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Substituent Effects in Heterogeneous Catalysis

IX. Adsorption Strength and Reactivity of 4-Substituted Cyclohexanones in Platinum-Metal-Catalyzed Hydrogenation

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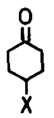
Substituent effects in platinum-metal-catalyzed hydrogenation were studied using 4-substituted cyclohexanones (substituent = OH, OMe, Cl, COOEt, Ph, C_6H_{11}, COOH, NMe_2) as reaction substrates. The hydrogenation rates of these derivatives were compared with that of cyclohexanone in both individual and competitive reactions. Despite the employment of several different metals and a variety of substituents, including acidic COOH and basic NMe_2, all of the relative rates fell within a rather limited range: 0.05–6.3 for competitive reactions and 0.10–2.1 for individual reactions. An analysis of these relative rate data indicates that in most cases the adsorption strength of the substituent-bearing cyclohexanones is greater than that of cyclohexanone, thus suggesting an attractive substituent–metal surface interaction. Palladium was distinguished from other platinum-group metals in its unusual weakness of carbonyl adsorption. In order to better understand the substituent effects of COOH and NMe_2, the effects of acid and base addition were also examined.

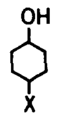
INTRODUCTION

Most of the papers in this series (*1*) have dealt with the alkyl substituent effects in cyclohexanone hydrogenation. In general an alkyl group substituted on cyclohexanone is so inert that little or no electronic influence on the carbonyl group is expected even if the two groups are located close to each other (*2*). The alkyl substituent effects so far observed in our laboratory could indeed be accounted for in terms of the steric and "ponderal" effects only (*3, 4*). The ponderal effect, pointed out by Ingold (*5*), pertains to mass distribution within the substrate molecule, and indicates the substituent effects due to variation in the mass and the moment of inertia caused by substitution. In the present work we extend our studies concerning substituent effects to include substituents other than alkyls. For the sake of simplicity of mechanistic interpretation, we deal with only 4-substituted cyclohexanones on which no electronic effects on the carbonyl group are expected by virtue of the remoteness of the substituent.

Among the 4-substituted cyclohexanones employed here are the carboxyl and dimethylamino derivatives. In order to better understand the role of these acidic and basic substituents, we examined the effect of acid and base addition upon cyclohexanone hydrogenation. We also made some comparative studies of benzene and cyclohexanone hydrogenation in connection with the phenyl substituent effects in cyclohexanone hydrogenation.



1-X



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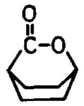

3

4-X

1,4-epoxycyclohexane

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EXPERIMENTAL

Materials

Ketones. 4-Methoxycyclohexanone (**1**-OMe) was prepared by hydrogenation of 4-hydroxyanisole over Raney-Ni, followed by chromic acid oxidation. The product was purified by distillation: bp 89.4°C/85 mm Hg.

4-Carboethoxycyclohexanone (**1**-COOEt) was prepared by hydrogenation of ethyl *p*-hydroxybenzoate over Raney-Ni, followed by chromic acid oxidation. The product was purified by distillation: bp 135°C/18 mm Hg.

4-Carboxycyclohexanone (**1**-COOH) was prepared by hydrolysis of **1**-COOEt with dilute hydrochloric acid. The product was purified by recrystallization: mp 67°C.

4-Phenylcyclohexanone (**1**-Ph). 4-Phenylphenol was partially hydrogenated over Raney-Ni to give 4-phenylcyclohexanol and this product was subjected to chromic acid oxidation to yield **1**-Ph (*6*). The product was purified by recrystallization: mp 77°C.

4-Cyclohexylcyclohexanone (**1**-C_6H_{11}). Hydrogenation of *p*-phenylphenol over Raney-Ni under pressure (about 80 atm) gave 4-cyclohexylcyclohexanol, and chromic acid oxidation of this product yielded **1**-C_6H_{11} (*6*), which was recrystallized: mp 29°C, bp 155°C/20 mm Hg.

4-Chlorocyclohexanone (**1**-Cl) was prepared by the reaction of 1,4-cyclohexanediol with hydrochloric acid, followed by chromic acid oxidation (*7*). The product was purified by distillation: bp 102.2°C/24 mm Hg.

4-Dimethylaminocyclohexanone (**1**-NMe_2) was prepared as follows (*8*). 4-Aminophenol was acetylated with acetic anhydride to form 4-acetamidophenol. Hydrogenation of this product over Raney-Ni gave 4-acetamidocyclohexanol, which was then hydrolyzed to form 4-aminocyclohexanol. Treatment of this amine with formic acid and formaldehyde yielded 4-dimethylaminocyclohexanol. Chromic acid oxidation of this alcohol gave **1**-NMe_2, which was purified by distillation: bp 115°C/24 mm Hg.

4-Hydroxycyclohexanone (**1**-OH) was prepared as follows (*9*). 1,4-Cyclohexanediol was converted into 4-benzoylcyclohexanol by the reaction with benzoyl chloride. The benzoate was subjected to chromic acid oxidation, and the resulting 4-benzoylcyclohexanone was hydrolyzed to yield **1**-OH, which was purified by distillation: bp 99.0°C/0.3 mm Hg.

All of these ketones were >99% pure, and were stored in a freezer. The five ketones [**1**-X(X = OH, OMe, Cl, COOEt, NMe_2)], which are liquid at room temperature, were redistilled just before use.

Alcohol isomers. In the hydrogenation of **1**-X to the corresponding alcohol **2**-X, both *cis* and *trans* isomers are expected to form. For the assignment of these isomeric products, authentic alcohol isomers were synthesized.

trans-Isomers of **2**-OMe and **2**-Cl were prepared using as a common starting material 1,4-epoxycyclohexane, which was obtained according to the procedure described in the literature (*10, 11*). This epoxide was converted to *trans*-**2**-OMe by heating in methanol containing a small amount of hydrochloric acid, and to *trans*-**2**-Cl by the reaction with concentrated hydrochloric acid.

trans-4-Phenylcyclohexanol (*trans*-**2**-Ph) and *trans*-4-cyclohexylcyclohexanol (*trans*-**2**-C_6H_{11}) were prepared by metallic sodium reduction in ethanol of **1**-Ph and **1**-C_6H_{11}, respectively (*6*). *cis*-4-Carboethoxycyclohexanol (*cis*-**2**-COOEt) was prepared by the esterification of *cis*-**2**-COOH, which was obtained by hydrolysis of lactone **3** (*11*). *cis*- and *trans*-1,4-Cyclohexanediol (*cis*- and *trans*-**2**-OH) were prepared according to literature procedures (*10*).

Other chemicals. Benzene (Wako Special Grade) was distilled over calcium hydride. Triethylamine (Wako Special Grade) and dimethylaminocyclohexane (Tokyo

Kasei Guaranteed Reagent) were fractionally distilled. These distillates (>99% pure) were stored with sodium, and redistilled just before use. Cyclohexanecarboxylic acid (Tokyo Kasei Guaranteed Reagent) was dried over phosphorus pentoxide, and distilled just before use. Acetic acid (Wako Super Special Grade, stated purity 99.7%) was used without further purification. *t*-Butyl alcohol (*t*-BuOH, Wako Special Grade) was purified according to a procedure given in the literature (*12*). It was refluxed over calcium hydride (1 g/liter) for 24 h, and then distilled. The center fraction was redistilled after addition of benzoic acid (25 mg/liter).

Catalysts. The metal catalysts used were all in the form of fine powders or black. The starting materials used for the preparation were OsO_4 for Os and the appropriate chlorides for the other metals. These starting materials were converted to the metal powders according to the same procedures as given before (Ref. (*13*) for Pt and Ref. (*2*) for the rest of the metals) except that a temperature of 80°C was chosen for the reduction of all the intermediate metal hydroxides.

Methods

Apparatus. The glass reaction vessel used for catalyst pretreatment and ketone hydrogenation is shown in Fig. 1. This reaction vessel (8 cm high, 2.6 cm in greatest o.d., and *ca.* 8 cm^3 in capacity) could be snugly inserted in a 100-cm^3 stainless-steel autoclave for *in-situ* high-pressure hydrogen pretreatment of catalyst samples. In designing this reaction vessel, the following two points were also taken into account in order to permit accurate measurements of hydrogenation rates. First, stirring splashes formed anywhere on the inside walls can easily flow down back into the bulk liquid. Second, the upper part of the reaction vessel is constricted to minimize the undesirable effect that part of the powder catalyst sample may stick to the walls, especially around the gas–liquid boundaries, thereby lowering the hydrogenation rate.

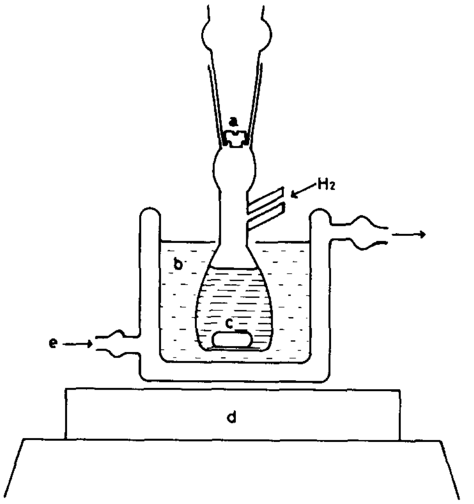

FIG. 1. The glass reaction vessel and its surroundings. (a) Septum adapter, (b) water bath, (c) Teflon-coated magnetic bar, (d) magnetic stirrer, (e) thermostated water.

Kinetic procedure. All the measurements of hydrogenation rate were preceded by the *in-situ* hydrogen pretreatment of the catalysts according to the following procedure. A catalyst sample (*ca.* 80 mg for Pd, 1–2 mg for other metals) was weighed into the reaction vessel, which was then charged with 5 cm^3 of *t*-BuOH and a 15-mm-long Teflon-covered stirring bar. The reaction vessel was then placed in the autoclave, followed by hydrogen admission to 80 atm. The autoclave was heated in the electric furnace to 80°C, and maintained at that temperature for 20 min. To ensure a sufficient hydrogen supply to the whole catalyst sample during this 20-min period, the autoclave was occasionally withdrawn from the electric furnace and placed on a magnetic stirrer for a short time.

After this pretreatment, the reaction vessel was taken out of the autoclave and weighed to determine the loss of *t*-BuOH due to the pretreatment operation. It was then recharged with *t*-BuOH to an extent that would just compensate the loss, set up in the assembly shown in Fig. 1, and flushed with hydrogen. Whenever the reaction vessel was taken out of the autoclave, a fine stream of hydrogen bubbles was seen to come out of the catalyst sample. While there was still a steady bubble stream from the catalyst, substrate ketone **1**-X (in singles or in pairs including **1**-H) was quickly added either neat or as a concentrated solution in *t*-BuOH (for solid **1**-COOH and **1**-Ph), and hydrogenation was commenced immediately by switching on the magnetic stirrer. The reaction temperature was maintained at 30°C and the hydrogen pressure at atmospheric. The reaction mixture was sampled at appropriate time intervals and analyzed. Sampling could be done without turning off the magnetic stirrer.

Analysis. Analysis of each reaction mixture was made by gas chromatography using a column of polyethylene glycol 20000 or bis(2,3-dihydroxypropyl)ether. In the case of **1**-COOH hydrogenation, the gas chromatographic analysis was preceded by the treatment of the reaction mixture with *N*,*N*-dimethylformamide dimethylacetal (*14*, *15*). By this treatment **1**-COOH and **2**-COOH were converted to the corresponding methyl esters.

RESULTS AND DISCUSSION

Preliminaries. With vigorous magnetic stirring, it was possible to cause foaming in the reaction solution. When such foam was seen, the hydrogenation rate was independent of the rotating speed of the magnetic bar, and increased in proportion to the catalyst amount. This means that the hydrogenation rate was not diffusion-controlled. As shown in Fig. 2, the catalyst activity was exactly constant for some time after the start of hydrogenation reaction. The duration of this constant activity period ranged from about 20 min for Ru to about 100 min for Pd. The amount of the catalyst sample weighed into the reaction vessel was chosen so that the percentage conversion of a substrate ketone **1**-H in competitive hydrogenation would be about 5% in the initial 20-min period. All the rate data in this report were obtained in this initial period, where pseudo-zero-order kinetics was followed, as shown in Fig. 2. The measurements of reaction rates were reproducible to within 5% for individual reactions and within 2% for competitive reactions.

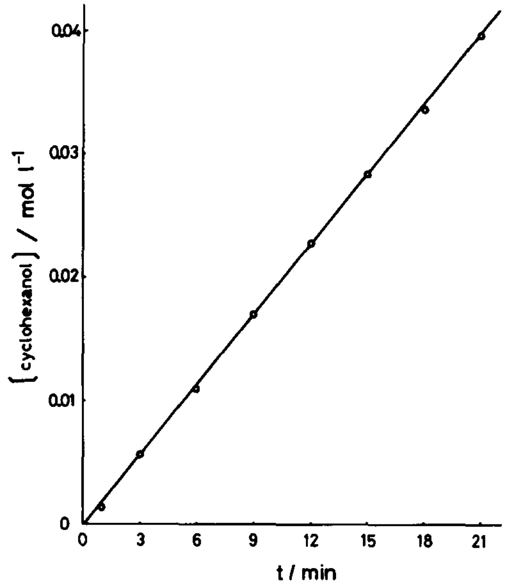

FIG. 2. A typical pseudo-zero-order plot. [**1**-H] = 0.5 mol/liter, reaction temperature = 30°C, catalyst (Ru) weight = 14.6 mg, solvent = *t*-BuOH.

Side reactions. As reported previously (*16*), hydrogenation of **1**-OCH_3 was accompanied by hydrogenolysis to cyclohexylmethylether over Pt, and to **1**-H and **2**-H over Pd. The extent of this side reaction reached 18% of the total conversion of **1**-OCH_3 for Pt, and 3.1% for Pd. It is to be noted that in the reaction of **1**-Cl, no dechlorination occurred with any catalyst. Hydrogenation of **1**-COOH yielded a large proportion of lactone **3**, which was formed by dehydration of product alcohol *cis*-**2**-COOH. The quantitative data on lactone formation will be given in a later section. Lactone formation might also be suspected for **1**-COOEt hydrogenation, but actually no corresponding lactone was formed. With **1**-Ph hydrogenation, **2**-Ph was the only product over Os, but over the other metals a small fraction of **1**-C_6H_{11} (<4% compared with **2**-Ph) was also produced.

Data analysis. As previously shown (*17*), the relative rate R/R_0 in competitive reaction and the relative rate R'/R'_0 in individual reaction may be given by

$$R/R_0 = (k/k_0)(K/K_0)(\beta/\beta_0) \qquad (1)$$

and

$$R'/R'_0 = (k/k_0)(\beta/\beta_0), \qquad (2)$$

respectively, where k is the rate constant referred to the unit fraction of the surface covered, K is the adsorption equilibrium constant, β is the adsorption amount at monolayer saturation, and the subscript (0) signifies the parent compound. Usually, the factor (β/β_0) in these equations is omitted on the tacit assumption that the molecular size is nearly the same for the parent and substituted substrate compounds. In the present work, however, this approximation is not necessarily true, *e.g.*, **1**-C_6H_{11} is much larger than **1**-H. Combining Eqs. (1) and (2) yields

$$(K/K_0) = (R/R_0)/(R'/R'_0). \qquad (3)$$

The experimental data will be analyzed using Eqs. (2) and (3) for k/k_0 and K/K_0. Rate R' as well as R'_0 was estimated from the slope of the appropriate pseudo-zero-order plot, such as Fig. 2, in a high ketone concentration region where the saturation rate is attained. Relative rate R/R_0 was determined on the basis of the linear first-order log–log plot of ketone concentrations (*13*). In the case of **1**-COOH hydrogenation, the estimation of R and R' was made allowing for lactone formation.

TABLE 1

Kinetic Data for Hydrogenation of Cyclohexanones **1**-X with Neutral X

X	Relative quantities					
	Ru	Rh	Pd	Os	Ir	Pt
	(A) $R/R_0 = (k/k_0)(K/K_0)(\beta/\beta_0)$					
H	1	1	1	1	1	1
OH	2.4	4.0	—	1.7	2.0	6.3
OMe	1.45	1.84	1.87	1.17	1.54	1.82
Cl	3.02	4.20	4.87	1.53	1.86	2.36
COOEt	2.20	2.39	3.22	1.24	1.36	2.61
Ph	1.55	1.69	4.57	0.98	1.89	2.29
C_6H_{11}	0.62	0.96	1.77	0.57	0.93	1.01
	(B) $R'/R'_0 = (k/k_0)(\beta/\beta_0)$					
H	1	1	—	1	1	1
OH	0.67	0.49	—	0.64	0.51	0.51
OMe	0.97	0.65	—	0.62	1.13	1.21
Cl	1.04	0.28	—	0.56	1.23	0.92
COOEt	0.47	0.50	—	0.36	0.42	0.66
Ph	0.65	0.67	—	0.38	0.43	0.98
C_6H_{11}	0.33	0.41	—	0.23	0.36	0.42
	(C) K/K_0					
H	1	1	—	1	1	1
OH	3.6	8.2	—	2.7	3.9	12.4
OMe	1.5	2.8	—	1.9	1.4	1.5
Cl	2.9	15	—	2.7	1.5	2.6
COOEt	4.7	4.8	—	3.4	3.2	4.0
Ph	2.4	2.5	—	2.6	4.4	2.3
C_6H_{11}	1.9	2.3	—	2.5	2.6	2.4

Neutral substituents. Table 1 summarizes the results of the hydrogenation of those ketones **1**-X that possess neutral substituents (X ≠ COOH, NMe_2). At present we cannot unambiguously explain all of these data, but several comments may be in order. The lack of the R'/R'_0 and K/K_0 data with Pd is due to the fact that a saturation of R'_0 was not reached even at a concentration as high as 4 mol/liter (*ca.* 40 vol%), in contrast to the attainment of the saturation rate at as low as 0.5 mol/liter over other metals. Such an anomaly with Pd was also observed for hydrogenation of other **1**-X; it is also in accord with our previous work (*18*). This suggests that the adsorption of the carbonyl group on Pd surface is unusually weak compared with that on other metals.

In Table 1C, the K/K_0 values are greater than unity for all the cyclohexanone derivatives. This suggests that all the neutral substituents interact attractively with the metal surfaces. Most K/K_0 values fall in a relatively narrow range of 2 to 4 or its immediate vicinity, with only a few exceptions of **1**-OH/Rh, **1**-OH/Pt, and **1**-Cl/Rh. It is unlikely that substituent X would exert any significant steric hindrance to adsorption in view of the molecular shape of **1**-X and of the remoteness of the substituent from the carbonyl group. Thus there seem to be only two factors exerted by substituents on adsorption, *i.e.*, the assisting substituent–metal interaction mentioned above and an inhibiting entropy effect (*3, 13, 19*) outlined below. The observed K/K_0 values greater than unity indicate that the former assisting effect exceeds the latter inhibiting effect.

Upon adsorption on metal surfaces, ketones **1**-X, as well as other organic molecules, ought to lose their translational and rotational degrees of freedom partially or completely. The larger the molecule, the larger this entropy effect, owing to the greater mass and the greater moment of inertia. The intrinsic substituent–metal interaction not masked under this entropy effect must, therefore, be much greater than expected from the observed K/K_0 data.

In order to discuss the data for $R'/R'_0 = (k/k_0)(\beta/\beta_0)$ in Table 1B, it is desirable to separate out the β/β_0 factor, and this β/β_0 separation is also desirable for $R/R_0 = (k/k_0)(K/K_0)(\beta/\beta_0)$. In the case of **1**-OH, **1**-OMe, and **1**-Cl, the size of the substituents is quite small in comparison with that of the cyclohexanone ring, and therefore $\beta \approx \beta_0$. In the case of **1**-COOEt, **1**-C_6H_5, and **1**-C_6H_{11}, the substituents are roughly as large as the cyclohexanone ring, and therefore it could be assumed that $2\beta \approx \beta_0$. Keeping these β/β_0 values in mind, inspection of the R/R_0 data indicates that the $(k/k_0)(K/K_0)$ values are close to or somewhat larger than unity for all the **1**-X/metal systems employed. The R'/R'_0 data indicate that the (k/k_0) values fall in a relatively narrow range of 0.5 to 2, with the exception of the **1**-Cl/Rh system, whose value is somewhat below the range. It was rather unexpected that such small variations in reactivity would be obtained from such a variety of substituent—metal combinations.

Comparing the $(k/k_0)(\beta/\beta_0)$ values for all the catalyst metals, it is seen that the retardation of carbonyl hydrogenation due to substitution is most prominent with Os for most substituents. Interestingly, substitution of OMe or Cl exhibits significant retardation over Rh and Os, but little retardation or even slight acceleration over Ru, Ir, and Pt.

Table 2 summarizes the stereoselectivity data for product alcohols **2**-X. Apparently there is no significant difference in *cis* percentage between individual and competitive reactions. This seems reasonable since it is unlikely that the nature of the *t*-BuOH solution of **1**-X(X ≠ H) would be affected significantly by the addition of **1**-H. Over Ru, Rh, and Os catalysts, with the exception of the Rh-catalyzed **1**-Cl, the observed *cis* percentages fall in a relatively narrow range of 52 to 69%. In contrast, the other metals exhibit a diversity of substrate-to-substrate variations in product *cis* percentage; 13–85% on Pd, 47–92% on Ir, 33–94% on Pt. It is also to be noted that Ir and Pt are similar in *cis* percentage for each substrate ketone.

Acidic substituent COOH. The data obtained in **1**-COOH hydrogenation are given in Table 3. The observed $(k/k_0)(\beta/\beta_0)$ values of much less than unity indicate that COOH substitution retards ketone hydrogenation.

TABLE 2

Stereoselective Data for Hydrogenations of Cyclohexanones **1**-X

X	Percentage *cis* of **2**-X					
	Ru	Rh	Pd	Os	Ir	Pt
	For individual reaction					
OH	59	60	—	62	55	59
OMe	57	65	—	54	86	77
Cl	65	75	—	64	92	94
COOEt	63	58	—	63	80	65
Ph	66	55	—	64	47	35
C_6H_{11}	64	55	—	63	61	52
	For competitive reaction					
OH	61	60	—	63	60	60
OMe	57	69	77	61	87	75
Cl	62	71	85	62	92	94
COOEt	61	57	74	64	80	62
Ph	65	52	13	61	48	33
C_6H_{11}	65	54	31	64	60	48

TABLE 3

Hydrogenation of **1**-COOH and Related Data

	Relative quantities				
	Ru	Rh	Os	Ir	Pt
(A) Comparison with **1**-H					
$(k/k_0)(K/K_0)(\beta/\beta_0)$	0.45	0.15	0.20	0.06	0.05
$(k/k_0)(\beta/\beta_0)$	0.16	0.14	0.10	0.15	0.12
K/K_0	2.8	1.1	2.0	0.40	0.42
(B) Product distribution in **1**-COOH hydrogenation					
cis	29	33	26	18	19
trans	16	20	14	4	8
lactone	15	47	60	78	73
(C) Effect of acid addition on **1**-H hydrogenation					
$\frac{R'_0(\mathbf{4}\text{-COOH})^a}{R'_0} \equiv f$	0.35	0.78	0.27	0.77	0.48
$\frac{R'_0(CH_3COOH)^b}{R'_0}$	0.64	0.58	0.59	0.58	0.63
(D) Intrinsic K/K_0 values					
$(K/K_0)_i \equiv f(K/K_0)$	0.98	0.86	0.54	0.31	0.20

[a] R'_0(**4**-COOH) stands for the rate of **1**-H hydrogenation in the presence of equimolar **4**-COOH.

[b] $R'_0(CH_3COOH)$ stands for the rate of **1**-H hydrogenation in the presence of equimolar CH_3COOH.

The value of the molecular dimension factor β/β_0 could not be smaller than 2/3, judging from inspection of molecular models. Thus the observed retardation effect should be attributed largely to the interaction of the carboxyl group with the catalyst surface. Is this interaction attractive or repulsive? The answer to this question would be given simply by estimating the value for K/K_0 if Eqs. (1)–(3) were applicable even to **1**-COOH irrespective of its strong acidic nature. However, it is suspected that the hydrogenation rate of **1**-H is significantly affected by the addition of **1**-COOH, and thus that k_0 in Eq. (1) (competitive reaction) is not identical with k_0 in Eq. (2) (individual reaction). In order to clarify this, we examined the effect of acid addition on **1**-H hydrogenation using two acids—acetic acid as the simplest carboxylic acid and cyclohexanecarboxylic acid as an analog of **1**-COOH. Table 3C suggests that **1**-H hydrogenation is considerably retarded by the addition of any carboxylic acid. The apparent K/K_0 value worked out using Eq. (3) is close to unity for Rh, and considerably lower than unity for Ir and Pt. Had the retardation effect due to **1**-COOH itself been taken into account, still lower intrinsic K/K_0 values $[(K/K_0)_i]$ would be obtained. There seem to be no means for estimating this intrinsic value by considering precisely the COOH retardation effect. However, it may not be unreasonable to make its rough estimation on the basis of the following considerations. Suppose that the rate of **1**-H hydrogenation is altered by a factor f by the addition of **1**-COOH in equimolar amount of **1**-H. Taking this addition effect into account for the competitive hydrogenation system of the **1**-COOH/**1**-H pair, then the denominator product $k_0\beta_0$ in Eq. (1) has to be varied to $fk_0\beta_0$. This variation leads to a modification of Eq. (1):

$$R/R_0 = (1/f)(k/k_0)(K/K_0)_i(\beta/\beta_0). \qquad (4)$$

Combining Eqs. (2) and (4), and taking Eq. (3) into account, we obtain

$$(K/K_0)_i = f(K/K_0). \qquad (5)$$

In view of the molecular similarity between **1**-COOH and **4**-COOH, we now assume that the f value for each metal catalyst is closely approximated by the corresponding R'_0(**4**-COOH)/R'_0 value in Table 3C. The values of $(K/K_0)_i$ calculated on this assumption are listed in Table 3D. Since they are close to or considerably less than unity, the COOH group may interact repulsively with the metal surfaces. If this is not so, the metal surface attraction with the COOH group is weaker than that with any neutral group, as revealed from a comparison with the K/K_0 values in Table 1. This conclusion is rather surprising, and remains to be explained.

Basic substituent NMe_2. Although conceivable as a more typical base-substituted derivative, **1**-NH_2 was not chosen as the reaction substrate on account of its tendency to form intermolecular Schiff's bases in neat or concentrated solution.

The relative rate data are listed in Table

TABLE 4

Hydrogenation of **1**-NMe_2 and Related Data

	Relative quantities				
	Ru	Rh	Os	Ir	Pt
(A) Comparison with **1**-H					
$(k/k_0)(K/K_0)(\beta/\beta_0)$	1.47	1.54	1.31	2.40	2.24
$(k/k_0)(\beta/\beta_0)$	2.1	1.4	0.15	0.10	0.83
K/K_0	0.70	1.1	8.7	24	2.7
(B) Effect of base addition on **1**-H hydrogenation					
$\frac{R_0'(4\text{-NMe}_2)^a}{R_0'} \equiv g$	0.36	1.00	0.17	0.23	0.35
$\frac{R_0'(\text{NEt}_3)^b}{R_0'}$	0.76	1.50	0.15	0.05	0.65
(C) Intrinsic K/K_0 values					
$(K/K_0)_i \equiv g(K/K_0)$	0.25	1.1	1.5	5.5	0.95

[a] R_0'(**4**-NMe_2) stands for the rate of **1**-H hydrogenation in the presence of equimolar **4**-NMe_2.

[b] $R_0'(NEt_3)$ stands for the rate of **1**-H hydrogenation in the presence of equimolar NEt_3.

4A along with K/K_0 values. Notable is the diversity of the $(k/k_0)(\beta/\beta_0)$ and K/K_0 data; each of these quantities varies from catalyst to catalyst more widely than has been observed in the case of the neutral substituents or of the COOH group. Table 4B indicates that **1**-H hydrogenation is considerably affected by base addition, thus suggesting that the K/K_0 values in Table 4A should not be taken too seriously. As in the case of **1**-COOH, however, a rough estimation of the intrinsic K/K_0 values could be made by a similar consideration. In place of Eq. (5) we have

$$(K/K_0)_i = g(K/K_0), \tag{6}$$

and we approximate g by R_0'(**4**-NMe_2)$/R_0'$, whose values are given in Table 4B. The $(K/K_0)_i$ values worked out are listed in Table 4C. It is seen that $(K/K_0)_i$ is considerably lower than unity for Ru, close to unity for Rh, Os, and Pt, and much greater than unity for Ir. Thus it is likely that the dimethylamino group interacts rather repulsively with the Ru surface, but attractively with the Ir surface.

Phenyl and carbonyl. As mentioned in the section *Side reactions*, hydrogenation of **1**-Ph usually afforded a small amount of **1**-C_6H_{11} besides the main product **2**-Ph. The proportions of **1**-C_6H_{11}, at most 4.4% for Ru, are listed in Table 5A. These values represent the relative reactivity of the phenyl and carbonyl groups for each catalyst; apparently the phenyl group is hydrogenated with much more difficulty than the carbonyl group. This comparison concerns the two functional groups attached on the same molecule. In this case the adsorption of either one or both of the functional groups would be sterically hindered to some extent owing to the conformational restrictions. It is of interest to study what relative reactivities would be observed if each functional group were free from such conformational restrictions on adsorption. To probe this question we hydrogenated benzene and cyclohexanone in both competitive and individual reactions. The observed relative reactivities are summarized in Table 5B, together with related data. It is seen that the relative reactivity R_b/R_0 as well as R_b'/R_0' is one order of magnitude greater than the product selectivity in Table 5A for most catalysts. Especially over Ru, benzene and cyclohexanone exhibited identical reactivities.

Concluding remarks. Somewhat surprisingly, despite the variety of the substituents

TABLE 5

The Relative Reactivity of Phenyl and Carbonyl Groups

	Relative quantities				
	Ru	Rh	Os	Ir	Pt
(A) Product selectivity in **1**-Ph hydrogenation					
1-C_6H_{11}/**2**-Ph	0.044	0.032	0.000	0.037	0.014
(B) Relative reactivity of benzene and cyclohexanone in competitive reaction (R_b/R_0) and individual reaction (R_b'/R_0')					
R_bR_0	0.80	1.00	0.00	0.14	0.92
R_b'/R_0'	0.80	0.59	0.18	0.20	0.23
K_b/K_0	1.00	1.69	0.00	0.70	4.0

employed, including acidic COOH and basic NMe_2, no remarkable substituent effects were exhibited in terms of R'/R'_0 for carbonyl hydrogenation over any of the metals studied. Although the most pronounced retardation effect was observed with the COOH/Os and NMe_2/Ir systems, their R'/R'_0 values were still as large as 0.1. The retardation of **1**-H hydrogenation by acid or base addition was not remarkable either. From the viewpoint of organic synthesis, these results suggest that the platinum metals other than Pd are useful enough as catalysts for hydrogenating carbonyl groups under a diversity of chemical environments.

In competitive reaction with **1**-H, it was in most cases the substituted ketone that was more reactive. The opposite trend, retardation by substituent, was most pronounced with the COOH/Pt system, which gave rise to $R/R_0 = 0.05$. This extent of substituent retardation is, however, still trivial in comparison with the $R/R_0 \approx 10^{-4}$ previously observed with 2-*t*-butylcyclohexanone over Ru and Rh. These results suggest that the steric factor plays a dominant role in metal-catalyzed hydrogenation of carbonyl compounds.

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