

Substituent Effects in Heterogeneous Catalysis

I. Competitive Hydrogenation of Cyclohexanone and Methylcyclohexanones over Group VIII Metals

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Cyclohexanone and one of its methyl-substituted derivatives (2-, 3-, or 4-methylcyclohexanone) were hydrogenated competitively in pairs in cyclohexane solvent at 30°C over group VIII metal catalysts. All of the methyl-substituted ketones were less reactive than cyclohexanone. The reactivity of a methylcyclohexanone relative to cyclohexanone was dependent upon the reaction mechanism and the atomic radius of the catalyst. INDO calculations, on the other hand, revealed that the carbonyl groups of the substituted and unsubstituted ketones are nearly identical in charge distribution and bond order, thus suggesting that the methyl substituent effect upon the hydrogenation rate is due primarily to steric hindrance to adsorption.

INTRODUCTION

The influence of substituents upon reaction rates has been a subject of continuing interest. While most of the investigations have dealt with homogeneous reactions, there have also been some studies in the field of heterogeneous catalysis (1-3). For such studies in heterogeneous catalysis it has been a conventional practice to compare the relative reactivities of a series of substituted compounds on a single solid catalyst. Relative reactivities obtained were usually correlated with the so-called reaction and substituent constants using the Hammett equation or similar ones (1, 2). However, one might suspect that in heterogeneous catalysis the relative reactivity depends not only upon the substituent and the reaction but may also be affected by the catalyst employed. Indeed, in the work of Smith and Campbell on the competitive catalytic hydrogenation of benzene and its methyl-substituted derivatives (3), the relative reactivities observed

for Rh and Pt were apparently different. However, we are aware of no systematic studies of the relationship between the effect of the substituent and the nature of the catalyst. We considered, therefore, that a study of competitive reactions using a series of solid catalysts would be valuable. The hydrogenation of cyclic ketones was employed for this study because the reaction mechanism has been revealed in some detail in earlier work at our laboratory (4).

EXPERIMENTAL METHODS

Materials. Four different procedures were used in preparing the catalysts. The Co and Ni catalysts were prepared, usually a few days before use, from Raney alloys (Nikko Shokai Raney-Co R-400 of Co: Al = 1:1 by wt and Kawakami Fine Chemicals Raney-Ni ND_H of Ni:Al = 1:1 by wt) using a method which was similar to that described by Nishimura (5) for preparation of his type T-4 catalyst. The

actual procedure was as follows. To a stirred suspension of 2 g of a Raney alloy in 10 ml of water was added dropwise 0.4 ml of 20% NaOH. The resulting alkaline mixture was warmed to 50°C, maintained at that temperature for about 1.5 hr with occasional stirring, and then 6 ml of 40% NaOH were added. After this addition the suspension was allowed to stand at the same temperature for another 1–2 hr. The resulting metal black catalyst was washed with water until the washings were neutral to litmus, and further washed successively with ethanol and cyclohexane.

The Os catalyst was prepared by reducing osmium tetroxide in isopropyl alcohol for 20 min at an initial hydrogen pressure of 80 kg/cm² (1 kg/cm² = 9.8 × 10⁴ N/m²) at progressively increasing temperatures to 60°C using a stirred autoclave. The resulting metal black was separated by filtration, washed with water, dried under reduced pressure at room temperature, and stored over silica gel.

The Pt catalyst was prepared by reducing Adam's oxide (PtO₂) in water at a hydrogen pressure of 35 kg/cm² for 40 min at room temperature using the stirred autoclave. The resulting metal black was washed, dried, and stored as in the case of the Os catalyst.

The rest of the catalysts (Ru, Rh, Pd, Ir) were prepared by the following procedure. To an appropriate hot aqueous metal chloride, with or without added HCl, was added 5–10 wt% aqueous NaOH in small portions. The resulting precipitate was filtered, washed with water until the filtrate was neutral, and then placed in the autoclave together with some water for reduction. In the case of Pd, the reduction of the precipitate suspended in water was carried out by stirring it at temperatures up to 30°C and an initial hydrogen pressure of 80 kg/cm² until the pressure drop was imperceptible (ca. 40 min). In the case of Ru, Rh, and Ir, the reduction was conducted using the same initial hydrogen pressure (80 kg/cm²) but at higher temperatures up to 80°C for 20 to 40 min. The resulting metal black was washed, dried, and stored as described above for Os.

The ketones used as reactants were all commercially available: cyclohexanone (CH) and 2-methylcyclohexanone (2-MCH) were Wako "Tokkyu" grade, and 3- and 4-methylcyclohexanone (3- and 4-MCH) were Tokyo Kasei G. R. grade. The purity of these ketones was shown by gas chromatography to be 99.7, 99.2, 98.3, and 98.8%, respectively. The latter two ketones were yellow tinted, contaminated with a trace of the corresponding alcohol, and resulted in slightly turbid solutions upon dissolution in cyclohexane. The cyclohexane, used as a solvent without further purification, was Wako "Tokkyu" grade.

Apparatus. Figure 1 illustrates the glass reaction vessel used for the competitive hydrogenations. The reaction vessel is jacketed, and fitted with a gas feed tube (A), a gas flushing tube (B), and a septum adapter (C). The reaction vessel proper (D) has a capacity of about 10 ml. The entire apparatus could be shaken back and forth by connecting the fitting (E) to a motor-driven plunger. The gas feed tube (A) was connected either to a hydrogen reservoir or to a gas burette filled with liquid paraffin. The reaction vessel plus the gas burette constituted a closed system in which the competitive hydrogenations were conducted.

Procedures. Competitive hydrogenations were carried out with a ketone pair dissolved in cyclohexane in the sequence described in the following. In the reaction vessel a weighed sample of catalyst (range, 4–200 mg) was placed along with 5 ml of an equimolar mixture of CH and a MCH (0.5 or 1 mol/liter of each) dissolved in cyclohexane. The reaction vessel was flushed with hydrogen while it was being cooled by cold water (8–10°C) in the jacket to minimize evaporative loss of the solvent. The cold jacket water was then replaced by warm water maintained at the reaction temperature of 30°C, and the reaction vessel was allowed to stand for 10 to 20 min to reach thermal equilibrium. Hydrogenation was started by shaking the reaction vessel and continued at approximately atmospheric pressure (1–1.05 atm). The reaction was followed volumetrically

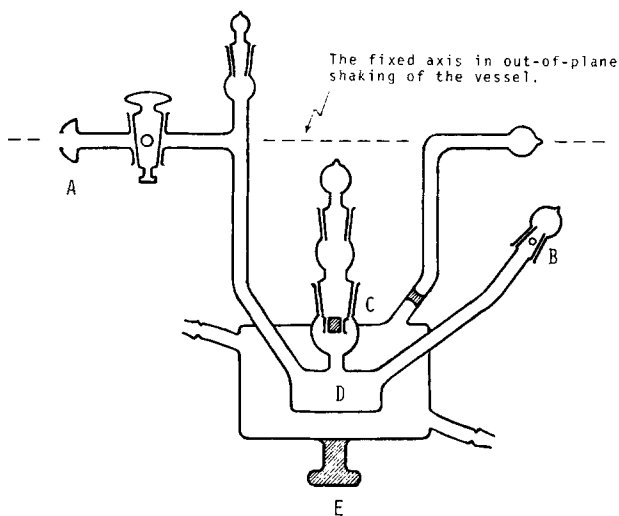


FIG. 1. Jacketed glass reaction vessel.

by measuring the hydrogen consumption and also gas chromatographically by analyzing aliquots of the reaction mixture at appropriate time intervals.

Using this procedure, 24 runs were carried out with 24 different combinations of eight metal catalysts and three ketone mixtures; 2-MCH and CH, 3-MCH and CH, and 4-MCH and CH (subsequently abbreviated to 2-MCH/CH, 3-MCH/CH, and 4-MCH/CH, respectively). The gas chromatography was performed on a Shimadzu Model GC-4BP instrument using helium as the carrier gas. A 3.5 m \times 3 mm i.d. column of 10 wt% diglycerol on 60–80 mesh C-22 SK at 85°C was employed for the runs started with the 2-MCH/CH mixture, and a 6 m \times 3 mm i.d. column of 10 wt% polyethylene glycol 20 M ABA on 60–80 mesh chromosorb WAW at 100 or 120°C for the runs started with the 3-MCH/CH or 4-MCH/CH mixture. Base line resolution was obtained for all the ketones and alcohols except for the two adjacent peaks due to *cis*- and *trans*-3-methylcyclohexanol and also for those due to *cis*- and *trans*-4-methylcyclohexanol. The resolution of these adjacent peaks as defined by Ambrose (6) was 1.4 when the column packing was fresh, and gradually fell to 1.1 with use. Quantitative analyses were performed using standard solutions of

known amounts of the ketones and alcohols.

TREATMENT OF KINETIC DATA

In this report, we are dealing with hydrogenation of a ketone pair (CH and one MCH). Let us assume that the hydrogenation of each ketone is first order in the amount of the adsorbed species, and that the adsorption obeys the Langmuir isotherm. Based on these assumptions, the rate of CH hydrogenation may be given by

$$\frac{dC_P}{dt} = \frac{k_0 K_A C_A}{1 + K_A C_A + K_B C_B}, \quad (1)$$

where C_A , C_B and C_P are the concentrations of CH, MCH, and cyclohexanol, respectively, K_A and K_B are the adsorption coefficients, and k_0 is the rate constant. Similarly, for the reaction of MCH we have

$$\frac{dC_Q}{dt} = \frac{k K_B C_B}{1 + K_A C_A + K_B C_B}, \quad (2)$$

where C_Q is the concentration of the methylcyclohexanol produced, and k is the rate constant. Note that as far as the initial stage of the reaction is concerned the alcohols produced are present only in very small amounts, and therefore the terms due to alcohol adsorption are not included in Eqs. (1) and (2). Dividing Eq. (2) by Eq. (1) gives rise to

$$\frac{dC_Q}{C_B} = \frac{kK_B}{k_0K_A} \frac{dC_P}{C_A} \quad (3)$$

Let $C_{A(i)}$ and $C_{B(i)}$ represent the initial concentrations of CH and MCH, respectively. Then

$$C_A = C_{A(i)} - C_P \quad (4)$$

and

$$C_B = C_{B(i)} - C_Q \quad (5)$$

Inserting Eqs. (4) and (5) into Eq. (3) and integrating between $C_P = 0$ and $C_P = C_P$ and between $C_Q = 0$ and $C_Q = C_Q$ leads to

$$\log \left(\frac{C_{B(i)}}{C_{B(i)} - C_Q} \right) = \frac{kK_B}{k_0K_A} \log \left(\frac{C_{A(i)}}{C_{A(i)} - C_P} \right) \quad (6)$$

The factor kK_B/k_0K_A represents the ratio of the reactivity for MCH (R) to the reactivity for CH (R_0), and will subsequently be referred to as the relative rate or relative reactivity. Equation (6) is then rewritten as

$$\begin{aligned} \frac{R}{R_0} &\equiv \frac{kK_B}{k_0K_A} \\ &= \log \left(\frac{C_{B(i)}}{C_{B(i)} - C_Q} \right) / \log \left(\frac{C_{A(i)}}{C_{A(i)} - C_P} \right) \end{aligned} \quad (7)$$

If the assumed first-order kinetics are valid, the plot of $\log[C_{B(i)}/(C_{B(i)} - C_Q)]$ against $\log[C_{A(i)}/(C_{A(i)} - C_P)]$ should be linear, and the relative reactivity R/R_0 can be obtained from such a linear plot.

RESULTS

Side reactions. In the derivation of Eq. (7), it was tacitly assumed that there were no side reactions. Therefore, before discussing the relative reactivity it is desirable to refer to side reactions observed in some cases. In catalysis over Pd, the reaction mixture 2-MCH/CH developed two unidentified gas chromatographic peaks as the reaction progressed, but the combined amount of these impurities was less than 3% of all the products. With catalysis over Pt, the molar excess of hydrogen uptake

over ketone consumption and also the molar excess of the ketone consumption over alcohol formation were indicative of accompanying hydrogenolysis, but its extent usually did not exceed 10% of the total conversion. There were no indications of any side reactions for the rest of the catalysts. Therefore, Eq. (7) is applicable to the correct or approximate evaluation of the relative reactivity.

Substituent effects. The relative reactivity R/R_0 may be regarded as a measure of the methyl substituent effect upon the reaction rate in hydrogenation of CH and MCH's. The first-order log-log plots from Eq. (7) were either linear or slightly curved depending upon the catalyst and the reaction mixture. Values for R/R_0 were determined from the slope of such a plot when it was linear, and from the tangent at zero conversion when it was curved. Table 1 lists the R/R_0 values thus determined. It is seen that all of the R/R_0 values, with the exception of that for the system 4-MCH/CH-on-Pd, are less than unity. This indicates that methyl substitution generally retards the hydrogenation of the carbonyl linkage. The exceptional R/R_0 value greater than unity for Pd should not be taken too seriously unless it is confirmed by further experiments. If the three R/R_0 values are compared for a certain catalyst it may be seen that as the substituted methyl group is located further away from the carbonyl linkage (in the order of the carbon positions 2, 3, and 4)

TABLE I
RELATIVE REACTIVITIES

Catalyst	R/R_0		
	2-MCH/ CH	3-MCH/ CH	4-MCH/ CH
Co	0.043	0.43	0.87
Ni	0.047	0.37	0.75
Ru	0.044	0.33	0.49
Rh	0.033	0.64	0.81
Pd	0.141	0.94	1.04
Os	0.055	0.37	0.51
Ir	0.111	0.47	0.57
Pt	0.79	0.75	0.66

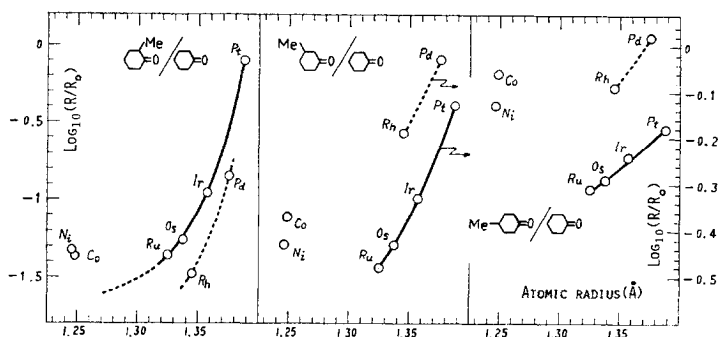


FIG. 2. Correlation of relative reactivity with atomic radius of catalyst metal.

the effect of methyl substitution decreases except in the case of Pt catalysis where rather an opposite trend is observed. In Fig. 2, $\log(R/R_0)$ is plotted 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 (7).

Before considering the results of Fig. 2, it may be useful to refer to our previous work (4) on the deuteration of 4-*tert*-butylcyclohexanone over platinum metals. This tracer study revealed that over four platinum metals, Ru, Os, Ir, and Pt, a simple addition mechanism predominates which is characterized by direct addition of two hydrogen atoms to the carbonyl linkage. By contrast, over the other platinum metals, Rh and Pd, a more complex mechanism is operative which involves a C_1 , C_2 - or C_1 , C_6 -diadsorbed species as an intermediate.

Interestingly, the results given in Fig. 2 also distinguish Rh and Pd from the other platinum metals. While the tetrad (Ru, Os, Ir, Pt) falls on a smooth curve the dyad (Rh and Pd) deviate from it; downward in the case of the 2-MCH/CH mixture, and upward in the case of both mixtures 3-MCH/CH and 4-MCH/CH. In each of these two metal groups, the greater the atomic radius of catalyst metal the greater the value for $\log(R/R_0)$, whatever the reaction mixture. In other words, as the atomic radius is increased the effect of methyl substitution becomes less pronounced. Co and Ni, like Rh and Pd, deviate

from the tetrad curve, but always upward.

INDO calculations. In order to see whether the observed methyl substituent effects are steric or electronic, calculations were made of the charge distributions and the bond orders for CH and MCH's using the INDO method on a Fujitsu computer Facom 230-60. For these calculations, the bond lengths and bond angles of CH and 2-MCH in the chair conformation were taken from the electron diffraction studies of Romers (8). The methyl group of 2-MCH may be regarded as occupying the equatorial orientation (8), and the methyl hydrogens as taking the staggered position with respect to the hydrogen on the vicinal carbon. Because of a lack of crystallographic data on 3- and 4-MCH, it was assumed that upon methyl substitution the geometry of the cyclohexanone ring in the chair form remains unaltered, and that the methyl group takes the equatorial position with its hydrogen atoms staggered with respect to the hydrogen on the vicinal carbon.

Details of these calculations will be published elsewhere, but some of them are given in Table 2. There is no significant difference between CH and any of the MCH's in either the charge distribution or the bond order of the carbonyl group. This result rules out any electronic factor as the main cause of the methyl substituent effect upon the hydrogenation rate, and leads us to the conclusion that the effect must be explained largely, if not exclusively, by steric factors.

TABLE 2
 INDO CALCULATIONS OF CYCLOHEXANONE AND ITS METHYL-SUBSTITUTED DERIVATIVES

		CH	2-MCH	3-MCH	4-MCH
Charge	O	-0.311	-0.312	-0.312	-0.312
	C ₁	0.295	0.293	0.291	0.295
	C ₂	-0.007	-0.002	-0.008	-0.010
	C ₆	-0.007	-0.009	-0.006	-0.010
	Me		0.007	-0.011	-0.011
Bond order	C ₁ =O	1.873	1.875	1.872	1.873
	C ₁ -C ₂	1.006	0.986	1.008	1.006
	C ₁ -C ₆	1.006	1.006	1.006	1.006
	C ₂ -Me		1.023		
	C ₃ -Me			1.023	
	C ₄ -Me				1.023

DISCUSSION

Equation (7) indicates that the relative reactivity R/R_0 is determined by two factors, the ratio of the rate constants k/k_0 and the ratio of the adsorption coefficients K_B/K_A . In other words, methyl substitution may lower the reactivity of the adsorbed species or hinder the adsorption of the reactant molecules. While the present experiments do not aid in determining which is the main factor, most of the results can be interpreted qualitatively in terms of K_B/K_A , or more conveniently in terms of the relative surface concentrations of CH and MCH.

2-MCH. Upon adsorption, whatever the adsorption mode, the methyl group of 2-MCH is expected to be close enough to the catalyst surface to undergo repulsive interaction. If this is true, steric hindrance to 2-MCH adsorption would be greater than steric hindrance to CH adsorption. The lower reactivity of 2-MCH relative to CH may be attributed to this excess hindrance because of which the catalyst surface would be more densely populated by CH than by 2-MCH upon contact with the equimolar 2-MCH/CH mixture.

In the case of the tetrad metals, the observed correlation of the relative reactivity with the atomic radius may be easily understood in terms of the distance between the methyl group and the catalyst surface. Since a simple addition mechanism is obeyed by these metals, as mentioned in a

foregoing section, both CH and 2-MCH must be adsorbed at either the C₁ position or the carbonyl oxygen in their half-hydrogenated state. In either case the length of the adsorption bond should increase with increasing radius in the catalyst metal because the radius of the carbon or oxygen atom plus the radius of the metal atom is equivalent to the adsorption bond length. The greater the adsorption bond length, the greater would be the distance between the methyl group of 2-MCH and the catalyst surface, and consequently the smaller would be the nonbonding repulsive interaction between the methyl group and the surface. The observed correlation between $\log(R/R_0)$ and atomic radius for the tetrad metals thus appears very reasonable.

As was mentioned in a foregoing section, the reaction mechanism over Rh and Pd is complex, and is characterized by the existence of a C₁, C₂- or C₁, C₆-diadsorbed species as an intermediate. In order to explain the downward deviation of these metals from the tetrad curve shown in Fig. 2, let us assume that the C₁, C₂-intermediate rather than the C₁, C₆-intermediate is predominant in the reaction of 2-MCH. Since the C₁, C₂-intermediate may be regarded as an adsorbed tetrasubstituted olefin whose hydrogenation is effected only with difficulty owing to large steric hindrance, it is not surprising that Rh and Pd are especially low in $\log(R/R_0)$ value for their atomic radii. Trying to test the assumption of the C₁, C₂-diadsorbed inter-

mediate, we are now studying deuteration of 2-MCH.

3- and 4-MCH. When these substituted ketones are adsorbed, the methyl group is expected to be too remote from the catalyst surface to cause any appreciable steric hindrance to adsorption. However, the results shown in Fig. 2 undoubtedly demonstrate a definite substituent effect upon the hydrogenation rate even for 3- and 4-MCH. Such an effect is understandable if the cross sections of the two competing ketones are compared. Due to the presence of a bulky methyl group, 3- and 4-MCH are greater than unsubstituted CH in the cross section. Consequently, in adsorption from a binary equimolar mixture of CH and 3- or 4-MCH, the unsubstituted ketone would exceed the substituted one in surface concentration unless interaction among adsorbed ketone molecules is negligible. This difference in surface concentration may possibly be responsible for the observed negative values for $\log(R/R_0)$.

Additional remarks. Relevant to our discussion of the substituent effects is the study of Sparks (9) on hydrogenation of a binary mixture of 2- and 4-MCH using Rh, Pt, and PtO₂ as catalyst. The reaction rates of the two ketones were similar over the Pt and PtO₂ catalyst, but over the Rh catalyst 4-MCH reacted much more rapidly than 2-MCH. This is consistent with our observation that 2-MCH/CH and 4-MCH/CH mixtures were very similar in R/R_0 value over Pt while over Rh the value for 4-MCH/CH was much greater than that of 2-MCH/CH.

It is instructive to refer to the study by Mitsui and his coworkers (10-12) dealing with stereochemistry in catalytic hydrogenation of a variety of cyclic olefins and aziridines. Based on this study, Mitsui (13) concluded that "catalyst hindrance" decreases in the sequence, Ni > Pd > Pt, i.e., decreases as the atomic radius increases. Here, "catalyst hindrance" is the concept defined by Linstead and others (14) as a steric hindrance between the catalyst and the substrate. In this paper, this concept has been referred to as "steric

hindrance to adsorption" rather than called by Linstead's term.

Interestingly, the work of Mitsui and others agrees with ours in emphasizing the importance of "catalyst hindrance" in catalytic hydrogenation, and also in claiming that "catalyst hindrance" decreases with increasing atomic radius in catalyst metal. The observed unique feature of Rh and Pd in $\log(R/R_0)$, on the other hand, suggests that the reaction mechanism is as important as the atomic radius in determining the substituent effects in heterogeneous catalysis.

ADDITIONAL DATA

In addition to the relative reactivity or the substituent effects, it seems worthwhile to note some of the other data which concern reaction order, catalyst activity, and a few more subjects.

Reaction order. If the assumed first order-kinetics in the adsorbed ketones is valid, the log-log plot based on Eq. (7) will be linear. If zero-order kinetics holds instead, we obtain

$$C_Q = (k/k_0)C_P, \quad (8)$$

and hence the plot of C_Q against C_P must be linear. All of the runs were examined for these two types of linearity, and the results are summarized in Table 3. Obviously, in the case of the reaction mixture 2-MCH/CH, all the metals except Pt obeyed first-order kinetics and deviated from zero-order linearity. Figure 3 shows a typical example of such a kinetic behavior. The other two reaction mixtures either did not follow any of the kinetics or arbitrarily obeyed both kinetics, depending upon the catalyst. Possibly this complication is due to participation of the product alcohols in hydrogenation kinetics. A typical example of the deviation from both kinetics is given in Fig. 4. From this it is seen that in the initial stage of the reaction the deviation from first-order linearity is so slight that the R/R_0 values (Table 1) calculated based on this linearity may be accepted with reasonable confidence.

Catalyst activity. Let U_0 represent

TABLE 3
COMPARISON BETWEEN FIRST-ORDER LOG-LOG PLOT BASED ON EQ. (7) AND
ZERO-ORDER C_P - C_Q PLOT BASED ON EQ. (8)

Catalyst	Linearity of first-order plot for			Linearity of zero-order plot for		
	2-MCH/CH	3-MCH/CH	4-MCH/CH	2-MCH/CH	3-MCH/CH	4-MCH/CH
Co	Yes	No	Yes	No	No	Yes
Ni	Yes	No	Yes	No	No	Yes
Ru	Yes	No	No	No	No	No
Rh	Yes	Yes	Yes	No	Yes	Yes
Pd	Yes	Yes	Yes	No	Yes	Yes
Os	Yes	No	No	No	No	No
Ir	Yes	No	No	No	No	No
Pt	No	No	No	No	No	No

$k_0 K_A / (1 + K_A C_A + K_B C_B)$ in Eq. (1), and insert Eq. (4) into Eq. (1). Then, we have

$$\frac{dC_P}{dt} = U_0(C_{A(i)} - C_P). \quad (9)$$

If we neglect the variation of U_0 with time, Eq. (9) represents a first-order rate law. Integration of this equation leads to

$$U_0 = \frac{2.303}{t} \log_{10} \left(\frac{C_{A(i)}}{C_{A(i)} - C_P} \right). \quad (10)$$

Similarly, from Eqs. (2) and (5) we have

$$U = \frac{2.303}{t} \log_{10} \left(\frac{C_{B(i)}}{C_{B(i)} - C_Q} \right), \quad (11)$$

where U represents $kK_B / (1 + K_A C_A + K_B C_B)$. The sum $U_0 + U$ divided by the

catalyst weight may be regarded as a measure of catalytic activity. In order to make an estimation of this catalytic activity, the logarithmic terms of Eqs. (10) and (11) were plotted against time for all of the runs conducted with 2-MCH/CH. With the exception of the Pt-catalyst run, straight lines were obtained for all or most of the regions investigated. Values for the sum $U_0 + U$ were then estimated from the slopes of these linear plots. For the Pt run, the catalyst activity was estimated by drawing tangents to the curved plots at the points of half conversion. Table 4 shows comparisons of the catalyst activities thus determined. From this it may be seen that Pt and Ru are the most and Pd the least active among the platinum metals.

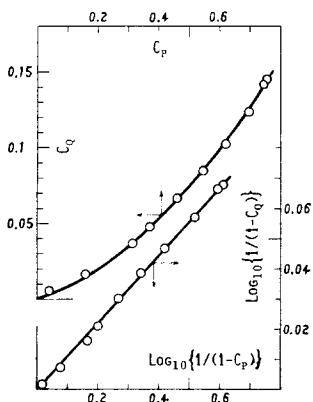


FIG. 3. Obedience to first-order kinetics and deviation from zero-order linearity: reaction mixture 2-MCH/CH over Ir.

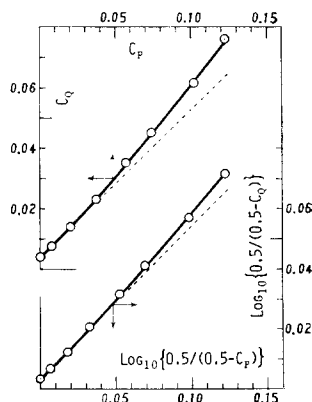


FIG. 4. Deviations from both first- and zero-order linearities: reaction mixture 4-MCH/CH over Os.

TABLE 4
ESTIMATES OF CATALYST ACTIVITY BASED ON
2-MCH/CH SERIES RUNS

Catalyst	$(U + U_0)/W$ (hr ⁻¹ g ⁻¹)	Comparison of activities
Co	0.27	0.003
Ni	1.08	0.01
Ru	86	1
Rh	35	0.4
Pd	0.27	0.003
Os	25	0.3
Ir	20	0.2
Pt	88	1

Stereoselectivity. The molar ratio between the *cis*- and *trans*-alcohol produced was invariant with time or conversion in most of the runs, but in some runs it varied slightly with conversion. In the latter case the isomeric ratio was determined by drawing a tangent to the *cis*- versus *trans*-alcohol concentration curve at zero conversion and by reading the slope of the tangent. Table 5 lists the values of the isomeric ratios for all the runs. Note that the numerical values for 3-MCH refer to the *trans/cis* ratio while those for 2- and 4-MCH refer to the *cis/trans* ratio. Hence, all the values in Table 5 approximate the molar ratios of the axial- to the equatorial-alcohol.

In contrast to the relative reactivity R/R_0 , there appears to be no direct cor-

relation between the stereoselectivity and the atomic radius, although the difference in stereoselectivity among the substituted ketones becomes less distinct in the sequence, Pt > Ir > Os \approx Ru, namely, an order of decreasing atomic radius. Interestingly, Rh and Pd are again distinguished from the other metals in that only these two display a marked rise in axial/equatorial ratio when going from 2-MCH to either 3- or 4-MCH.

Certain features of Raney-Ni. When this catalyst was used, ketone hydrogenation by the hydrogen inherent in the catalyst occurred in advance of the admission of gas phase hydrogen. Whatever the reaction mixture, this particular hydrogenation by inherent hydrogen gave a lower axial- to equatorial-alcohol ratio and a greater value for R/R_0 (smaller substituent effect) in comparison to ordinary hydrogenation by gas phase hydrogen. This result suggests that the adsorbed state of hydrogen has some bearing on substituent effects and stereoselectivity, and stimulates further study to verify it.

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TABLE 5
ISOMERIC RATIOS IN HYDROGENATION OF BINARY
MIXTURES OF CYCLOHEXANONE AND
A METHYLCYCLOHEXANONE

Catalyst	Reactant ketone and product alcohol		
	2-MCH <i>cis/trans</i>	3-MCH <i>trans/cis</i>	4-MCH <i>cis/trans</i>
Co	1.8	0.9	1.2
Ni	2.5	1.9	2.6
Ru	2.3	2.7	3.2
Rh	1.3	3.2	2.9
Pd	2.2	4.0	4.7
Os	2.4	1.7	2.3
Ir	1.4	0.8	1.0
Pt	3.3	0.8	1.7

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