent. The present work tests this prediction. For a comparison, **1** and **2ip** are also examined; these are expected to behave quite differently from the triad.

Experimental

Materials. Commercial decalin (Wako Pure Chemical Ind., "First Grade," a mixture of cis and trans isomers) was purified by refluxing with calcium hydride (*ca.* 1 g per liter decalin) for 24 h, followed by distillation. The middle was collected and redistilled with benzoic acid (*ca.* 25 mg per liter decalin).

The catalysts used were the same as those employed previously,[2,3] *i.e.*, Ru/Al_2O_3, Rh/Al_2O_3, and Pt/Al_2O_3, each in the form of pellets (Engelhard Ind., 1/8 inch in diameter containing 0.5 wt% metal).

Kinetic Procedure. The relative rates of hydrogenation of five ketones (**1**, **2m**, **2e**, **2p**, **2ip**) were measured either separately with one of the individual ketones or competitively with an equimolar mixture of **1** and **2** (**2** represents any one of **2m**, **2e**, **2p**, and **2ip**). Hydrogenation runs were conducted by the procedures described previously,[2] with an exception that decalin was used as the solvent in place of cyclohexane. The reaction temperature ranged from −5 °C to 68 °C, and the hydrogen pressure was atmospheric. Decalin was chosen because its liquid-state temperature range is wider than that of cyclohexane and its vapor pressure is lower (9.7 mmHg at 66.1 °C for the isomeric mixture[5]).

Results and Discussion

The linearity of Arrhenius plots was satisfactory over the whole temperature range (−5 °C—68 °C) as shown in Fig. 1. The rate data obtained at both ends of this range are listed in Table 1. Before discussing these data, let us consider the physical meaning of the relative rates involved.

According to a common practice in heterogeneous catalysis, the relative rate R_2/R_1 in competitive reactions may be expressed as

$$R_2/R_1 = k_2K_2/k_1K_1, \quad (3)$$

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

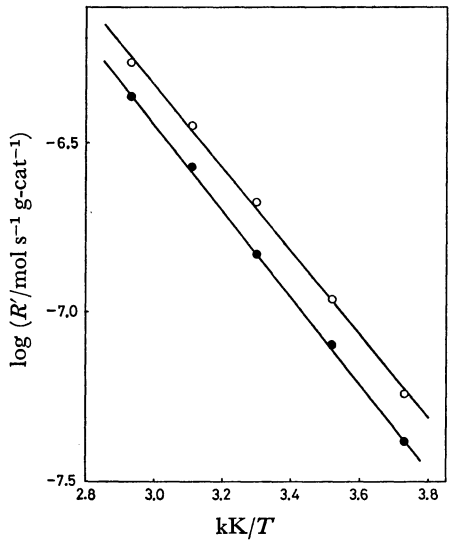

Fig. 1. Typical Arrhenius plots.
Hydrogenation of **1** and **2m** on Ru/Al_2O_3.
○: **1**, ●: **2m**.

brium constant. On the other hand, for the relative rate R'_2/R'_1 in individual reactions we have

$$R'_2/R'_1 = k_2/k_1, \tag{4}$$

provided that the concentrations of **1** and **2** are sufficiently high that R'_2 and R'_1 are concentration independent. The establishment of this prerequisite under our reaction conditions has been confirmed by preliminary experiments.[6]

Entropy Factors. Based on Eqs. 3 and 4 we obtain

$$\frac{K_{2e}}{K_{2m}} = \frac{K_{2e}}{K_1}\frac{K_1}{K_{2m}} = \frac{(R_{2e}/R_1)}{(R'_{2e}/R'_1)}\frac{(R_1/R_{2m})}{(R'_1/R'_{2m})}. \tag{5}$$

Since sequence (1) indicates $R'_{2e}=R'_{2m}$, Eq. 5 is reduced to

$$\log(K_{2e}/K_{2m}) = \log(R_{2e}/R_1) - \log(R_{2m}/R_1). \tag{6}$$

Since the numerical values for the two terms of the right side are given in Table 1, we can estimate the experimental $\log(K_{2e}/K_{2m})$ values using Eq. 6. On the other hand, a theoretical $\log(K_{2e}/K_{2m})$ value has previosuly[2] been worked out based on the equation

$$\log\left(\frac{K_{2e}}{K_{2m}}\right) = \frac{3}{2}\log\left(\frac{m_{2m}}{m_{2e}}\right) + \frac{1}{2}\log\left(\frac{I_{2m}}{I_{2e}}\right) - \frac{\omega_{2e}-\omega_{2m}}{2.303\,kT}, \tag{7}$$

where ω is the heat of adsorption (negative values for exothermic). In the calculation of the theoretical $\log(K_{2e}/K_{2m})$ value, it was assumed that $\omega_{2e}=\omega_{2m}$. Both experimental and theoretical $\log(K_{2e}/K_{2m})$ values are listed in Table 2. Also for a pair **2e**+**2p**, we can write down two equations which are analogous to Eqs. 6 and 7. The experimental and theoretical $\log(K_{2p}/K_{2e})$ values obtained are also included in Table 2. It is seen that, except for a value of −0.39 for Pt, the agreement between theory and experiment is satisfactory. Since the last term in Eq. 7 has been taken as zero in the theoretical calculations, this agreement provides indirect evidence for the assumed identity in heats of adsorption between the triad ketones, *i.e.*, $\omega_{2m}=\omega_{2e}=\omega_{2p}$.

Table 1. The observed rates

Catalyst	Competitive reaction: Ketone pair	$\log_{10}(R_2/R_1)$ −5 °C	$\log_{10}(R_2/R_1)$ 68 °C	Individual reaction: Ketone	$10^8 R'_i$ / mol s⁻¹ g-cat⁻¹ −5 °C	$10^8 R'_i$ / mol s⁻¹ g-cat⁻¹ 68 °C
Ru/Al_2O_3				**1**	5.75	54.4
	2m/1	−1.18	−0.74	**2m**	4.16	43.4
	2e/1	−1.48	−1.01	**2e**	3.91	37.4
	2p/1	−1.76	−1.23	**2p**	3.73	39.1
Rh/Al_2O_3	**2m/1**	−0.98	−0.85			
	2e/1	−1.22	−1.10			
	2p/1	−1.49	−1.35			
Pt/Al_2O_3				**1**	5.62	59.6
	2m/1	−0.47	−0.48	**2m**	3.10	33.7
	2e/1	−0.86	−0.74	**2e**	3.26	37.4
	2p/1	−1.13	−0.98	**2p**	3.11	37.1
	2ip/1	−1.96	−1.57	**2ip**	1.02	13.1

Table 2. The experimental and theoretical values for relative equilibrium constants

Catalyst		Obsd −5 °C	Obsd 68 °C	Calcd
Ru/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.30	−0.27	−0.28
	$\log_{10}(K_{2p}/K_{2e})$	−0.27	−0.23	−0.27
Rh/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.23	−0.25	−0.28
	$\log_{10}(K_{2p}/K_{2e})$	−0.27	−0.25	−0.27
Pt/Al_2O_3	$\log_{10}(K_{2e}/K_{2m})$	−0.39	−0.26	−0.28
	$\log_{10}(K_{2p}/K_{2e})$	−0.28	−0.24	−0.27

Energy Factors. The relation between the rate constant k_i referred to adsorbed **1** or **2** and the activation energy is

$$R\frac{\mathrm{d}\ln k_i}{\mathrm{d}(1/T)} = -(\varepsilon_i-\omega_i). \tag{8}$$

Herein R with no subscript is the gas constant and ε_i is the energy required for bringing the substrate i in the bulk solution up to the activated state on the catalyst surface (apparent activation energy). The quantity $\varepsilon_i-\omega_i$, therefore, represents the energy required for bringing the adsorbed i to the activated state (true activation energy), as shown in Fig. 2. The following relation is also available:

$$R\frac{\mathrm{d}\ln K_i}{\mathrm{d}(1/T)} = -\omega_i. \tag{9}$$

From Eqs. 3, 4, 8, and 9 we obtain

$$R\frac{\mathrm{d}\ln(R_2/R_1)}{\mathrm{d}(1/T)} = -(\varepsilon_2-\varepsilon_1) \equiv -\Delta\varepsilon_{2,1} \tag{10}$$

and

$$R\frac{\mathrm{d}\ln(R_2/R_1)}{\mathrm{d}(1/T)} - \left\{R\frac{\mathrm{d}\ln R'_2}{\mathrm{d}(1/T)} - R\frac{\mathrm{d}\ln R'_1}{\mathrm{d}(1/T)}\right\} = -(\omega_2-\omega_1) \equiv -\Delta\omega_{2,1}. \tag{11}$$

TABLE 3. THE VALUES FOR ENERGETIC QUANTITIES

Catalyst	Ketone pair	$\Delta\varepsilon_{2,1}$[a] / kcal mol^{-1}	$\Delta\omega_{2,1}$ / kcal mol^{-1}	Ketone	$\varepsilon_i-\omega_i$ / kcal mol^{-1}
Ru/Al_2O_3				**1**	5.6
	2m/1	2.5	2.3	**2m**	5.8
	2e/1	2.7	2.7	**2e**	5.6
	2p/1	3.0	2.7	**2p**	5.8
Rh/Al_2O_3	**2m/1**	0.8			
	2e/1	0.7			
	2p/1	0.8			
Pt/Al_2O_3				**1**	5.9
	2m/1	−0.1	−0.1	**2m**	5.9
	2e/1	0.7	0.5	**2e**	6.1
	2p/1	0.9	0.6	**2p**	6.2
	2ip/1	2.2	1.8	**2ip**	6.3

a) 1 kcal = 4.184×10^3 J.

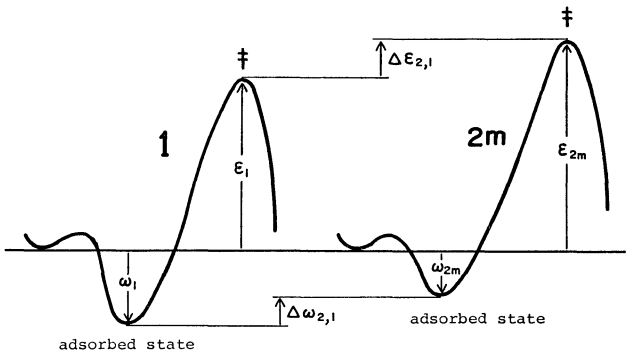

Fig. 2. Comparison of reaction coordinates between **1** and **2m**.

The values for $\Delta\varepsilon_{2,1}$ and $\Delta\omega_{2,1}$ can be estimated from Table 1 using Eqs. 10 and 11, respectively, if $\ln(R_2/R_1)$, $\ln R_2'$, and $\ln R_1'$ are linearly correlated with $1/T$. This sort of linearity has been confirmed with several representative reaction systems which are different in ketone or ketone pair. Table 3 summarizes the values for $\Delta\varepsilon_{2,1}$, $\Delta\omega_{2,1}$ and derived quantities.

Except for the **2m/1** system on Pt, the $\Delta\varepsilon_{2,1}$ values are nearly identical for **2m/1**, **2e/1**, and **2p/1** on each catalysts. This indicates that there is no significant difference in ε between **2m**, **2e**, and **2p**, as predicted in Introduction. In contrast to this near identity, a small but significant jump in ε is seen on going from **1** to **2m** and also for Pt on going from **2p** to **2ip**. Thus, the ε sequence for ketones is

$$\mathbf{1} < \mathbf{2m} \approx \mathbf{2e} \approx \mathbf{2p} < \mathbf{2ip}, \qquad (12)$$

which is the inverse of sequence (1). With respect to $\Delta\omega_{2,1}$ also, sequence (12) holds both for Ru and Pt although the value for **2m** on Pt is again exceptional. At present we cannot explain the unexpected result with **2m** on Pt.

Interestingly, little difference is seen in the true activation energy $(\varepsilon_i-\omega_i)$ for **1** and **2**'s; there is no gap when going from **1** to **2m** or from **2p** to **2ip**. This indicates that there is a compensation relation between $|\varepsilon_i|$ and $|\omega_i|$, *i.e.*, the greater the $|\varepsilon_i|$ value, the lower the $|\omega_i|$ value. Although this compensation must reflect certain characteristic features of the surface reaction, they are not clear at present.

In summary, the predicted near identity in the heat of adsorption and in the activation energy for the triad ketones **2m**, **2e**, and **2p** has been confirmed. This near equivalence is understood in terms of the particular conformation of the side chains in the adsorbed state (*cf.* Introduction). Comparing **1** with the triad, the latter is more weakly adsorbed and has a higher activation barrier, as shown in Fig. 2. The same is true for a comparison of the triad with **2ip**.

The present work was partially supported by Grant-in-Aid for Scientific Research No. 454134 from the Ministry of Education, Science and Culture.

References

1) T. Chihara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **52**, 507 (1979).
2) T. Chihara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **52**, 512 (1979).
3) T. Chihara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **52**, 633 (1979).
4) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), pp. 396—399.
5) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, (Vol. II of the Technique of Organic Chemistry Series), Wiley-Interscience, New York, (1970), p. 99.
6) For instance, R_i' was independent of concentration of **1** at concentrations above 1/8 mol/l for all the catalysts at both temperatures, −5 and 68 °C.