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Linear Free Energy Relationships in Heterogeneous Catalysis

IX. Kinetic Study of Catalytic Dehydrogenation of Cyclohexanes by the Pulse Technique

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The dehydrogenation of methyl-substituted cyclohexanes catalyzed by chromia–alumina and molybdena–alumina was studied by means of the pulse technique. In the case, where the rate is expressed as $v = \alpha\beta p/(1 + \alpha p)$, the relation between the conversion, x, and the maximum partial pressure, p_m, of a triangular pulse can be formulated as follows, under the ideal conditions:

$$\frac{xF}{2W} = \beta \frac{\alpha p_m - \ln(\alpha p_m + 1)}{\alpha p_m^2}.$$

By using this equation, α and β of all the reactants used were obtained at a few temperatures. From the fact that α increases with increasing temperature as well as from the results of some supplementary experiments, it is demonstrated that $\alpha\beta$ stands for the rate constant of the first hydrogen abstraction and β for that of the second one. It was found that $\alpha\beta$ varied remarkably with the reactants used and was correlated to the delocalizability, a quantum-chemical reactivity index, though β was almost invariant. Therefore, it is concluded that the slowest step is the dehydrogenation to cyclomonoolefin, where each of two hydrogens is abstracted stepwise, and that the first hydrogen abstraction from an original hydrocarbon determines the relative reactivity.

INTRODUCTION

In a previous paper (*1*), the authors reported a well-defined relation between the dehydrogenation rates of cyclohexanes and the delocalizability, i.e., a quantum-chemical reactivity index for hydrogen abstraction reactions. This relation is consistent with the hitherto proposed mechanism, where the step to cyclomonoolefin is the slowest.

In order to obtain a more universal information from a viewpoint of the LFER (Linear Free Energy Relationships) (*2*), it will be an effective approach to apply the LFER not only to the overall rate itself but also to each elementary step of any proposed mechanism. The study of the LFER and the kinetics, complemented by one another, may play an important role in the generalization of the LFER and thus makes possible the more precise understanding of catalysis.

On the kinetics of cyclohexane dehydrogenation over chromia–alumina, MacIver *et al.* (*3*) found the reaction to be first order in cyclohexane by using the mixed gas with hydrogen and argon. By taking into consideration all elementary steps of the reaction in nitrogen, Herington and Rideal (*4*) proposed a Langmuir-type rate equation.

The pulse technique (*1*) was employed in the present work in order to obtain easily the rate equations of various reactants at several temperatures and, moreover, on nearly fresh catalysts. An application of the pulse technique to the kinetic analysis of Langmuir-type rate equations is developed in the present work, which will expand the usefulness of the pulse technique to catalysis.

NOMENCLATURE

l	distance from the front edge of the pulse
t	time after the entrance into the catalyst bed
p_0	total pressure of the system
$h(t,l)$	molar fraction of the reactant at the point l at the time t
$p(t,l)$	partial pressure of the reactant $p(t,l) = p_0h(t,l)$
p_{m}	maximum partial pressure at the entrance of a catalyst bed
W	weight of a catalyst
F	flow rate of the carrier gas
t_0	contact time $t_0 = W/F$
x	conversion
α, β	constants

EXPERIMENTAL METHODS

Materials. All the reactants and the catalysts used are the same as those in the previous paper (*1*).

Procedures and apparatus. The procedures and the apparatus are also the same as those in the previous paper, except those mentioned in the following sections. The reactions were carried out between 375 and 450°C over Cr-1, and between 375 and 425°C over Mo-2–Na-1.

Mathematical treatment of experimental data. The pulse technique developed by Kokes *et al.* (*5*) had been considered to be restricted to first-order reactions for kinetic studies (*6*). However, Gaziev *et al.* (*7*) analyzed theoretically the relation between the pulse shape and the conversion in the case of zero- and second-order reactions as well as first-order reactions. Recently, Hattori and Murakami (*8*) have carried out a theoretical investigation of irreversible, reversible, and consecutive reactions of both first and *n*th orders in the case of a rectangular, a triangular, and an error function-shaped pulses. These methods supposed a linear adsorption isotherm and a surface reaction of the *n*th order. However, monomolecular reactions of *n*th order are generally considered to involve the first-order surface reaction with a nonlinear adsorption isotherm. In the present work, a treatment of the Langmuir-type kinetics, which had been widely applied to heterogeneous catalysis, is attempted under the following ideal conditions: (I) the shape of a pulse is approximated to be triangular throughout a catalyst bed; (II) the shape of a pulse is not disturbed through the catalyst bed; and (III) the change in the volume is negligible and that in the concentration is small during the course of the reaction. For a Langmuir-type rate equation, the rate is expressed for the pulse component at t and l as Eq. (1), under the condition II.

$$v = -\frac{dp(t,l)}{dt} = \frac{\alpha\beta p(t,l)}{1 + \alpha p(t,l)} = \frac{\alpha\beta p_0h(t,l)}{1 + \alpha p_0h(t,l)}. \qquad (1)$$

Equation (2) can be derived by integrating Eq. (1) with respect to t.

$$\frac{1}{\alpha}\ln\frac{h(t_0,l)}{h(0,l)} = -p_0[h(0,l) - h(t_0,l)] - \beta t_0. \qquad (2)$$

When the conversion is less than 10%, Eq. (3) holds as a good approximation. This approximation coincides with the condition III.

$$\ln\frac{h(t_0,l)}{h(0,l)} \simeq \frac{h(t_0,l)}{h(0,l)} - 1. \qquad (3)$$

On the other hand, the conversion should be formulated as follows.

$$x = \frac{\int p_0[h(0,l) - h(t_0,l)]\,dl}{\int p_0h(0,l)\,dl}. \qquad (4)$$

By using Eqs. (2) and (3), Eq. (4) is converted to the following relation.

$$x = \frac{\int[\alpha\beta p_0h(0,l)/1 + \alpha p_0h(0,l)]t_0\,dl}{\int p_0h(0,l)\,dl}. \qquad (5)$$

Under the condition I, $h(0,l)$ is composed of two linear functions of l crossing at $h = p_{\mathrm{m}}/p_0$ (Fig. 1). Finally, integration of

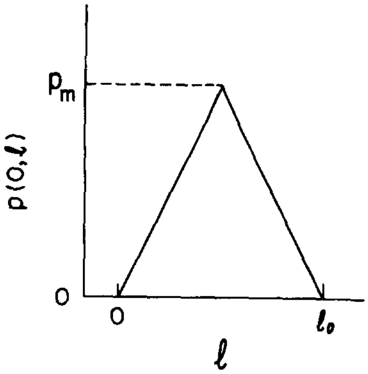

FIG. 1. Illustration of a triangular pulse.

Eq. (5) leads to the relation between x and p_m.

$$\frac{xF}{2W} = \beta \frac{\alpha p_m - \ln(\alpha p_m + l)}{\alpha p_m^2}. \qquad (6)$$

Since the left-hand side of Eq. (6) and p_m are obtained experimentally, the best values of α and β can be fitted by the nonlinear method of least squares. Variation of p_m can be realized by varying the pulse sizes, as mentioned below.

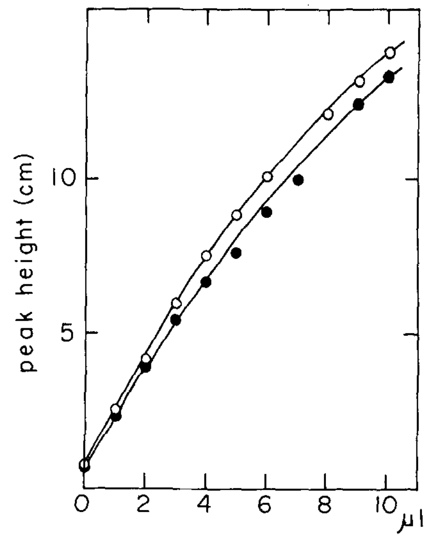

FIG. 2. Change in the maximum partial pressure with sample sizes: ○, without a catalyst bed; ●, after the passage of a catalyst bed at 450°; catalyst: Cr-1, 1.0 g.

Experimental procedures for the realization of the ideal conditions. A rapid evaporation at the instant of injection is preferred, in order to maintain the reproducibility, and consequently to give the pulse of the error function shape which is well approximated to a triangular pulse.

For the instantaneous evaporation, an evaporator of stainless steel kept at 300°, which was stoppered with a silicone rubber serum cap and was packed with metal gauze, was used. A Pyrex glass reactor (6-mm i.d.) was placed after the evaporator, and in the rear of the evaporator the whole tubing was sufficiently heated so that no condensation could occur. The dependence of the pulse shapes on the pulse sizes was examined with or without a catalyst bed. As shown in Fig. 2, the peak height increases almost linearly with increasing pulse sizes and, furthermore, the broadening of the pulses is negligible even in the presence of catalyst. Peak heights in the absence of catalyst can be regarded as those at the entrance of the catalyst bed. The peak heights corresponding to 1 to 10 μl for all the reactants used were measured, from which the maximum partial pressures were calculated.*

In the measurement of the conversion, the weight of catalyst was selected so that the conversion did not exceed 10%.

Prior to a run, 10 μl each of methylcyclohexane was injected 10 times to eliminate the uncertainty due to the initial marked fouling. In order to compensate the still remaining minor fouling, the pulse sizes were randomized as in the following man-

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[*] The maximum partial pressure, p_m, was calculated as follows. For the injection of 2.5 μl (this is 0.5 μl larger than the graduation of the microsyringe owing to the evaporation from the tip), the peak height recorded on the chromatogram was 4.1 cm and the half-width corresponded to 5.0 sec. Using the values of the flow rate at room temperature, 40 cm³/min, the density of cyclohexane, 0.77, the molecular weight, 84, and the relative sensitivity, 111, the maximum partial pressure of any reactant can be obtained for the peak height of h cm at the entrance to the catalyst bed at the total pressure of p_0.

$$p_m = \frac{(2.5 \times 10^{-3} \times 0.77/84) \times (22.4 \times 298/273)}{40 \times 5.0/60} \times \frac{h}{4.1} \times \frac{111}{S_R} \times p_0 = 4.55 \times p_0 \times h/S_R,$$

where S_R is the relative sensitivity of the reactant R.

ner, 4, 1.5, 3, 2, 2.5, 1, and 6 μl; moreover, the run of the aimed reactant was inserted between runs of methylcyclohexane.

RESULTS

Results wich the pulse technique. By using the observed conversions for various pulse sizes, the constants α and β were calculated according to Eq. (6) by the nonlinear method of least squares with a computer program named PRMT-1H. Examples of α' and β' are shown in Table 1, where α' and β' are the values of α and β for each run. The values of α' and β' thus obtained were normalized in respect of those of methylcyclohexane to eliminate the effect of the catalyst fluctuation. Examples of this normalization are given in Table 2, where α'(MCH) and β'(MCH) are the average values for the two measurements of methylcyclohexane. The average values of α'(MCH) and β'(MCH) for all the measurements at certain temperature were regarded as α and β of methylcyclohexane at that temperature, by which α' and β' of other reactants were normalized as Eq. (7).

$$\alpha = \alpha' \frac{\alpha(\mathrm{MCH})}{\alpha'(\mathrm{MCH})} \qquad \beta = \beta' \frac{\beta(\mathrm{MCH})}{\beta'(\mathrm{MCH})}. \tag{7}$$

The Arrhenius plots of normalized α, β, and $\alpha\beta$ are given in Figs. 3, 4, and 5, respectively, and both the activation energies and the pre-exponential factors are shown in Table 3. As is evident from Fig. 3, α increases with temperature, that is, α stands for a process involving an activation energy but not for an exothermicity in

TABLE 1

EXAMPLES OF α' AND β' CALCULATED BY THE NONLINEAR METHOD OF LEAST SQUARES

Catalyst: Cr-1; catalyst wt: 0.50 g; flow rate of carrier gas: 39 ml cm³/min; reaction temp: 450°C; total pressure: 1.43 atm. The percentages in the parentheses are the standard deviations.

Reactant (R)	Pulse size (μl)	p_m (atm)	Conversion (100x) (%)	$xF/2W$ (cm³/min g)
Methylcyclohexane	1	0.134	10.7	4.17
	1.5	0.179	10.0	3.90
	2	0.220	9.19	3.58
	2.5	0.262	8.88	3.46
	3	0.298	8.24	3.21
	4	0.364	7.95	3.10
	6	0.493	6.80	2.65
		α' = 3.36(8%), β' = 3.18(5%)		
Cyclohexane	1	0.144	7.80	3.04
	1.5	0.190	7.41	2.89
	2	0.236	6.55	2.55
	2.5	0.287	6.42	2.50
	3	0.328	6.23	2.43
	4	0.431	5.90	2.30
	6	0.620	4.90	1.91
		α' = 2.33(15%), β' = 3.11(10%)		
Methylcyclohexane	1	0.134	9.97	3.89
	1.5	0.179	9.11	3.55
	2	0.220	8.72	3.40
	2.5	0.262	8.08	3.15
	3	0.298	7.88	3.07
	4	0.364	7.05	2.75
	6	0.493	6.29	2.45
		α' = 3.58(6%), β' = 2.83(4%)		

TABLE 2

An Example of the Normalization of α and β Using Eq. (6)

Catalyst: Cr-1; reaction temp: 450°C.

Reactant (R)	α'	β'	α'(MCH)	β'(MCH)	α	β	$\alpha\beta$
Cyclohexane	2.33	3.11	3.47	3.01	2.46	2.91	7.2
trans-1,2-Dimethylcyclohexane	4.15	2.83	3.82	2.78	3.98	2.87	11.4
cis-1,2-Dimethylcyclohexane	4.40	2.87	3.37	2.53	4.78	3.20	15.3
1,3-Dimethylcyclohexane	3.88	2.91	3.76	2.45	3.78	3.35	12.7
1,4-Dimethylcyclohexane	3.87	4.03	4.16	3.32	3.40	3.42	11.6
1,3,5-Trimethylcyclohexane	4.21	4.13	3.38	2.80	4.56	4.16	19.0
Methylcyclohexane		av	3.66	2.82	3.66	2.82	10.3

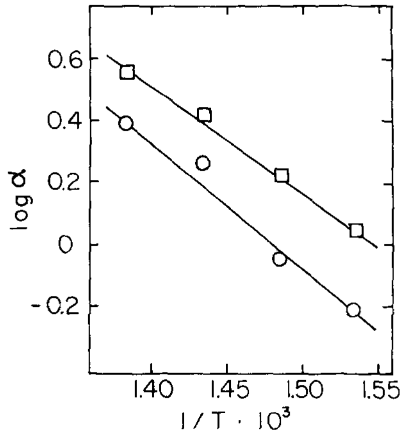


Fig. 3. Arrhenius plots for α: ○, cyclohexane; □, methylcyclohexane.

enthalpy change. This behavior is contrary to the ordinary meaning of a Langmuir-type rate equation. Furthermore, from Figs. 4 and 5, it is obvious that the difference among the reactants used are remarkable in $\alpha\beta$ but almost inperceptible in β. From the discussion of these features of the results, it is demonstrated below that $\alpha\beta$ is approximately equal to the rate constant of the first abstraction of hydrogen and β is to that of the second abstraction. Similar results were obtained for the runs of methylcyclohexane and *cis*-1,2-dimethylcyclohexane over Mo-2–Na-1.

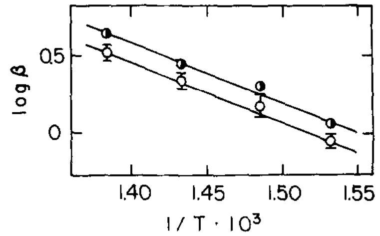


Fig. 4. Arrhenius plots for β: ◑, 1,3,5-trimethylcyclohexane; ○, the reactants except 1,3,5-trimethylcyclohexane.

Results with the continuous flow method. The results of the preliminary experiments with the continuous flow method are compared with those with the pulse technique. The apparatus was in most part the same as that used for the pulse technique. The cyclohexane feed was injected by a microfeeder at a constant rate. The results are well represented by a Langmuir-type rate equation as shown in Fig. 6, and the values of α at 475, 500, and 520° are 4.3, 4.5, and

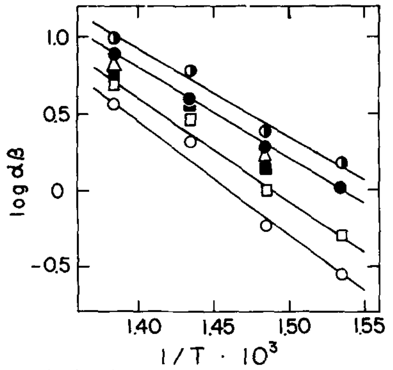


Fig. 5. Arrhenius plots for $\alpha\beta$: ○, cyclohexane; □, methylcyclohexane; ●, *cis*-1,2-dimethylcyclohexane; ■, *trans*-1,2-dimethylcyclohexane; △, 1,3- and 1,4-dimethylcyclohexane; and ◑, 1,3,5-trimethylcyclohexane.

TABLE 3

THE ACTIVATION ENERGIES AND THE PRE-EXPONENTIAL FACTORS OF $\alpha\beta$ AND β OF VARIOUS REACTANTS
Catalyst: Cr-1.

	$\alpha\beta$		β	
Reactant (R)	Activation energy (kcal/mole)	Pre-exponential factor	Activation energy (kcal/mole)	Pre-exponential factor
Cyclohexane	36.1	11.83	16.9	5.62
Methylcyclohexane	31.5	10.56		
cis-1,2-Dimethylcyclohexane	27.4	9.49		
1,3,5-Trimethylcyclohexane	26.5	9.34	16.9	5.74

5.5 atm^{-1}, respectively. This shows a qualitative agreement between both the technique in the rate equation as well as in the temperature effect on α. However, the value of the conversion divided by W/F is one third compared with that with the pulse technique. This will be an inevitable consequence due to a severe poisoning in the flow system.

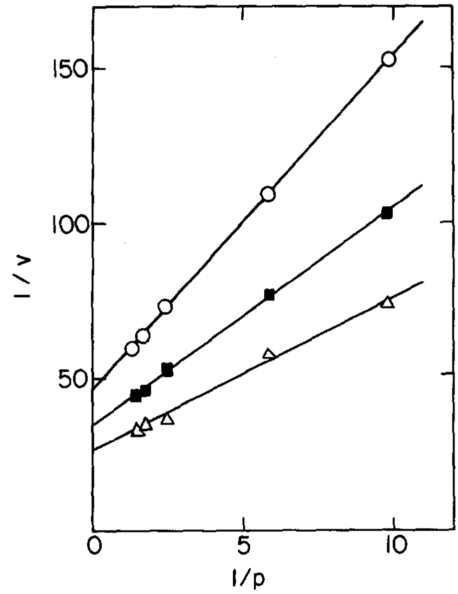


FIG. 6. Langmuir plots obtained by the continuous flow method: reactant: cyclohexane; catalyst: Cr-1; ○, 475°; ■, 500°; △, 520°.

DISCUSSION

The pressure dependence of reaction rates in catalysis have usually been measured by means of the continuous flow method or the circulating flow method, where the catalyst surface is considered to be in a stationary state, being covered with poisons, if any, or with strongly adsorbed molecules. On the other hand, in the case of the pulse technique, the catalyst is considered to be in a relatively fresh and transient state. Owing to this difference in the surface state, some discrepancy may result among these methods, not only in the conversions but also in the aspects of reactions. For example, the sites, on which reactants are enough strongly adsorbed, hardly contribute to the reaction in the continuous flow system. On the contrary, in the microcatalytic gas chromatographic system, the reactants, products or poisons are in most part desorbed during the pulse interval, thus the regenerated sites can contribute to the reaction at the passage of the next pulse. However, for a sufficiently long pulse, the aspect of the reaction may be regarded as almost identical with that in the continuous flow system. As another example, the reduction of the catalyst surface by reactants in catalytic oxidation will possibly bring about a similar discrepancy between these methods. Therefore, much precaution should be paid in order to draw some conclusion from the results with the pulse technique.

In the present work, the catalysts used were sufficiently reduced in a hydrogen flow prior to the reaction, and consequently there may probably be no change in the nature of the catalyst due to the evolved hydrogen. No inhibition by the produced aromatics is deduced from the fact that the conversion of methylcyclohexane for the pulse of the one-to-one mixture with benzene is approximately equal to that for the pulse of methylcyclohexane only. However, the activity of this kind of reactions generally declines owing to a small amount of coke. Such phenomena were observed also in the present work. The gradual fouling caused by successive pulses was observed, and the rate in the continuous flow method was much smaller than that in the microcatalytic gas chromatographic system. However, the activity decline due to a single pulse was not so large as to obscure the variation of the conversion with the pulse sizes. The error due to such an activity decline was avoided as mentioned earlier. From the above considerations, the obtained rate equation is not the spurious one due to the change of the catalyst surface, but an essential one which represents the pressure dependence in the transient fresh state.

The scheme of cyclohexane dehydrogenation to benzene has been considered to be a consecutive one through cyclohexene (*4*, *9*). In the present work, some supplementary experiments were carried out to establish a more detailed scheme. The dehydrogenation conversion of cyclohexane and cyclohexene under the same conditions are, respectively, 3 and 50%, which are qualitatively identical with the results by Herington and Rideal (*4*). This fact indicates that the step from cyclohexane to cyclohexene is approximately rate-determining. At the 50% conversion of cyclohexene to benzene, the cyclohexane produced through hydrogenation by evolved hydrogen or through disproportionation is only less than 5%. From this result, it is deduced that the backward reaction, where cyclohexene that is assumed as the reaction intermediate may be hydrogenated to cyclohexane, is negligible compared with the further reaction producing benzene. Therefore, the rates of cyclohexane dehydrogenation represents approximately the rates at which the two hydrogens are abstracted from cyclohexane.

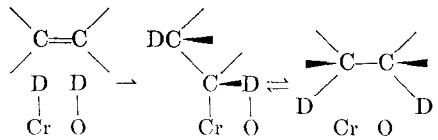
The following Langmuir-type rate equation was proposed by Herington and Rideal (*4*) as the approximate representation of the dehydrogenation rate.

$$\frac{1}{v} \sim \frac{1}{\beta}\left(1 + \frac{1}{\alpha p}\right). \tag{8}$$

This representation was confirmed in the present work by means of both the pulse technique and the continuous flow method. They obtained a considerably interesting result that α of cyclohexane was different from that of methylcyclohexane (1.2 and 1.9, respectively), whereas those reactants are very similar in β. This result, on which no comment was made by them, is coincident with that in the present work. These identical features of reactions with the two methods also confirm the reliability of the rate equation by means of the pulse technique.

On the other hand, however, Herington and Rideal concluded that α was the equilibrium constant of the physical adsorption, without examining the temperature dependence of α. In the present work, the result was obtained that α increased with temperature, which indicates that α can hardly be interpreted as an adsorption constant. Such a phenomenon was observed by Hughes and Hill in carbon monoxide oxidation over vanadium pentoxide (*10*).

From the studies of the H–D exchange reaction and the deuteration reaction of various hydrocarbons over chromia gel, Burwell *et al.* (*11*) proposed the main process as follows:



Taking this mechanism and the above features into consideration, the reaction scheme as in Eq. (9) is the most plausible for the dehydrogenation reaction.

$$C_6H_{12} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_{11}(a) + H(a) \xrightarrow{k_2} C_6H_{10}(a) + H_2 \xrightarrow{\text{fast}} C_6H_6 + 3H_2. \tag{9}$$

If the occupation of the dehydrogenation sites by the produced hydrogen atoms or molecules is neglected, Eqs. (10) and (11) can be derived for the coverage of adsorbed cyclohexyl radical and the overall rate, respectively, by using the method of stationary state.

$$\theta = \frac{k_1 p}{k_{-1} + k_2 + k_1 p}, \qquad (10)$$

$$v = \frac{k_1 k_2 p}{k_{-1} + k_2 + k_1 p} = k_2 \frac{[k_1/(k_{-1} + k_2)]p}{1 + [k_1/(k_{-1} + k_2)]p}. \qquad (11)$$

This equation is entirely identical with the equation obtained experimentally, where α stands for $k_1/(k_{-1} + k_2)$ and β for k_2. Therefore, the activation energy of α, $E_{A,\alpha}$, can be represented as Eq. (12),

$$E_{A,\alpha} = E_{A,1} - \frac{k_{-1}E_{A,-1} + k_2 E_{A,2}}{k_{-1} + k_2}, \qquad (12)$$

where $E_{A,1}$, $E_{A,-1}$ and $E_{A,2}$ are the activation energies of k_1, k_{-1} and k_2, respectively. Since, in general, $E_{A,1} < E_{A,-1}$, the conditions that $k_2 \gg k_{-1}$ and $E_{A,1} > E_{A,2}$ must be satisfied for the sake of the positive value of $E_{A,\alpha}$ in the wide temperature range. Under these conditions $\alpha\beta$ is nearly equal to k_1 and β is to k_2. Thus, the rates of the first and second abstraction of hydrogens can be calculated from the experimental data.

While k_1 varies remarkably with reactants, k_2 is almost invariable within experimental errors, as is shown in Fig. 4. This fact can be explained as follows. For example, the heats of reaction* for hydrogen abstraction from n-butane are the following:

$$n\text{-}C_4H_{10} \rightarrow n\text{-}C_4H_9 + H \qquad -98\ \text{kcal/mole} \qquad (13)$$

$$n\text{-}C_4H_9 \rightarrow 1\text{-}C_4H_8 + H \qquad -36 \qquad (14)$$

$$n\text{-}C_4H_{10} \rightarrow sec\text{-}C_4H_9 + H \qquad -94.5 \qquad (15)$$

$$sec\text{-}C_4H_9 \rightarrow 2\text{-}C_4H_8 + H \qquad -37 \text{ or } -38. \qquad (16)$$

There is large difference in the heats of reaction between (13) and (15), whereas there is little difference in the second abstraction of hydrogen [Eqs. (14) and (16)]. Hence, if the Polanyi rule is assumed, little difference of reactivity in the second hydrogen abstraction can be expected.

On the other hand, the observed rate should be represented as the sum of the reactivity of each ring hydrogen. This treatment gives the following Eq. (17) for the overall rate, which will be derived in the appendix.

$$v(R,T) = \frac{[\Sigma w(R,m)k_1^H(m,T)]k_2 p}{k_2 + [\Sigma w(R,m)k_1^H(m,T)]p}, \qquad (17)$$

where $w(R,m)$ and $k_1^H(m,T)$ are the number and the rate constant of the mth hydrogens of reactant R. The superscript H denotes the rate constant per one *hydrogen*. Thus, the overall value of k_1, which is identical with $\alpha\beta$, is expressed by Eq. (18).

$$k_1(R,T) = \Sigma w(R,m)k_1^H(m,T). \qquad (18)$$

Since Eq. (18) is equivalent to the relation between $v(R,T)$ and $v^H(m,T)$ derived in the preceding paper, the analysis of $k_1(R,T)$ from a viewpoint of the LFER is possible in the same way as in the preceding paper. A linear plots of the logarithm of $k_1^H(m,T)$ vs. $D_r^R(H^m)$, the delocalizability of the mth hydrogen, is shown in Fig. 7. Finally, $k_1^H(R,T)$ is expressed as the following equation in such an analogous

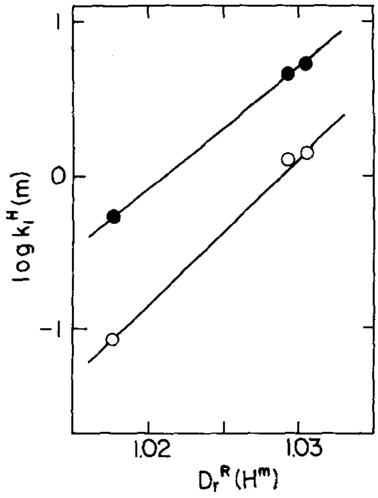


FIG. 7. The rate constant of the first hydrogen abstraction as a function of the delocalizability of hydrogen: catalyst: Cr-1; ○, 400°; ●, 450°.

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* Calculated from the values in Refs. (*12* and *13*). The heats of reaction for Eqs. (13) and (15) are approximated to be equal to the bond dissociation energies.

way as derived in the preceding paper (*1*).

$$k_1{}^{\mathrm{H}}(\mathrm{R},T) = k_1{}^{\mathrm{H}}(0,\infty) \exp[-E_{\mathrm{A}}(0)/RT]\Sigma w(\mathrm{R},m) \exp\{\gamma^D(1 - T/T_s)\Delta D_r{}^R(H^m)/RT\}, \quad (19)$$

where $k_1{}^{\mathrm{H}}(0,\infty)$ and $E_{\mathrm{A}}(0)$ are, respectively, the pre-exponential factor and the activation energy of a hypothetical hydrogen whose delocalizability is 1.0. T_s is the isokinetic temperature and γ^D is a constant independent of temperature. The calculated values of these four catalyst constants are given in Table 4.

TABLE 4

CALCULATED VALUES OF THE FOUR PARAMETERS

Catalyst: Cr-1.

$\log k_1{}^{\mathrm{H}}(0,\infty)$	14.7 ± 2.3
$E_{\mathrm{A}}(0)$ (kcal/mole)	49.3 ± 7.5
γ^D	906 ± 344
T_s(°K)	936 ± 123

In conclusion, the slowest step in dehydrogenation of cyclohexanes over chromia–alumina or molybdena–alumina is the dehydrogenation to cyclomonoolefin. In this step, each of two hydrogens is abstracted stepwise, and the first hydrogen abstraction from reactant determines the relative reactivity. There is also an agreement between the proposed reaction mechanism and the physical meaning of delocalizability, to which the reactivity of the first hydrogen abstraction is linearly correlated.

APPENDIX

As for the reactant R, where the number of mth hydrogens is $w(\mathrm{R},m)$, the rate equation can be derived in the following way. When the stationary state is assumed in the reaction scheme (9),

$$\frac{d\theta(m)}{dt} = w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)[1 - \Sigma\theta(m)]p - [k_{-1}{}^{\mathrm{H}}(m) + k_2{}^{\mathrm{H}}(m)]\theta(m) = 0, \quad (20)$$

where $\theta(m)$ is the coverage of cyclohexyl radical which has been produced with loss of one mth hydrogen. If $k_{-1}{}^{\mathrm{H}}(m) \ll k_2{}^{\mathrm{H}}(m)$ and $k_2{}^{\mathrm{H}}(m)$ is constant, then Eq. (21) holds by neglecting $k_{-1}{}^{\mathrm{H}}(m)$ and substituting $k_2{}^{\mathrm{H}}(m)$ by k_2.

$$w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)[1 - \Sigma\theta(m)]p - k_2\theta(m) = 0. \quad (21)$$

For example, the following equation holds for $m = 1$.

$$[w(\mathrm{R},1)k_1{}^{\mathrm{H}}(1)p + k_2]\theta(1) + w(\mathrm{R},1)k_1{}^{\mathrm{H}}(1)p \sum_{m' \neq 1} \theta(m') = w(\mathrm{R},1)k_1{}^{\mathrm{H}}(1)p. \quad (22)$$

When the ring hydrogens are classified into five, the coverage can be represented as follows, by solving the five simultaneous equations for m of 1 to 5.

$$\theta(m) = \frac{w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)p}{k_2 + [\Sigma w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)]p}. \quad (23)$$

As $v^{\mathrm{H}}(m) = k_2\theta(m)/w(\mathrm{R},m)$ and $v(\mathrm{R}) = \Sigma w(\mathrm{R},m)v^{\mathrm{H}}(m)$, Eq. (17′) can be derived.

$$v(R) = \frac{[\Sigma w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)]k_2p}{k_2 + [\Sigma w(\mathrm{R},m)k_1{}^{\mathrm{H}}(m)]p}. \quad (17')$$

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REFERENCES

1. HISHIDA, T., UCHIJIMA, T., AND YONEDA, Y., *J. Catal.* **11**, 71 (1968).

2. MOCHIDA, I., AND YONEDA, Y., *J. Catal.* **7**, 386 (1967).

3. BRIDGES, J. M., RYMER, G. T., AND MACIVER, D. S., *J. Phys. Chem.* **66**, 871 (1962).

4. HERINGTON, E. F. G., AND RIDEAL, E. K., *Proc. Roy. Soc., Ser. A* **190**, 289 (1947).

5. KOKES, R. J., TOBIN, H., AND EMMETT, P. H., *J. Amer. Chem. Soc.* **77**, 5860 (1955).

6. BASSETT, D. W., AND HABGOOD, H. W., *J. Phys. Chem.* **64**, 769 (1960).

7. GAZIEV, G. A., FILINOVSKII, B. Y., AND YANOVSKII, M. I., *Kinet. Katal.* **4**, 688 (1963).

8. HATTORI, T., AND MURAKAMI, Y., *J. Catal.* **10**, 114 (1968).
9. CIAPETTA, F. G., DOBRES, R. M., AND BAKER, R. W., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 6, Chap. 6. Reinhold, New York, 1958.
10. HUGHES, M. F., AND HILL, G. R., *J. Phys. Chem.* **59**, 388 (1955).
11. BURWELL, R. L., JR., LITTLEWOOD, A. B., CARDEW, M., PASS, G., AND STODDART, C. J. H., *J. Amer. Chem. Soc.* **82**, 6272 (1960).
12. BENSON, S. W., *J. Chem. Educ.* **42**, 502 (1965).
13. ROSSINI, F. D., *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." Carnegie Press, Pittsburgh, Pa., 1953.