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The Effect of the Structure of Aliphatic Ketones in Their Hydrogenation Over Metal Catalysts

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The kinetics of the gas-phase hydrogenation of homologous aliphatic ketones of the type R-CO-CH_3 (where R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, i-C_4H_9, t-C_4H_9) was studied at 150°C on Cu-, Pt- and Rh-catalysts. Using Langmuir–Hinshelwood kinetic models the reaction constants and adsorption coefficients were calculated.

Estimated values of kinetic quantities were successfully correlated applying the Taft equation. On all investigated metals the reactivity of ketones decreases with increasing electropositivity of the alkyl groups. For the adsorptivity the opposite trend was found. The structure effects are more strongly reflected in the adsorptivity than in the reactivity of the ketones. This phenomenon was found to be more pronounced on Cu, than on Pt and Rh catalysts. Furthermore, some correlation between the *d*-character of the metals and the adsorption or reaction parameters of the Taft equations was observed. Information resulting from linear free energy relationships complete the mechanistic picture of the ketone hydrogenation on metals.

NOMENCLATURE

E_s	constants expressing the steric effect of substituents
F	feed rate of ketone (mol/hr)
G	linear mass velocity (mol/hr cm^2)
k	rate constant of hydrogenation (mol/hr kg_{cat})
K	adsorption coefficient (atm^{-1})
p	partial pressure (atm)
P	total pressure of reactants and nitrogen (atm); max $P = 1$ atm
Q	least sum of squared deviations
$\bar{R}$	correlation coefficient of the linear regression
r_0	initial reaction rate (mol/hr kg_{cat})
W	weight of catalyst (kg)
W/F	time factor (kg_{cat} hr/mol)
x	conversion (mol)

Greek Letters

δ	constants expressing the structure effects of substituents
ρ^*	parameter of the Taft equation
σ^*	constants expressing the polar effects of substituents

Subscripts

a	adsorption
A	ketone
B	hydrogen
AB	reaction intermediate — "half hydrogenated state"
crit	critical
cat	catalyst
r	reaction

INTRODUCTION

In recent years our interest has been focused on the reactivity of organic compounds in heterogeneously catalyzed reactions. In our first studies (*1*, *2*) only qualitative information concerning this problem was obtained. Later the Taft and Ham-

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mett equations were applied to the quantitative description of the structural effects in reactions over solid catalysts (*3–5*). The results of these studies were mentioned in a review (*6*) devoted to the general applicability of linear free energy relationships (LFER) in heterogeneous catalysis.

In our most recent studies, dealing with the dehydration (*7*) and dehydrogenation (*8*) of alcohols, we have found that LFER can serve not only in the elucidation of reaction mechanism but can also be used for the characterization of solid catalysts.

The aim of the present work was to estimate the effects of the structure of aliphatic ketones on the rate of their hydrogenation in the gaseous phase over various metal catalysts which have been formerly used in the dehydrogenation of secondary alcohols (*8*). For the quantitative expression of structure effects on the reactivity of ketones the Taft equation should be applied.

Attention has recently been paid to the study of structure effects in the hydrogenation of aliphatic ketones in the liquid phase (*9–12*). In these studies, in which various types of nickel catalysts were used, the following order in the reactivity of aliphatic ketones was found:

$$CH_3COCH_3 > C_2H_5COCH_3 > n\text{-}C_3H_7COCH_3 > i\text{-}C_4H_9COCH_3 > i\text{-}C_3H_7COCH_3.$$

Recently Iwamoto, Yoshida, and Aonuma (*12*) have successfully correlated estimated rate constants and adsorption coefficients in liquid-phase hydrogenations in the coordinates of the Taft equation. The additional treatment of other published data (*9–11*) using the Taft equation has revealed that in some cases the rate data for acetone deviate from the linear correlation. The reaction parameter (ρ_r^*) was found to depend on reaction conditions, especially on the solvent used (*9, 12*).

A short communication (*13*) was devoted recently to the gas-phase hydrogenation of aliphatic ketones over a copper catalyst. The reactivity was described through the Taft equation using polar constants for alkyl substituents.

EXPERIMENTAL METHODS

Chemicals. The quality of hydrogen and nitrogen and their purification were described previously (*14*). Ketones were commercial preparations of Koch-Light Laboratories, B.D.H. and Fluka. Before use, ketones were carefully dried with $CaCl_2$ and distilled over a laboratory column (35 TP). Their purity was checked by gas–liquid chromatography.

Catalysts. Copper catalyst (43% (w/w) Cu on kieselguhr) was a commercial product. Platinum (Pt 0.5%, w/w) and rhodium (Rh 3.0%, w/w) were supported on kieselguhr. Their preparation, activation and physical properties are described in our previous communications (*8, 14*).

Apparatus. The hydrogenation of ketones in the gaseous phase was carried out in a glass flow reactor placed in a silicone oil bath. The apparatus was described in detail in our previous paper (*14*).

Analysis. The reaction products consisting only of alcohols and unreacted ketones, were analyzed by gas–liquid chromatography using diglycerol (15%, w/w) supported on Celite (*14*). The analyses were performed on a commercial gas chromatograph equipped with a flame ionization detector at 90 or 110°C, depending on the molecular weight of the ketone and alcohol.

RESULTS AND DISCUSSION

Activity and Selectivity of the Catalysts

In preliminary experiments we examined the activity and stability of the catalysts at reaction conditions analogously as in the hydrogenation of acetone (*14*). On the copper catalyst we found the same decrease of the initial activity for all investigated ketones as in the hydrogenation of acetone. For this reason it was necessary to keep the chosen estimated reduction conditions strictly reproducible and to use a fresh portion of copper catalyst for each kinetic experiment. The decrease in the activity of Pt and Rh catalysts was much lower than that of the copper catalyst. The activity of the palladium catalyst (3.0%, w/w Pd on kieselguhr) which has also been used for the hydrogenation of acetone (*14*), was too low for 2-butanone and other investigated ketones at 150°C. The increase of the metal content to 5 or 10% (w/w) of Pd in the catalyst brought only a small effect on their catalytic activity, so that the kinetic measurements could not be performed on palladium. On the nickel catalyst (10%, w/w on kieselguhr) at 150°C the reaction rate of all investigated ketones was too high. On diminishing the metal content to 1.0% (w/w) of nickel, the catalytic activity decreased to a desirable level, but the stability of such a catalyst during the kinetic measurement was too low.

The selectivity of the hydrogenation of all investigated ketones on copper, platinum and palladium catalysts at 150°C was satisfactory. Only the corresponding alcohols were found as reaction products; no hydrocarbons were detected.

Effect of Heat- and Mass-transfer in Kinetic Measurements

Using the glass flow reactor placed in the silicone oil bath and keeping the conversion of ketones below 10 mole %, the heat transfer from the catalyst bed was sufficient and the reaction occurred under isothermal conditions.

If the mass velocity (G) of the ketones was kept higher than 0.1 mol/hr cm^2 the effect of external diffusion on kinetic measurements on the copper catalyst was eliminated. On platinum and rhodium catalysts the external diffusion had no effect on measured kinetic quantities if G was higher than 0.06 mol/hr cm^2.

With the 0.3–0.6 mm particle size fraction of Cu, Pt and Rh catalysts, internal diffusion did not affect the measured initial reaction rate of any of the ketones under the experimental conditions studied.

Kinetic Analysis

In the hydrogenation of acetone on copper (*14*) we found that Eq. (1) describes the experimental data best.

$$r_0 = kK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2} + K_Bp_B]^4. \quad (1)$$

At 150° the following values of kinetic constants were estimated: $k = 5700$, $K_A = 15.0$, $K_B = 0.72$.

In the present study we first checked if the hydrogenation of homologous aliphatic ketones on the copper catalyst obeyed the same kinetic equation. As a model substance 3-methyl-2-butanone was used. The results are given in Fig. 1.

From these data the optimal values of kinetic parameters (k, K_A, K_B, or K_{AB}) for the 23 derived equations (*14*) using the "gridsearch" method (*4, 8, 14, 16*) were calculated. In order to find the best kinetic models which fit the experimental data, the values of the least sum of squared deviations (Q) were compared with the critical value of $Q(Q_{crit})$ calculated with the aid of Beale's criterion (*8, 14*), analogously as in our previous studies (*4, 8, 14*). This treatment has revealed that the sums of Q for Eq. (1) and for Eq. (2) are smaller than the estimated value of Q_{crit}.

$$r_0 = kK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2} + (K_Bp_B)^{1/2}]^4. \quad (2)$$

This fact indicates that both equations describe the kinetic data obtained in the hydrogenation of 3-methyl-2-butanone sufficiently. For this reactant the following values of kinetic constants were esti-

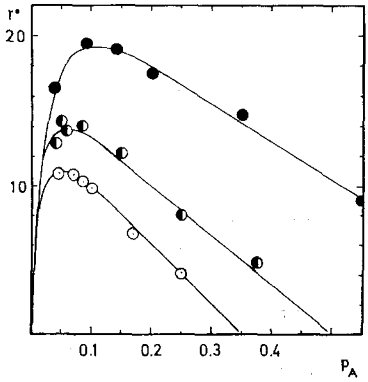


FIG. 1. Dependence of initial reaction rate of 3-methyl-2-butanone hydrogenation on partial pressure of ketone at 150°C over Cu-catalyst; total pressure of reactant [(●) 1.0, (◐) 0.5, (○) 0.35 atm]; curves correspond to Eq. (1).

mated: Eq. (1), $k = 1341$, $K_A = 18.8$, $K_B = 0.63$; Eq. (2), $k = 939$, $K_A = 43.4$, $K_B = 2.1$.

Since Eq. (1) was also found to describe the experimental data in the hydrogenation of acetone (*14*), we have also applied it to other aliphatic ketones on copper catalyst.

Assuming that the adsorption coefficient of hydrogen (K_B) calculated from the kinetic data of the hydrogenation of different aliphatic ketones on the same catalyst is the same, the kinetic procedure for homologous ketones which obey the same rate law can be simplified. Rate constants and adsorption coefficients of ketones can be calculated from values of the initial reaction rates measured at different partial pressures of ketone but at only one total pressure of reactants. The values of the adsorption coefficient of hydrogen as calculated from the kinetic analyses of the acetone ($K_B = 0.72$ atm^{-1}) and 3-methyl-2-butanone hydrogenations ($K_B = 0.63$ atm^{-1}), regarding the error of their estimation from Eq. (1), agree quite well.

Using the mean value of the adsorption coefficient of hydrogen ($K_B = 0.68$ atm^{-1}) and the simplified form (3) of Eq. (1),

$$r_0 = 0.68kK_Ap_Ap_B/(1 + (K_Ap_A)^{1/2} + 0.68p_B)^4, \quad (3)$$

k and K_A for the investigated ketones were calculated from the experimental data presented in Fig. 2.

The parameters for 2-butanone, 4-methyl-2-pentanone and 2-hexanone hydrogenation at 150°C on the copper catalyst are summarized in Table 1.

An analogous procedure was adopted for the hydrogenation of ketones on platinum and rhodium catalysts. The dependence of the initial reaction rate on the partial pressure of ketone at 150° is represented in Fig. 3 for Pt and in Fig. 4 for Rh. For these two catalysts, Eqs. (4) and (5) gave

$$r_0 = kK_AK_Bp_Ap_B/(1 + K_Ap_A + K_Bp_B)^4, \quad (4)$$

$$r_0 = kK_AK_Bp_Ap_B/[1 + K_Ap_A + (K_Bp_B)^{1/2}]^4 \quad (5)$$

the best fit in acetone hydrogenation (*14*)

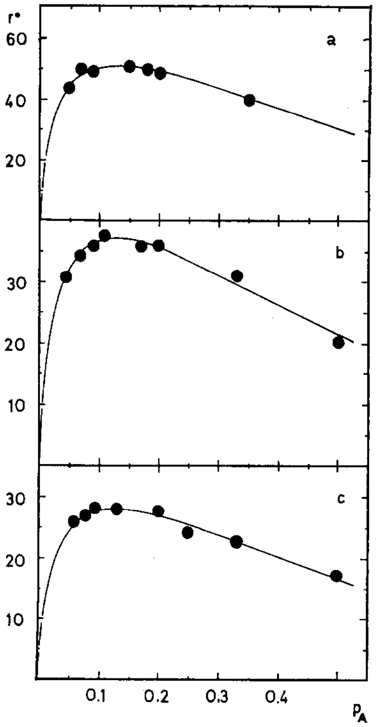


FIG. 2. Dependence of initial reaction rate of (a) 2-butanone, (b) 4-methyl-2-pentanone and (c) 2-hexanone on partial pressure of ketones at 150°C over Cu catalyst; total pressure of reactants 1.0 atm; curves correspond to Eq. (1).

TABLE 1

RATE CONSTANTS AND ADSORPTION COEFFICIENTS OF ALIPHATIC KETONES IN THEIR HYDROGENATION AT 150°C ON DIFFERENT CATALYSTS

Ketone $RCOCH_3$ (R =)	Metal					
	Cu[a]		Pt[b]		Rh[c]	
	k	K_A	k	K_A	k	K_A
CH_3	5700	15.0	22636	3.7	4025	3.9
C_2H_5	3510	17.5	18860	4.5	3075	6.4
i-C_3H_7	1341	18.8	5625	6.0	1522	8.4
n-C_4H_9	1935	17.8	—	—	—	—
i-C_4H_9	2537	17.7	9751	4.9	1569	7.0
t-C_4H_9	—	—	3628	7.5	716	14.4

[a] Calculated from Eq. (1); $K_B = 0.68$.
[b] Calculated from Eq. (4); $K_B = 0.01$.
[c] Calculated from Eq. (4); $K_B = 0.25$.

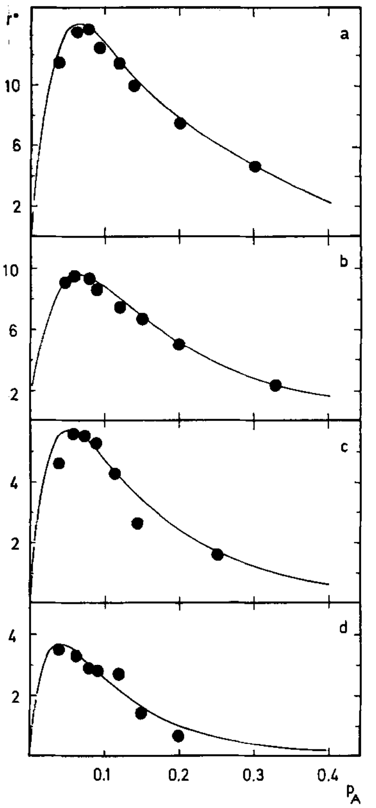


Fig. 3. Dependence of initial reaction rate of (a) 2-butanone, (b) 4-methyl-2-pentanone, (c) 3-methyl-2-butanone and (d) 3,3-dimethyl-2-butanone on partial pressure of ketones at 150°C over Pt catalyst; total pressure of reactants 1.0 atm; curves correspond to Eq. (4).

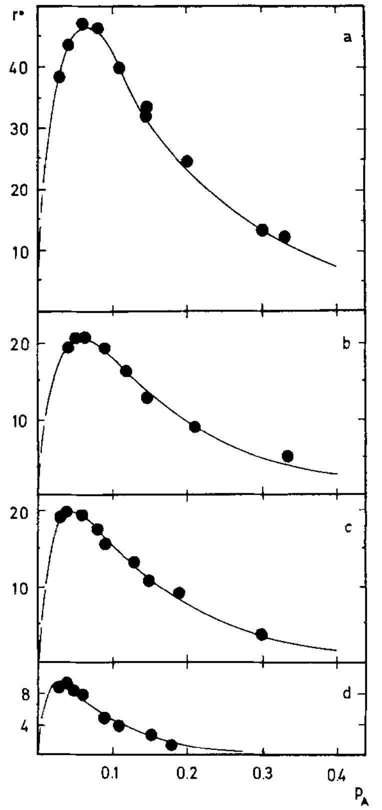


Fig. 4. Dependence of initial reaction rate of (a) 2-butanone, (b) 4-methyl-2-pentanone, (c) 3-methyl-2-butanone and (d) 3,3-dimethyl-2-butanone on partial pressure of ketones at 150°C over Rh catalyst; total pressure of reactants 1.0 atm; curves correspond to Eq. (4).

and the k, K_A and K_B values are shown in Table 2. The data obtained in the hydrogenation of the other aliphatic ketones on platinum and rhodium catalysts were treated using Eqs. (4) and (5) and inserting K_B values from Table 2. Results are summarized in Table 1. Since the relative values of k and K_A of homologous ketones with respect to acetone were found to be practically identical for Eqs. (4) and (5), only the values of kinetic constants using Eq. (4) are given here.

Effect of Structure of Aliphatic Ketones on Rate Constants and Adsorption Coefficients in Their Hydrogenation

Table 1 shows that on Pt and Rh catalysts the reactivity of alkylketones ($RCOCH_3$) decreases in the order R = $CH_3 > C_2H_5 > i\text{-}C_4H_9 > i\text{-}C_3H_7 > t\text{-}C_4H_9$, as has been found previously for the hydrogenation of aliphatic ketones in the liquid phase (*9–12*). The adsorption co-

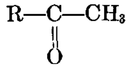
TABLE 2

Kinetic Constants of Acetone Calculated for Kinetic Eqs. (4) and (5) Describing Hydrogenation Over Pt- and Rh-Catalysts at 150°C (*14*)

Catalyst	Kinetic Eq. No.	k	K_A	K_B
Pt	4	22 636	3.7	0.01
Pt	5	39 800	4.0	0.01
Rh	4	4 025	3.9	0.25
Rh	5	5 600	5.1	0.28

efficients show an opposite trend on all metal catalysts. This fact is also in good agreement with the findings of Iwamoto, Yoshida, and Aonuma (*12*), who studied the hydrogenation of ketones in the liquid phase with Raney nickel catalyst.

For the quantitative expression of structure effects of ketones on their reactivity and adsorptivity, different types of Taft equations have been applied. These Eqs. (2)–(7) involving the operation of inductive and steric effects, were derived under the assumption that the hydrogenation proceeds through the carbonyl mechanism (*8*, *17*) and that the carbonyl group can be considered as being an adsorption or reaction center in the ketone molecule,



$$R{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

where R = CH_3, C_2H_5, i-C_3H_7, i-C_4H_9, t-C_4H_9.

$$\log K_A^{\mathrm{rel}} = \rho_a^* \sigma^*, \qquad (2)$$
$$\log K_A^{\mathrm{rel}} = \delta_a E_s, \qquad (3)$$
$$\log K_A^{\mathrm{rel}} = \rho_a^* \sigma^* + \delta_a E_s, \qquad (4)$$
$$\log k^{\mathrm{rel}} = \rho_r^* \sigma^*, \qquad (5)$$
$$\log k^{\mathrm{rel}} = \delta_r E_s, \qquad (6)$$
$$\log k^{\mathrm{rel}} = \rho_r^* \sigma_r^* + \delta_r E_s, \qquad (7)$$

where: $K_A^{\mathrm{rel}} = K_A^{\mathrm{alkylketone}}/K_A^{\mathrm{acetone}}$,

$k^{\mathrm{rel}} = k^{\mathrm{alkylketone}}/k^{\mathrm{acetone}}$.

The values of σ^* and E_s constants characterizing the structure of the alkyl group (R) were taken from the literature (*18*). Using the linear regression method, adsorption (ρ_a^*, δ_a) and reaction (ρ_r^*, δ_r) parameters and corresponding correlation coefficients ($\bar{R}$) were calculated for all types of Taft equations. The results are given in Tables 3 and 4. The values of the correlation coefficients indicate that in the hydrogenation of aliphatic ketones on copper the inductive effects play a predominant role. This fact is evident in the adsorption, as well as in the surface reaction. The adsorptivity and the reactivity of ketones on all the catalysts can be described well with Taft Eqs. (2) and (5), which express the function of the inductive effects in the hydrogenation. The graphical representation of these two equations is given in Figs. 5 and 6.

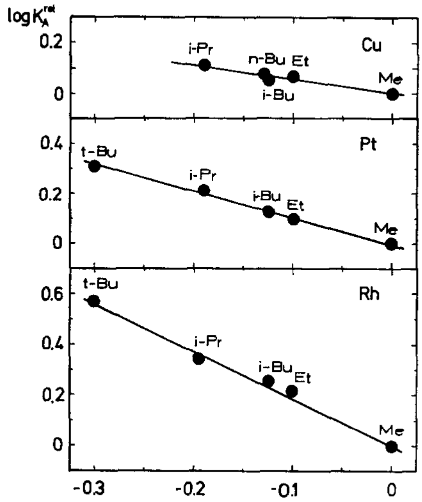


FIG. 5. Effect of structure of ketones ($RCOCH_3$) on adsorption coefficients in their hydrogenation over different metal catalysts at 150°C; expressed by Taft Eq. (2).

It is also evident from Table 3 that the adsorption parameters (ρ_a^*), [Eq. (2)] for all the catalysts are negative and increase from Cu to Pt and Rh. On the other hand, the reaction parameters (ρ_r^*) [Eq. (5)]

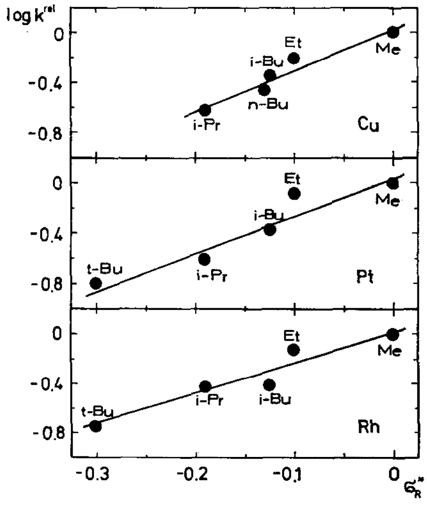


FIG. 6. Effect of structure of ketones ($RCOCH_3$) on reaction rates in their hydrogenation on different metal catalysts at 150°C; expressed by Taft Eq. (5).

TABLE 3

VALUES OF ADSORPTION PARAMETERS (ρ_a^*, δ_a) FOR HYDROGENATION OF ALIPHATIC KETONES ON Cu, Pt AND Rh CATALYSTS

Taft Eq. No.	Structure parameter	Cu[a]			Pt[b]			Rh[b]		
		ρ_a^*	δ_a	$\bar{R}$	ρ_a^*	δ_a	$\bar{R}$	ρ_a^*	δ_a	$\bar{R}$
2	σ^*	−0.52	—	0.986	−1.06	—	0.995	−1.84	—	0.996
3	E_s	—	−0.056	0.565	—	−0.15	0.849	—	−0.28	0.867
4	$\sigma^* + E_s$	−0.53	0.02	0.985	−1.08	0.01	0.995	−1.74	−0.02	0.996

[a] Calculated from adsorption coefficient of kinetic Eq. (1).

[b] Calculated from adsorption coefficient of kinetic Eq. (4).

are positive and their values decrease from Cu to Pt and Rh.

This agrees very well with Iwamoto, Yoshida and Aonuma (*12*), who also found negative values of adsorption parameters ($\rho_a^* = -0.78$) and positive values of reaction parameters ($\rho_r^* = 3.16$) for the hydrogenation of aliphatic ketones on Raney nickel using *n*-hexane as a solvent. Positive values of the reaction parameter (ρ_r^*) have been found also by other authors (*9, 10, 19*) for the hydrogenation of alkyl- or arylketones. However, quantitative comparison with our data has no importance because polar solvents, which strongly affect the values, have been used in the studies mentioned.

Mechanistic Concepts

The negative values of the adsorption parameter (ρ_a^*) of the Taft Eq. (2) indicate that the negative charge on the carbonyl group, which represents the adsorption center in the ketone molecule, increases with increasing electropositivity of the alkyl group; consequently, the adsorption ability of homologous ketones rises in the series from acetone to 2-butanone, 4-methyl-2-pentanone, 3-methyl-2-butanone and 3,3-dimethyl-2-butanone. One may therefore assume that the active sites on the surface of all the catalysts bear a charge opposite to the charge of the adsorption center of the ketone molecule. However, the reaction rate of the adsorbed ketone decreases with increasing electropositivity of the alkyl group attached to the carbonyl group. This fact can be explained under the assumption that adsorbed ketone molecules, as well as adsorbed hydrogen species, taking part in the rate limiting step of the surface reaction probably bear an electric charge of the same polarity. This mechanistic conception involving only the description of the action of electronic effects during the adsorption and the surface reaction of the ketone molecule does not exclude the presence of steric factors in these two processes, but changes in their effects for the series of compounds investigated are

TABLE 4

VALUES OF REACTION PARAMETERS (ρ_r^*, δ_r) FOR HYDROGENATION OF ALIPHATIC KETONES ON Cu, Pt AND Rh CATALYSTS

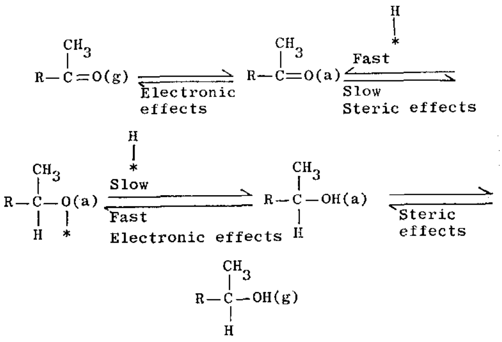
Taft Eq. No.	Structure parameter	Cu[a]			Pt[b]			Rh[b]		
		ρ_r^*	δ_r	$\bar{R}$	ρ_r^*	δ_r	$\bar{R}$	ρ_r^*	δ_r	$\bar{R}$
5	σ^*	3.36	—	0.966	2.90	—	0.952	2.53	—	0.958
6	E_s	—	0.37	0.567	—	0.45	0.856	—	0.44	0.954
7	$\sigma^* + E_s$	3.36	0.00	0.966	2.49	0.08	0.956	1.40	0.23	0.993

[a] Calculated from rate constants of kinetic Eq. (1).

[b] Calculated from rate constants of kinetic Eq. (4).

possibly too small to be detected in the Taft correlation.

It is interesting to note that steric effects were found to play a predominant role in the adsorption and in the surface reaction during the dehydrogenation of secondary alcohols of the type $RCH(OH)CH_3$ (where $R = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $i\text{-}C_4H_9$, $t\text{-}C_4H_9$) on Pt, Pd and Rh catalysts at 200°C (*8*). If we assume that the difference in the temperatures (150–200°C) at which hydrogenation and dehydrogenation were studied has no essential influence on the change in the operation of electronic or steric effects, then our results can be explained with a multi-step reaction mechanism, proposed by different authors (*12, 20*) and represented schematically as follows:



where (a) = adsorbed; (g) = gas.

Relation Between the Adsorption and Reaction Parameters of the Taft Equation and Characteristic Properties of Catalysts

In the dehydrogenation of alcohols (*8*) we found a relation between the adsorption and reaction parameters of the Taft equation and the *d*-character of the metals used as catalysts. Such relations also hold in the present case. As indicated by the data summarized in Table 5, values of adsorption parameters (ρ_a^*) decrease with increasing *d*-character of the metals. Reaction parameters (ρ_r^*) show the same trend.

Further it is interesting to note that values of adsorption and reaction parameters found by Iwamoto, Yoshida, and Aonuma (*12*) for Raney nickel (*d*-character 40%, $\rho_a^* = 0.78$, $\rho_r^* = 3.16$) agree very well with the values summarized in Table 5. The data in Table 1 indicate that characteristic properties of metals influencing the catalytic action are more important in the adsorption than in the reaction step. This fact was also observed in the dehydrogenation of alcohols (*8*) on metal catalysts.

TABLE 5
CORRELATION BETWEEN *d*-CHARACTER OF METALS AND ADSORPTION AND REACTION PARAMETERS OF TAFT EQS. (2) AND (5)

Metal	*d*-Character (%)	ρ_a^*	ρ_r^*
Cu	36	−0.52	3.36
Pt	44	−1.06	2.90
Rh	50	−1.84	2.53

Although correlations between the *d*-character of metals and rate data of various compounds in heterogeneously catalyzed reactions have often been published in the literature (*21–26*), the theoretical basis of such correlations has not yet been elucidated. For this reason it is necessary to regard the correlation between *d*-character and the parameters of the Taft equation as empirical only.

Appendix

If the observed correlation between the *d*-character of metals and the reaction or adsorption parameters of the Taft equation are to be checked quantitatively, it is necessary to use values calculated on the basis of rate constants or adsorption coefficients involving the same kinetic equation for all catalysts. In our case Eq. (4), which best describes the kinetic data on Pt and Rh catalysts, leads to a greater error, if used for the interpretation of experimental data obtained on the Cu catalyst. Nevertheless, the following values for the adsorption and reaction parameters on the Cu catalyst can be obtained: $\rho_a^* = -0.62$, $\rho_r^* = 3.32$. These values deviate relatively little from those given in Table 5, so that the previously mentioned trend remains valid at least qualitatively.

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