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Linear Free Energy Relationships in Heterogeneous Catalysis

V. An Application of Quantum Chemical Reactivity Indexes to Heterogeneous Catalysis*

ISAO MOCHIDA AND YUKIO YONEDA

From the Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, Japan

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An application of quantum chemical reactivity indexes is tried to find variables controlling the reactant effect in the LFER (Linear Free Energy Relationships) of heterogeneous systems. As examples, the reaction of halomethanes with solid acids and the catalytic dehydrogenation of alcohols on alumina-supported metal catalysts were analyzed with the aid of the simple LCAO-MO method. The delocalizability, a reactivity index for saturated compounds, was adopted for these reactions; that of halogen radical abstraction for halomethanes and that of α-hydrogen radical abstraction for alcohols. The correlations between the delocalizability and the kinetic data of these reactions, such as the rates and the activation energies, are satisfactory. The quantum chemical reactivity indexes are proved useful because they are semiempirical ones obtainable by calculations alone. The mechanisms of these reactions are briefly discussed on the basis of these reactivity indexes.

INTRODUCTION

A survey of the δ_R effect, the reactant effect, in the LFER (Linear Free Energy Relationships) of heterogeneous catalysis is not only useful for the estimation of the kinetic data such as the reaction rates and the activation energies of homologous reactions, but is also valuable as an approach to the elucidation of the reaction mechanism. At the same time, parameters in the LFER equations for the δ_R effect may give the characteristics of the catalyst in numerical values.

It was successful in previous work (*1*) to obtain the LFER in heterogeneous catalysis, using as δ_R variables the thermodynamic data, the empirical variables such as the Hammett σ, or the reaction rates of homologous reactions. The thermodynamic data concerned with the rate-determining steps of various catalyses, such as $\Delta H_C{}^+(R_1)$ in the dealkylation reactions cannot always be applicable because of their scantiness for unstable species. Even the Hammett σ or the Taft σ^* may not always be applicable owing to the lack of the data for the complex substituents or for unfamiliar groups such as the hydroxymethyl group.

The reactivity indexes based on the thermodynamic data regarding unstable species such as ions or radicals, if available, will explain the reaction data quite well in some cases and their meanings in the reaction schemes are clear, so that it is desirable to measure the heats of formation of various unstable species. Because difficulties are often met in these measurements, however, it is also necessary to seek for the method to obtain semiempirical or nonempirical reactivity indexes as another approach.

Recent progress in quantum chemistry, especially in the molecular orbital theory, together with the modern high-speed electronic computers, has contributed to the various fields of the science (*2*). The quan-

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tum chemical theory of organic reactions was founded by Huckel (*3*) for π-electron systems, and that for σ-electron systems has been developed by Fukui *et al.* (*4*). The semiempirical reactivity indexes derived from the simple molecular orbital theory have been adopted to the elucidation of chemical reactions. Many studies hitherto have dealt with comparatively simple homogeneous reactions such as a radical reaction with a simple attacking reagent like a methyl radical (*2*). As regards catalytic reactions, Fukui *et al.* (*5*) studied a homogeneous open-chain polymerization reaction by basic catalysts, but no research has been reported on heterogeneous catalyses or heterogeneous reactions.

In the present paper, an application of quantum chemical reactivity indexes for σ-electron systems will be tried for heterogeneous reactions. A discussion will be given of what kind of quantum chemical reactivity indexes are suitable as variables representing the δ_R effect in the LFER. Bold hypotheses were introduced by the present authors to get an appropriate understanding of the reactivities of the reactants. As examples, the reactions of halomethanes with alumina or alumina-boria (*6*) and the dehydrogenation of alcohols on alumina-supported metal catalysts observed by Brihta *et al.* (*7*) will be analyzed with the aid of the simple LCAO-MO method.

THEORY

Free valence (*8*), localization energy (*9*), frontier electron density (*10*), superdelocalizability (S_r) (*11*), delocalizability (D_r) (*4*), and so on, have been proposed as quantum chemical reactivity indexes.

According to Fukui *et al.* (*12*), the activation energy, E_A, of a simple reaction is given by the following equation for a particular reaction of homologous saturated compounds:

$$E_A = C - \Delta E_\sigma \qquad (1)$$

where ΔE_σ is the stabilization energy of the σ-electron system caused by the approach of an attacking radical and C is a constant for the definite type of reaction. Then, ΔE_σ is approximated by Eq. (2) for the abstraction reaction of the rth atom from a saturated compound (RX) by the sth atom of a radical attacking reagent (Y),

$$\Delta E_\sigma = \left(\sum_j^{\text{occ}} - \sum_j^{\text{unocc}}\right) \frac{(c_r{}^j)^2 (c_s{}^{\text{N}})^2}{\lambda_j(\text{RX}) - \lambda_{\text{N}}(\text{Y})} \qquad (2)$$

where $c_r{}^j$ and $c_s{}^{\text{N}}$ are the coefficients of the rth atomic orbital in the jth molecular orbital of RX, and of the sth atomic orbital in the nonbonding orbital of Y, respectively; $\lambda_j(\text{RX})$ is the energy of the jth molecular orbital of RX and $\lambda_{\text{N}}(\text{Y})$ is that of the nonbonding molecular orbital of Y. On the other hand, the delocalizability of the rth atomic orbital for the radical reactions, $D_r{}^{\text{R}}$, is defined by the following equation (*4*):

$$D_r{}^{\text{R}} = \left(\sum_j^{\text{occ}} - \sum_j^{\text{unocc}}\right) \frac{(c_r{}^j)^2}{\lambda_j(\text{RX})} \qquad (3)$$

The value of $\lambda_{\text{N}}(\text{Y})$ is nearly equal to zero when the attacking reagent is an alkyl radical, so that Eq. (4) can be approximated from Eqs. (2) and (3), as previously reported by Fukui *et al.* (*12*)

$$\Delta E_\sigma = D_r{}^{\text{R}} (c_s{}^{\text{N}})^2 \qquad (4)$$

In the present paper, it is assumed as the first approximation that an active site of a solid catalyst will abstract a radical from a reactant and that λ_{N} of the isolated orbital of the former is nearly equal to zero like that of an alkyl radical. Then, Eq. (4) will be applied even to the heterogeneous catalyses. The value of $(c_s{}^{\text{N}})$ will be constant for a particular catalyst and may be one of its attributes. As regards usual reactions with more than one elementary step, Eq. (2) does not hold in the strict sense. If the preliminary equilibrium constants preceding the rate-determining step are either related to $D_r{}^{\text{R}}$ or nearly independent of the reactant, Eq. (2) may hold for the activation energy of the overall reaction.

The reaction rate constant contains the activation entropy term as well as the activation energy term, but empirically the compensation effects often hold among the homologous reactions if the symmetry number of the reaction points is taken into consideration, or only the enthalpy term controls the reaction rate, as observed in many cases. Then both the activation energy and the reaction rate constant will have linear relationships with D_r^R through Eqs. (1) and (4).

The molecular orbitals of halomethanes and alcohols were calculated by means of the hydrocarbon method (*4*). The values of the Coulomb and resonance integrals used in this paper were adopted from Fukui *et al.* (*4, 13*), except for the resonance integral between the different atomic orbitals of the same carbon atom, the adopted value of which was 0.34 for both reactants. Oxygen atoms in alcohols were assumed to have an sp^2 configuration. Two computing programs, MO-13 that was considerably modified by one of the present authors (Y. Y.) from Wiberg's MO program (*14*), and MO-1D-2 by the classical Jacobian method, were used in this work.

RESULTS AND DISCUSSION

A. The Reactivity of Halomethanes with Alumina and Alumina-Boria

The reactants used in this work are listed in Table 1 together with the value of D_r^R of their halogen atoms. The solid acids used in this work were alumina and alumina-boria, whose properties are listed in Table 2. Reaction rates were measured at 300–450°C by means of the pulse technique. The details of the experimental procedures will be described in a subsequent paper (*6*). The activity of these catalysts in the dealkylation reaction may be found in our previous paper [*1*(b)].

TABLE 1
REACTANTS AND THEIR DELOCALIZABILITY FOR THE REACTIONS OF HALOMETHANES

No.	Reactant	D_r^R(X)	Symmetry number, *n*
1	CH_2Cl_2	1.755	2
2	CH_2Br_2	1.981	2
3	CH_2I_2	2.397	2
4	$CHCl_3$	3.018	3
5	CCl_4	3.839	4

TABLE 2
SOLID ACIDS FOR THE REACTIONS WITH HALOMETHANES

Symbol	Solid acid	Surface area (m^2/g)	Composition
A-3-550	Alumina[a]	170	
A-B-1	Alumina-boria[b]	290	10% B_2O_3

[a] F-110, an active alumina catalyst of Alcoa.

[b] Made by coprecipitation of aq. $Al_2(NO_3)_3$ and H_3BO_3 with NH_4OH.

The halomethanes in Table 1 gave carbon monoxide by the reaction with these solid acids except for carbon tetrachloride, which formed carbon dioxide instead of monoxide. In addition to these reaction products, the corresponding methyl halide was also formed from three methylene halides by reaction probably with the surface hydroxyl groups of the solid acids (*6*).

The reaction rates and activation energies of these reactions are correlated with D_r^R(X). These results are shown in Figs. 1 and 2 for alumina and in Figs. 3 and 4 for alumina-boria. The ordinate in Figs. 1 or 3, is the reaction rate divided by the

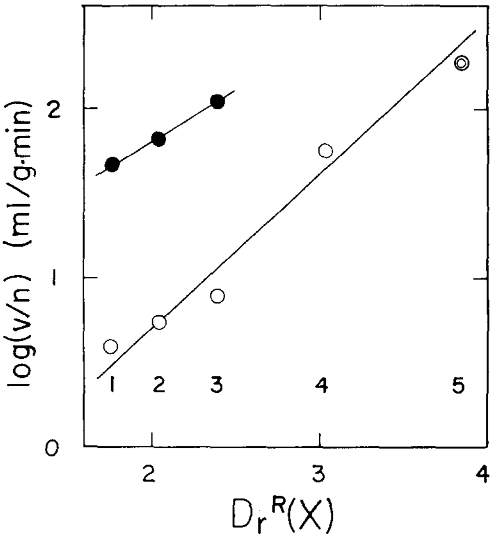

FIG. 1. The reactivity of halomethanes with alumina(A-3-550) as a function of the delocalizability for the radical reaction: reaction temperature, 300°C; numbers refer to Table 1; ●, methyl halide formation; ○, carbon monoxide formation; ◎, carbon dioxide formation (CCl_4).

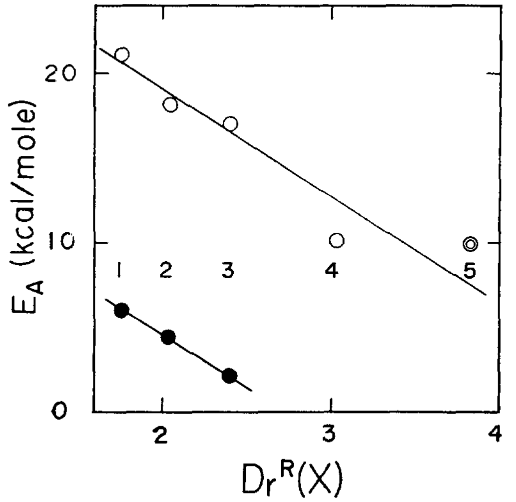

FIG. 2. Activation energy for halomethanes with alumina(A-3-550) as a function of the delocalizability for the radical reaction. Numbers refer to Table 1.

symmetry number of the reactants, that is, the number of halogen atoms in these cases. The activation energy as well as the reaction rate are well correlated with $D_r^R(X)$, although scattering around the straight line is observed in some cases. These kinetic data cannot be correlated with $D_r^E(X)$ nor $D_r^N(X)$ which Fukui *et al.* (*4, 5*) gave as the delocalizability for the electrophilic or nucleophilic reactions, respectively.

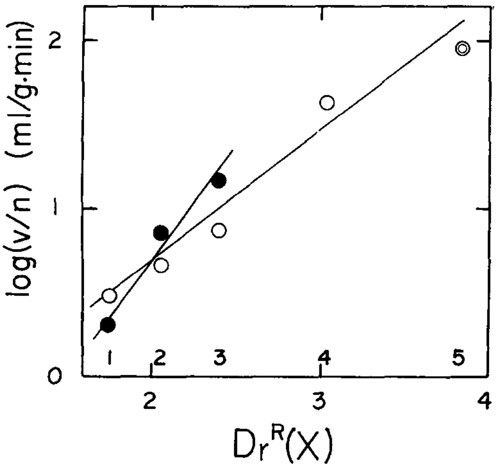

FIG. 3. The reactivity of halomethanes with alumina-boria(A-B-1) as a function of the delocalizability of the radical reaction: reaction temperature, 300°C; numbers refer to Table 1.

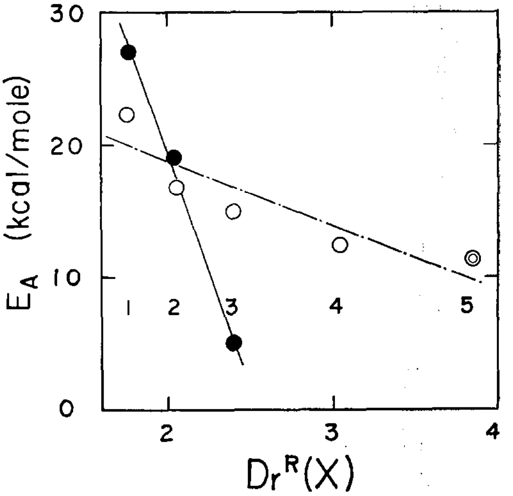

FIG. 4. Activation energy of halomethanes with alumina-boria(A-B-1) as a function of the delocalizability of the radical reaction. Numbers refer to Table 1.

Fukui *et al.* (*4*) correlated the hydrogen atom abstraction from halomethanes by a methyl radical with $D_r^R(H)$ and the bromine or chlorine atom abstraction by a hydrogen atom or a sodium atom with $D_r^R(X)$, both in homogeneous systems. It is worthy of attention that even the reaction with the solid surface is correlated with the same reactivity indexes as those for the reaction with simple radicals in the homogeneous phase.

Alumina-boria is more active than alumina in solid acid catalysis such as the dealkylation reaction (*1*b). On the contrary, alumina is much more reactive than silica-alumina in H_2–D_2 and D_2–CH_4 exchange reactions (*15*). These facts will suggest that the reaction of halomethanes with solid acids is a radical-like reaction. The linear relationships of the reactivity in carbon monoxide and methyl halide formation with $D_r^R(X)$ support the above postulation.

B. The Dehydrogenation of Alcohols over Alumina-Supported Metal Catalysts

Brihta *et al.* (*7*) reported the activation energies of dehydrogenation of five alcohols over five alumina-supported metal catalysts. The rate-determining step of this catalytic reaction has been considered to be either the α-hydrogen or the alcoholic hydrogen abstraction (*16*). The dehydrogenation reaction can resonably be assumed to proceed through a radical mechanism, therefore, the activation energies are correlated with $D_r^R(\alpha\text{-H})$ or $D_r^R(\text{alc-H})$. These values of alcohols are shown in Table 3 together with their numbers of α-hydrogens although the activation energy is independent of the symmetry number of the reaction points.

TABLE 3
DELOCALIZABILITY OF ALCOHOLS

No.	Alcohols	$D_r^R(\alpha\text{-H})$	$D_r^R(\text{alc-H})$	No. of α-H
1	Methanol	1.0419	0.9465	3
2	Ethanol	1.0590	0.9499	2
3	2-Propanol	1.0787	0.9536	1
4	1-Butanol	1.0606	0.9502	2
5	2-Butanol	1.0796	0.9540	1

The correlation of $D_r^R(\alpha\text{-H})$ with activation energies on all catalysts is satisfactory, as shown in Fig. 5. The values of $D_r^R(\text{alc-H})$ of these alcohols do not differ so much from one another, hence this index is not appropriate for this reaction. No correlation was found between activation energies and the delocalizabilities of other hydrogen atoms. These results based on the LFER approach with quantum chemical reactivity indexes support the mechanism that the α-hydrogen abstraction step may be rate-determining. The activation energies of alcohols other than those given in Table 3 will thus be estimated from the linear relationships with $D_r^R(\alpha\text{-H})$ in Fig. 5 as far as no anomaly would happen owing to unexpected reasons.

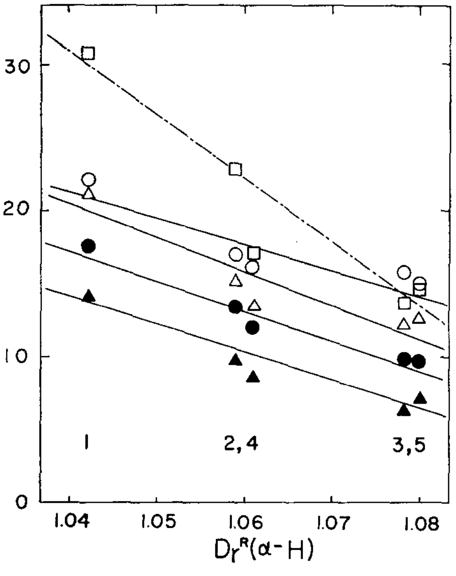

FIG. 5. Activation energy of dehydrogenation of alcohols over alumina-supported metal catalysts: □, Ag; ○, Fe; △, Ni; ●, Co; ▲, Cu. Numbers refer to Table 3.

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