JOURNAL OF CATALYSIS 11, 71–78 (1968)

Linear Free Energy Relationships in Heterogeneous Catalysis

VII. Reactivity of Ring Hydrogens in Catalytic Dehydrogenation of Cyclohexanes

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Received December 19, 1967

The rates of dehydrogenation of various methyl-substituted cyclohexanes catalyzed by chromia-alumina and molybdena-alumina were numerically analyzed in terms of the varying reactivities of the ring hydrogens classified into several groups, from the viewpoint of the LFER. It is demonstrated that the rate, $v(\mathrm{R},T)$, can be represented as the sum of the reactivities of the ring hydrogens, $v^{\mathrm{H}}(m,T)$, as $v(\mathrm{R},T) = \Sigma\, w(\mathrm{R},m)\, v^{\mathrm{H}}(m,T)$, where $w(\mathrm{R},m)$ is the number of mth hydrogens in a reactant R. The logarithm of the reactivity of ring hydrogen is, in turn, linearly related to the delocalizability, $D_r^{\mathrm{R}}(\mathrm{H})$, a quantum-chemical reactivity index for hydrogen abstraction reactions, as $\log v^{\mathrm{H}}(m,T) = \log v^{\mathrm{H}}(0,T) + \gamma(T)\Delta D_r^{\mathrm{R}}(\mathrm{H}^m)/2.303RT$, where $v^{\mathrm{H}}(0,T)$ is the reactivity of an imaginary hydrogen whose delocalizability is 1.0, and $\gamma(T)$ is a proportional constant. Furthermore, from the temperature dependence, $\gamma(T)$ has been correlated to the isokinetic temperature, T_s, and as the result the rates are expressed as follows:

$$v(\mathrm{R},T) = v^{\mathrm{H}}(0,\infty)\exp\left(\frac{-E_{\mathrm{A}}(0)}{RT}\right)\sum w(\mathrm{R},m)\exp\{\gamma^{\mathrm{D}}(1 - T/T_s)\Delta D_r^{\mathrm{R}}(H^m)/RT\}$$

where γ^{D} is a constant independent of temperature. Thus, the rate of dehydrogenation of any reactant at any temperature can be calculated with the knowledge of delocalizabilities inherent to ring hydrogens and four parameters characteristic for a catalyst, i.e., $v^{\mathrm{H}}(0,\infty)$, $E_{\mathrm{A}}(0)$, γ^{D}, and T_s. This equation is in accordance with the reaction scheme where the dehydrogenation to monoolefin is the slow step.

INTRODUCTION

The studies of LFER (Linear Free Energy Relationships) in heterogeneous acid catalyses such as dealkylation and isomerization have been carried out by Mochida and Yoneda (*1*) and Matsumoto, Take, and Yoneda (*2*); this approach has been proved to be effective to predict reaction rates and selectivities as well as to ascertain their reaction schemes.

The intention of the present paper is to find the LFER in the field of heterogeneous oxidation–reduction catalysis. Among the three categories of variables that may represent the reactivity of a reactant (*3*), the quantum-chemical approach was applied in the case of dehydrogenation of cyclohexanes over oxide catalysts.

In 1947, Herington and Rideal (*4*) studied in detail the kinetics and mechanism of this reaction over chromia-alumina and presented a theory concerned with the relative activation energies for various reactants. However, their theory became obsolete in view of present physical organic chemistry, which has progressed remarkably during these 20 years. Balandin *et al.* reported the dehydrogenation of alkylbenzenes (*5*), alkylcyclohexanes (*6*), and alcohols (*7*) over an oxide catalyst; Ritchie and Nixon (*8*) recently obtained rates and activation energies of dehydrogenation of cyclohexanes over platinum on alumina. Their results, however, have not yet been explained quantitatively.

The data of Herington and Rideal are restricted to the relative rates and activation energies over chromia-alumina. In the present work, absolute rate values are obtained on relatively fresh surfaces of chromia-alumina and molybdena-alumina so that the parameters introduced in the present paper will be correlated to the nature of catalysts in the future study. The data are analyzed numerically by using the delocalizability, a quantum-chemical reactivity index proposed by Fukui *et al.* (*9*) for abstraction reactions and applied further to heterogeneous catalysis by Mochida and Yoneda (*3*). In a succeeding paper, the relative rate constants will be interpreted in connection with the reaction scheme.

EXPERIMENTAL

Materials. The reactants used are listed in Table 1. Cyclohexane and methylcyclohexane were spectrograde reagents and the other cyclohexanes were guaranteed reagents from the Tokyo Kasei Co., except 1,3,5-trimethylcyclohexane. The last was synthesized from gas chromatographically pure mesitylene by hydrogenation over platinum (5%) on charcoal at 200° and contained less than 0.2% of mesitylene.

TABLE 1

PRE-EXPONENTIAL FACTORS AND ACTIVATION ENERGIES FOR THE DEHYDROGENATION OF CYCLOHEXANES OVER Cr-1 AND Mo-2-Na-1

	Cr-1			Mo-2-Na-1		
Reactants	$\log v(R, \infty)$	$E_A(R)_{obs}$ (kcal/mole)	$E_A(R)_{calc}$ (kcal/mole)	$\log v(R, \infty)$	$E_A(R)_{obs}$ (kcal/mole)	$E_A(R)_{calc}$ (kcal/mole)
1. Cyclohexane	7.74	23.8	23.8	8.66	24.2	24.9
2. Methylcyclohexane	6.73	20.2	19.9	8.73	24.0	22.0
3. *trans*-1,2-Dimethylcyclohexane	6.24	18.4	—	8.73	24.0	—
4. *cis*-1,2-Dimethylcyclohexane	5.92	17.0	17.1	7.73	20.1	20.1
5. 1,3-Dimethylcyclohexane	6.15	17.9	17.7	8.26	22.2	20.6
6. 1,4-Dimethylcyclohexane	6.15	17.9	17.7	8.26	22.2	20.6
7. 1,3,5-Trimethylcyclohexane	5.74	16.0	16.2	7.50	19.2	19.7

Chromia-alumina (Cr-1)* was Houdry Type A dehydrogenation catalyst and was used after being ground to a powder of 60 to 150 mesh size. Molybdena-alumina (Mo-2-Na-1)† was originally the Nalco polymerization catalyst (Mo-2); the catalyst used was prepared by impregnation with a solution of sodium nitrate, dried, and calcined at 450° in air. It was reduced further in hydrogen at 450° for 4 hr and the content of sodium ion was 0.11 wt % by analysis.

Tank hydrogen and helium were passed through an activated copper column at 180° and dried with a Dry Ice–ethanol trap and magnesium perchlorate.

Procedure. Before the reaction, Cr-1 and Mo-2-Na-1 were reduced in a hydrogen flow at 530° for 4 hr and 450° for 3 hr, respectively. The microcatalytic technique (*1*) was applied, since it is suitable for a rapid measurement of reaction rates of a series of reactants over a nearly fresh catalyst. The amount of catalyst (0.27 to 2.0 g) was selected so that the conversion did not exceed 20%. The cyclohexane feed, usually 2 μl, was injected into the carrier gas as a pulse through a serum cap at the top of the reactor and both the unchanged reactant and the products from the reactor were analyzed by a gas chromatograph attached directly to the reactor. An analyzing column packed with Diasolid M coated with tricresylphosphate (10%, the Nippon Chromato Ind. Co.) was used at 95° to 135°. The reaction temperature was 400° to 500° and 350° to 425° for Cr-1 and Mo-2-Na-1, respectively. Helium was used

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* About 20% Cr_2O_3 on γ-Al_2O_3; surface area, about 70 m^2/g.

† 20.7% MoO_3 on γ-Al_2O_3; surface area, 370 m^2/g.

as the carrier gas for the reaction at the flow rate of 40 ml/min.

The rate was calculated according to the following equation in units of ml/min g,

$$v(\mathrm{R},T) = \frac{(\text{conversion})}{(W/F)} \tag{1}$$

where F is the flow rate of the carrier gas and W is the weight of the catalyst.

RESULTS AND DISCUSSION

The reaction product of each alkylcyclohexane was mainly the corresponding alkylbenzene; a small amount of cycloolefin was detected in the reaction over Cr-1, whereas no cycloolefin was found and several percent of the product was the isomerized alkylbenzenes over Mo-2-Na-1. Prior to the rate measurements, a certain amount of cyclohexane or methylcyclohexane was injected to stabilize the catalyst, since the initial decrease of the catalytic activity was remarkable, especially for Mo-2-Na-1. In order to eliminate the effect due to the gradual fouling, the *round-trip* procedure was adopted. The seven reactants were injected in the order given in Table 1, from cyclohexane to 1,3,5-trimethylcyclohexane, then the procedure was repeated in the reverse order. The average of the two rate values was regarded as the rate at that temperature; after 14 pulses, the activity decreased by 10% to 20%.

The Arrhenius plots for all the seven reactants over Cr-1 and Mo-2-Na-1 are shown in Figs. 1 and 2, respectively. The activation energies, $E_A(\mathrm{R})$, and the pre-exponential factors, $v(\mathrm{R},\infty)$, are listed in Table 1. Clearly the compensation effect is recognized.

The dehydrogenation of cyclohexanes has been considered to proceed through a stepwise abstraction of ring hydrogens, where the formation of cyclomonoolefin is the rate-determining step (*4, 10*). Hence, their reactivities are probably to be determined by the reactivity of hydrogen abstraction. As is evident from Table 1, both the activation energy and the pre-exponential factor decrease with the number of methyl groups in the ring. This trend suggests that

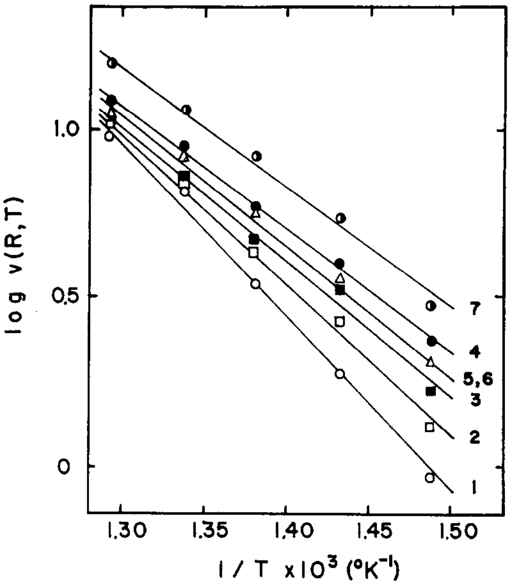


FIG 1. The Arrehenius plots for dehydrogenation of cyclohexanes over Cr-1: 1, ○, cyclohexane; 2, □, methylcyclohexane; 3, ■, *trans*-1,2- dimethylcyclohexane; 4, ●, *cis*-1,2-dimethylcyclohexane; 5,6, △, 1,3- and 1,4-dimethylcyclohexane; 7, ◐, 1,3,5-trimethylcyclohexane.

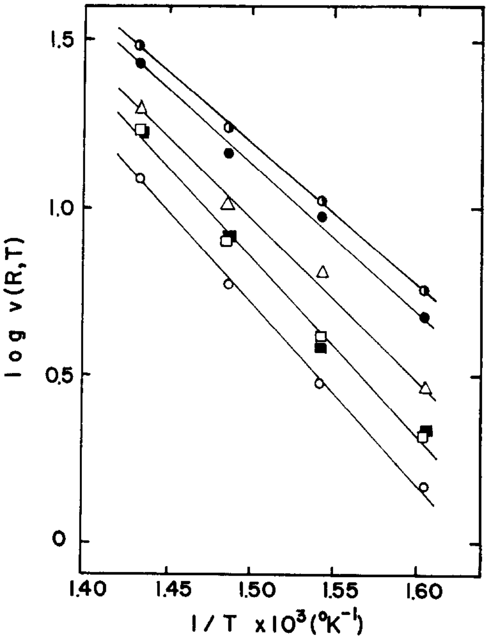
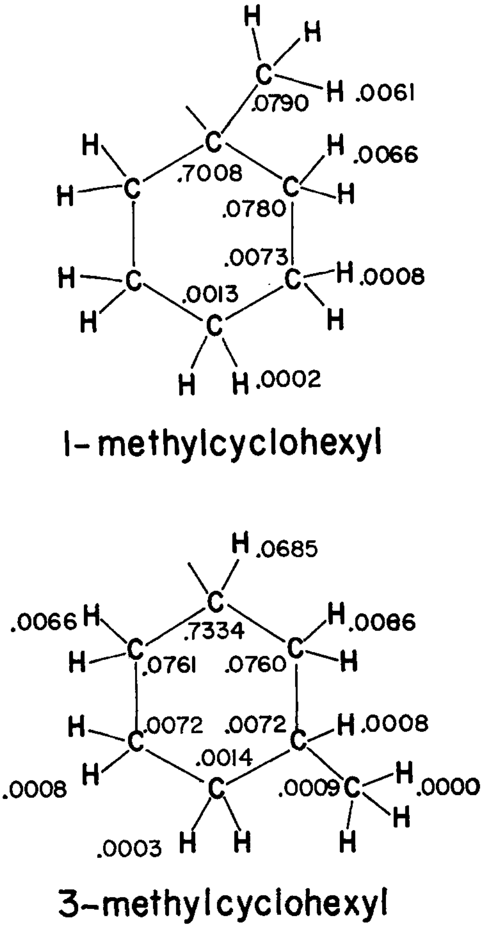


FIG. 2. The Arrhenius plots for dehydrogenation of cyclohexanes over Mo-2-Na-1. Symbols are the same as in Fig. 1.

the tertiary hydrogens are more reactive compared with the secondary ones. It is well known that the reactivity of hydrogen decreases in the order tertiary, secondary, and primary in various homogeneous reactions of saturated hydrocarbons, e.g., oxidation and halogenation, where a C–H bond splitting is considered to be homolytic (*11*). Since typical acid catalysts like silica-alumina scarcely have any catalytic activity for dehydrogenation, this reaction is considered to proceed through a radical mechanism rather than through a carbonium ion mechanism.

Previously, Herington and Rideal (*4*), who observed the relative rates for the dehydrogenation of cyclohexanes by means of the competitive reaction method, obtained a linear relationship between the relative activation energies and the numbers of the resonance structures for biradicals which were assumed as the intermediates. As regards a radical resulting from a saturated compound, however, the odd electron is much more highly localized compared with a radical of a conjugated hydrocarbon, hence the number of resonance structures of such a radical should not be directly connected to the stabilization energy. As concerns this point, Fukui *et al.* (*12*) found, by the use of the simple LCAO–MO method, that the odd electron densities in various alkyl radicals rapidly decrease with the distance from the unpaired hybridized orbital. In the present work, the distributions of the odd electron density for 1-methylcyclohexyl and 3-methylcyclohexyl radicals were calculated by using the method proposed by Fukui *et al.* (*9*). The result is shown in Fig. 3. Herington and Rideal preferred 3-methylcyclohexyl rather than 1-methylcyclohexyl radical as the most stable monoradical from methylcyclohexane on the basis of the resonance structures. However, Fig. 3 indicates that the latter radical is less localized in respect to the odd electron density and, as a result, is formed more preferentially. Thus, the theory proposed by them may be far from the concept of the present time.



1-methylcyclohexyl

3-methylcyclohexyl

FIG. 3. The odd electron distributions of 1-methylcyclohexyl and 3-methylcyclohexyl radicals.

As is evident from Figs. 1 and 2, the difference in the rates among these cyclohexanes is not so large that it is not attributable only to the difference in the number of tertiary hydrogens. Therefore, the observed rates should be represented as the sum of the contribution from each of ring hydrogens, which are tentatively classified into three groups according to the type of the hydrogen as shown in Case I of Fig. 4. The observed rate of a reactant R is represented as the following equation,

$$v(\mathrm{R},T) = \Sigma w(\mathrm{R},m)v^{\mathrm{H}}(m,T) \qquad (m = 1 \text{ to } 3) \tag{2}$$

where $v^{\mathrm{H}}(m, T)$ is the rate of one of the mth hydrogens at temperature T; $w(\mathrm{R}, m)$ is the number of mth hydrogens in the ring of the reactant R, and is given for each reactant in Table 2.

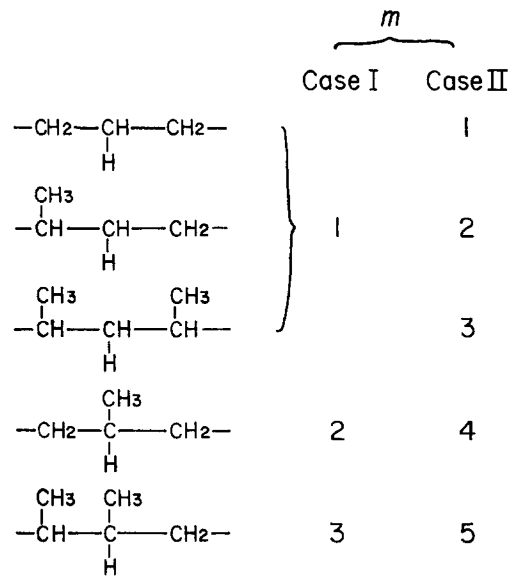


Fig. 4. The classification of ring hydrogens into (I) the three groups, and into (II) the five groups.

No steric hindrance was assumed in the derivation of Eq. (2). However, the lower reactivity and higher activation energy of *trans*-1,2-dimethylcyclohexane compared with *cis*-1,2-dimethylcyclohexane suggests that the two methyl groups of the former may hinder their two neighboring tertiary hydrogens from being abstracted, whereas those of the latter may not suffer from any steric hindrance. As for the other reactants, the hindrance by the methyl groups may scarcely have any effect on the rates since the neighboring hydrogens are secondary and consequently much less reactive. After this consideration, *trans*-1,2-dimethylcyclohexane was excluded, as an exception, from the following analysis.

Since Eq. (2) holds as to the six reactants except for *trans*-1,2-dimethylcyclohexane, the estimation of the three unknown values, $v^{\mathrm{H}}(1,T)$ through $v^{\mathrm{H}}(3,T)$, is possible by the method of least squares. This calculation provides satisfactory agreement between the calculated and the observed rate values.

The delocalizability, a quantum-chemical reactivity parameter for saturated compounds, is a measure of the stabilization energy due to the interaction between the electron of the hydrogen to be abstracted and the electron of the attacking radical (*9*). In the case of heterogeneous oxidation–reduction catalysis, a surface site can be regarded as an attacking radical (*3*). The delocalizability, $D_r^{\mathrm{R}}(\mathrm{H}^m)$, of the *m*th hydrogen in these cyclohexanes was computed according to the simple LCAO–MO method just as was proposed by Fukui *et al.* (*9*); the computed delocalizabilities are presented in Fig. 5. They are also summarized in Table 3 according to the type of the ring hydrogen.

A linear relationship between the logarithm of thus calculated rate of each hydrogen, $\log v^{\mathrm{H}}(m,T)$, and its delocalizability is revealed to be established as shown in Fig. 6 This relationship can be represented as Eq. (3),

$$\log v^{\mathrm{H}}(m,T) = \gamma(T)\Delta D_r^{\mathrm{R}}(\mathrm{H}^m)/2.303RT + \log v^{\mathrm{H}}(0,T) \quad (3)$$

where $v^{\mathrm{H}}(0, T)$ is the hypothetical rate of an imaginary hydrogen whose delocalizability is equal to 1.0, and $\gamma(T)$ is a proportionality constant.

TABLE 2

The Numbers of *m*th Hydrogens[a] in the Ring of Various Cyclohexanes

	m							
	Case I			Case II				
Reactants	1	2	3	1	2	3	4	5
Cyclohexane	12	0	0	12	0	0	0	0
Methylcyclohexane	10	1	0	6	4	0	1	0
1,2-Dimethylcyclohexane	8	0	2	4	4	0	0	2
1,3-Dimethylcyclohexane	8	2	0	2	4	2	2	0
1,4-Dimethylcyclohexane	8	2	0	0	8	0	2	0
1,3,5-Trimethylcyclohexane	6	3	0	0	0	6	3	0

[a] Ring hydrogens are classified into (I) the three groups, and into (II) the five groups.

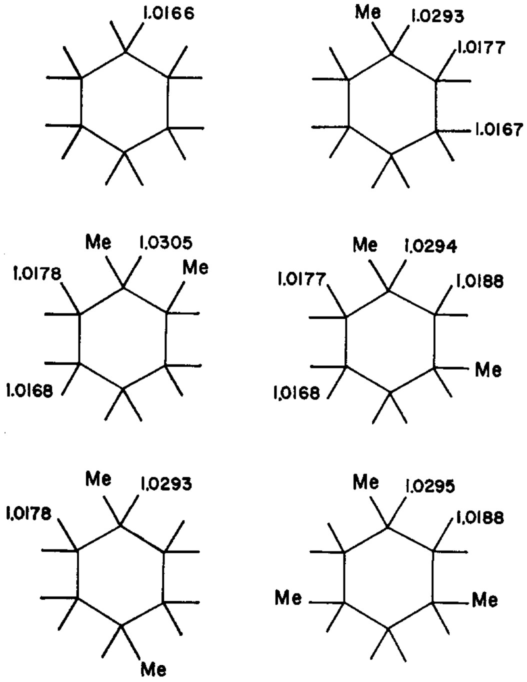


FIG. 5. The delocalizabilities of ring hydrogens of cyclohexanes.

In the preceding analysis, the classification of hydrogens into more than three groups was practically meaningless owing to the fewer degrees of freedom, whereas it becomes practical by the introduction of Eq. (3). The ring hydrogens were classified into five groups according to the values of delocalizability (Case II of Fig. 4) and the two parameters, $\gamma(T)$ and $v^{\mathrm{H}}(0,T)$, were obtained from Eqs. (3) and (4) by the nonlinear method of least squares with a computer program named PRT1H2.

$$v(\mathrm{R},T) = \Sigma w(\mathrm{R},m)v^{\mathrm{H}}(m,T) \qquad (m = 1 \text{ to } 5) \tag{4}$$

As in the previous case, a satisfactory agreement between the calculated and the observed rates was found, as shown in Fig. 7. However, the calculated values of cyclohexane and 1,3,5-trimethylcyclohexane are almost always lower than their observed ones and the reverse is the case for methylcyclohexane and 1,3- and 1,4-dimethylcyclohexanes. This fact may either be ascribed to any deficiency of the simple LCAO–MO method or be interpreted in terms of a certain steric effect.

TABLE 3
THE DELOCALIZABILITY OF *m*TH HYDROGEN

Case	m	$D_r(\mathrm{H}^{\mathrm{R}m})$
I	1	1.0166–1.0188
	2	1.0293–1.0295
	3	1.0305
II	1	1.0166–1.0168
	2	1.0177–1.0178
	3	1.0188
	4	1.0293–1.0295
	5	1.0305

The values of $\gamma(T)$ have a linear relationship to the temperature as shown in Fig. 8. Because $\gamma(T)$ should be equal to zero at the isokinetic temperature, T_s, this relationship can be reduced to

$$\gamma(T) = \gamma^{\mathrm{D}}(1 - T/T_s) \tag{5}$$

where γ^{D} is a proportional constant independent of temperature. By substituting Eq. (5) into Eq. (3), the pre-exponential factor and the activation energy of $v^{\mathrm{H}}(m,T)$ are represented as

$$\log v^{\mathrm{H}}(m,\infty) = \log v^{\mathrm{H}}(0,\infty) - \gamma^{\mathrm{D}}\Delta D_r{}^{\mathrm{R}}(\mathrm{H}^m)/2.303RT_s \tag{6}$$

$$E_{\mathrm{A}}(m) = E_{\mathrm{A}}(0) - \gamma^{\mathrm{D}}\Delta D_r{}^{\mathrm{R}}(\mathrm{H}^m) \tag{7}$$

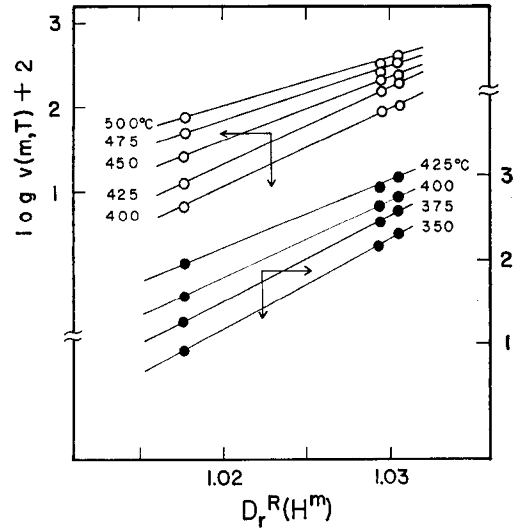


FIG. 6. The relationship between the delocalizability and the reactivity of *m*th hydrogen. Catalyst: ○, Cr-1; ●, Mo-2-Na-1.

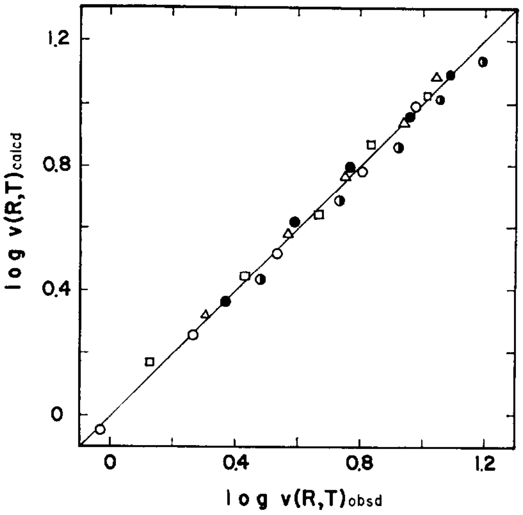


FIG. 7. Observed and calculated rates over Cr-1. Symbols are the same as in Fig. 1. Reaction temperature: 400° to 500°C.

where $v^{\mathrm{H}}(0,\infty)$ and $E_{\mathrm{A}}(0)$ are, respectively, a hypothetical pre-exponential factor and an activation energy of an imaginary hydrogen whose delocalizability is 1.0. Thus the activation energy for the abstraction of ring hydrogens from cyclohexanes by oxide catalysts is linearly related to the delocalizability. Equation (7) just corresponds with the relation proposed by Fukui *et al.* for homogeneous gas-phase reactions *(12)*.

By summarizing Eqs. (4), (6), and (7), the rate, $v(\mathrm{R},T)$, can be reduced to the following equation, as

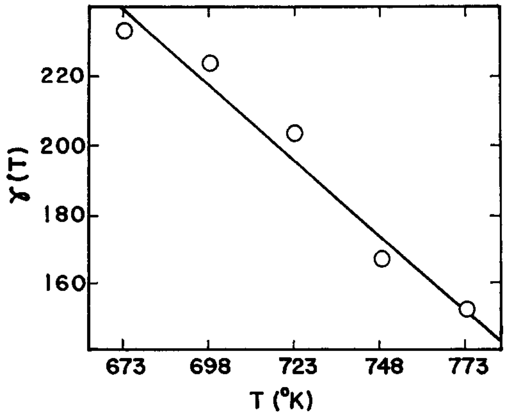


FIG. 8. Temperature dependence of $\gamma(T)$. Catalyst: Cr-1.

$$v(\mathrm{R},T) = v^{\mathrm{H}}(0,\infty)\exp\left[\frac{-E_{\mathrm{A}}(0)}{RT}\right] \times \sum w(\mathrm{R},m)\exp\left\{\gamma^{\mathrm{D}}\left(1-\frac{T_s}{T}\right) \times \frac{\Delta D_r{}^{\mathrm{R}}(\mathrm{H}^m)}{RT}\right\} \tag{8}$$

The calculation of this equation by the nonlinear method of least squares with a computer program named PRT1H5 was carried out with sufficient degrees of freedom, since the number of data is 24 or 30 (the number of reactants times the number of reaction temperatures) and that of unknown parameters is 4. The calculated values of four parameters, $v^{\mathrm{H}}(0,\infty)$, $E_{\mathrm{A}}(0)$, γ^{D}, and T_s, are tabulated in Table 4 with their standard errors. These parameters should have characteristic values depending on the combination of a catalyst and a type of reactions. The values of γ^{D} and T_s for Mo-2-Na-1 have large standard errors, but are not meaningless. The larger value of γ^{D} for Cr-1 suggests that Cr-1 abstracts ring hydrogens more selectively than Mo-2-Na-1. The calculated values of $v(\mathrm{R},T)$ according to Eq. (8) agree with the observed values as satisfactorily as in Fig. 7.

TABLE 4
CALCULATED VALUES OF THE FOUR PARAMETERS

Catalyst	Cr-1	Mo-2-Na-1
$\log v^{\mathrm{H}}(0,\infty)$	10.3 ± 1.2	10.1 ± 2.2
$E_{\mathrm{A}}(0)$ (kcal/mole)	36.0 ± 4.1	32.6 ± 7.3
γ^{D}	732 ± 188	460 ± 372
T_s(°K)	992 ± 93	1290 ± 1000

Evidently from Eq. (8), $v(\mathrm{R},T_s)/\Sigma w(\mathrm{R},m)$ is independent of R. Therefore, T_s should coincide with the isokinetic temperature T'_s, derived from the plot of $\log v(\mathrm{R},\infty)/\Sigma w(\mathrm{R},m)$ vs. $E_{\mathrm{A}}(\mathrm{R})$ approximately, but not strictly since $v(\mathrm{R},\infty)$ and $E_{\mathrm{A}}(\mathrm{R})$ vary with the reaction temperature according to Eq. (8). For Cr-1, T'_s is 912°K and for Mo-2-Na-1 it is 978°K. The coincidence between T_s and T'_s is not excellent but is bearable.

On the other hand, the overall activation energy, $E_A(\mathrm{R})$, should be the weighted mean of $E_A(m)$'s, as is given in Eq. (9).

$$E_A(\mathrm{R}) = \Sigma w(\mathrm{R},m)v^{\mathrm{H}}(m,T)E_A(m)/\Sigma w(\mathrm{R},m)v^{\mathrm{H}}(m,T) \quad (9)$$

where T is the intermediate reaction temperature. In Table 1 are presented the calculated activation energies, which coincide well with the observed values.

In conclusion, in spite of the minor disagreement between the observed and the calculated values, the rate and the activation energy of the catalytic dehydrogenation of cyclohexanes can be numerically interpreted on the following grounds; (1) the observed rate is attributable to the summation of the reactivities of all the hydrogens in the ring and (2) the logarithm of the reactivity of hydrogen is linearly related to its delocalizability.

The additional supports of this analysis are proved by the following interpretation of the data observed by the other researchers. The data by Herington and Rideal (*4*) were analyzed successfully in quite the same way as shown in Fig. 9. Also the fact that isopropylbenzene is dehydrogenated twice as fast as ethylbenzene (*5*) may be explained in terms of the larger delocalizability of the former. However, the reactivity pattern over platinum on alumina by Ritchie and Nixon (*8*) is different from that by the present authors; a possible, large steric hindrance by methyl groups over platinum on alumina, as was pointed out by them, may explain this discrepancy.

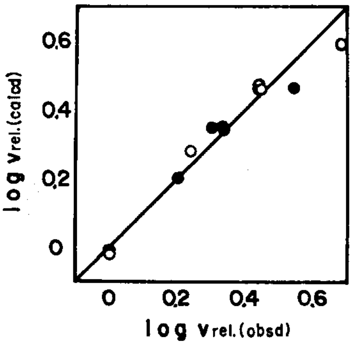


FIG. 9. Observed and calculated relative rates over chromia-alumina (Herington and Rideal). Reaction temperature: ○, 400°C; ●, 450°C.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Yasukazu Saito, Dr. Isao Mochida, and other colleagues for their valuable suggestions and discussions and Mr. Koichiro Kurokawa for the preparation of the modified molybdena-alumina catalysts. They are also indebted to the Furukawa Chemical Industries Co. for supplying the molybdena-alumina catalyst and to the Houndry Process Corp. and Nissho Trading Co. for the sample of chromia-alumina. The quantum-chemical computations were carried out on an HITAC 5020E at the Computer Center of the University of Tokyo.

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