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Linear Free Energy Relationships in Heterogeneous Catalysis

X. Temperature Effects in Dealkylation and Isomerization of Dialkylbenzenes over a Solid Acid Catalyst

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Temperature effects in dealkylation and isomerization of dialkylbenzenes at the temperature range of 200 to 500°C have been discussed from the viewpoint of linear free energy relationships (LFER). The effects of the second substituents on both reactions are well described by the Hammett law. The alkyl *shift* reaction, which is defined as the migration of an alkyl group in one direction on a monosubstituted ring, has been compared with the dealkylation of monoalkylbenzenes. The preexponential terms in both reactions have been shown to be constant independent of alkyl groups, whereas the activation energies are 24.8, 19.5, and 15.6 kcal/mole for the dealkylation of Et, isoPr, and *tert*-Bu groups, respectively, and 17.8, 14.1, 10.6, and 8.96 kcal/mole for the alkyl shift reaction of Me, Et, isoPr, and *tert*-Bu groups, respectively. The LFER equations for isomerization and dealkylation have been further extended over the temperature range of 200 to 500°C, as follows:

$$k_i(R^1,R^2;T) = \sum_{\mathrm{R}} w(r)k_i(0,\infty)\exp[-\{\gamma'_i\Delta H_{\mathrm{C}^+}(R) + E_{A,i}(0)\}/RT] + [2.3\rho(R)\sigma(\mathrm{R}^{f})]$$

where the Hammett ρ values are assumed to be practically independent of temperature. The generalized equation given above for dealkylation and isomerization has made it possible to predict the selectivity between two reactions of any kind of dialkylbenzenes.

The reaction mechanism of both reactions proposed in a previous paper has been refined on the basis of the LFER found in the present work.

INTRODUCTION

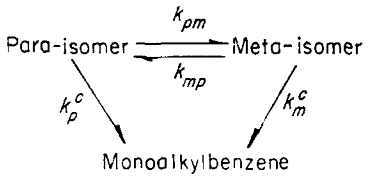
In the previous paper (*1*), the heterogeneous isomerization of dialkylbenzenes over solid acid catalysts was quantitatively discussed from the viewpoint of linear free energy relationships (LFER). The isomerization of alkyl aromatics was reasonably considered to take place through an intramolecular 1,2-shift mechanism. In order to compare it with the dealkylation of a monoalkylbenzene over solid acids, the idea of the alkyl shift reaction, which was defined as the migration of alkyl groups in one direction on a monosubstituted benzene ring, was introduced. The logarithms of the shift rate constants gave a linear relationship with ΔH_{C^+}, the enthalpy change for hydride abstraction from a corresponding paraffin, as was the case in dealkylation (*2*). These successes in LFER should make it possible to discuss the selectivity between two reactions over a solid acid catalyst quantitatively. Furthermore, the effects of the second substituted groups on isomerization were well described by the Hammett law.

In the present work, temperature effects in both dealkylation and isomerization of dialkylbenzenes over a solid acid catalyst were simultaneously studied in the temperature range from 200 to 500°C. The reaction schemes for isomerization and dealkylation of dialkylbenzenes, described in a previous paper (*1*), have been refined from the comparison between activation energies of both reactions.

EXPERIMENTAL METHODS

Materials and procedures. Reagents, apparatus, and procedures are, unless otherwise described, the same as those described in the previous paper (*1*). The catalyst used was SA-1-Na-3, a silica-alumina catalyst poisoned with NaOH aqueous solution. The previous samples of *m*-isopropyltoluene and *m*-*tert*-butyltoluene were further purified, better than 98%, by preparative gas chromatography. Dealkylation of ethylbenzene and *tert*-butylbenzene, GR grade reagents of 100% in purity, were measured in the present work besides that of the previously used reagents. The reaction temperatures were 200 to 500°C and the total conversion was kept below 15% in all runs. No products were detected except for those from isomerization and dealkylation.

Analysis of Rate Data. The rate constants were analyzed by assuming first order reaction for all alkylbenzenes (*1, 3*); the reverse isomerization and dealkylation after isomerization were taken into account, while the reverse reaction of dealkylation was neglected, as is shown in the following reaction model,



where k_{pm} and k_{mp} are the rate constants of para–meta and meta–para conversions, respectively, and k_p^c and k_m^c are cracking rate constants starting from para- and meta-isomers, respectively. The simultaneous differential equations for both isomerization and dealkylation of meta- and para-isomers were written and integrated (*4*). Each rate constant can be calculated from the integrated equations, if the conversion of dealkylation and isomerization of both meta- and para-isomers are measured by means of a gas chromatograph under identical conditions, i.e. at the same temperature and the same contact time.

RESULTS AND DISCUSSIONS

Substituent effects. By the application of the Hammett $\rho\sigma$ law to the second substituent effects on isomerization of dialkylbenzene (*1*), the overall rate constants for isomerization at T°K, $k_i(R^1, R^2; T)_r$, are represented as Eq. (1),

$$k_i(R^1, R^2; T)_r = \sum_{\mathrm{R^m}} w(r) k_i^s(\mathrm{R^m}, T) \exp\{2.3\rho_0^s(\mathrm{R^m}, T)\sigma(\mathrm{R^f})\}, \quad (1)$$

where $w(r)$ is a symmetry number; $w(r) = 2$ for para–meta conversion ($r = pm$) and $w(r) = 1$ for meta–para conversion ($r = mp$); $k_i^s(\mathrm{R^m})$ is the shift rate constant of an alkyl group $\mathrm{R^m}$, and $\mathrm{R^f}$ is an alkyl substituent fixed on the benzene ring.

A similar equation for dealkylation, which has been proposed for substituted alkylbenzenes by Mochida and Yoneda (*2*), cannot be applied to dealkylation of such a reactant as ethylisopropylbenzene, because it has two different alkyl groups to be eliminated by the same mechanism over solid acids. Therefore, the more generalized form of Eq. (2), analogous to Eq. (1) for isomerization, has been introduced for the dealkylation of dialkylbenzenes.

$$k_i^c(R^1, R^2; T) = \sum_{\mathrm{R^c}} k_i^c(\mathrm{R^c}, T) \exp\{2.3\rho_i^c(\mathrm{R^c}, T)\sigma(\mathrm{R^f})\}, \quad (2)$$

where $\mathrm{R^c}$ is the alkyl group capable of giving an olefin by cracking, i.e., Et, isoPr, *tert*-Bu, and so on. The rate constants of $k_i^c(\mathrm{R^c}, T)$ are equal to those for dealkylation at T°K of monoalkylbenzene, i.e. ethylbenzene, isopropylbenzene, and *tert*-butylbenzene.

The values of $k_i^s(\mathrm{R^m}, T)$ and $\rho_0^s(\mathrm{R^m}, T)$ in Eq. (1) ($\mathrm{R^m}$ = Me, Et, and isoPr) were determined from the data of various dialkylbenzenes used in the present work by means of the nonlinear method of least squares with a computer program named PR1P11-PLG7T4, where σ(*m*-isoPr) was assumed to be —0.07 (*1*). The values of

TABLE 1

THE CALCULATED VALUES OF $k_i^s(R^m)$ AND $k_i^c(R^c)$ AT SEVERAL TEMPERATURES

Alkyl group (°C):	250	300	350	400	450
Shift reaction: $k_i^s(R^m,T)$ (moles/g min atm)					
Me	2.02×10^{-7}	9.01×10^{-7}	3.16×10^{-6}	9.21×10^{-6}	2.32×10^{-5}
	(23.5%)[a]	(18.5%)	(25.5%)	(11.1%)	(8.9%)
Et	4.18×10^{-6}	1.39×10^{-5}	3.73×10^{-5}	8.74×10^{-5}	1.83×10^{-4}
	(15.2%)	(23.5%)	(9.9%)	(26.5%)	(26.9%)
isoPr	6.20×10^{-5}	1.47×10^{-4}	3.11×10^{-4}	5.92×10^{-3}	1.03×10^{-3}
	(28.5%)	(27.2%)	(12.7%)	(19.6%)	(22.2%)
tert-Bu	3.02×10^{-4}	6.46×10^{-4}	1.22×10^{-3}	2.10×10^{-3}	3.32×10^{-3}
	—	—	—	—	—
Dealkylation: $k_i^c(R^c,T)$ (moles/g min atm)					
Me	—	—	—	—	—
Et	8.94×10^{-8}	7.25×10^{-7}	4.08×10^{-6}	1.78×10^{-5}	6.47×10^{-5}
	(7.2%)	(17.4%)	(23.4%)	(12.1%)	(9.8%)
isoPr	1.03×10^{-5}	5.25×10^{-5}	2.09×10^{-4}	6.77×10^{-4}	1.87×10^{-3}
	(19.4%)	(8.2%)	(11.5%)	(9.4%)	(21.0%)
tert-Bu	3.48×10^{-4}	1.29×10^{-3}	3.90×10^{-3}	1.00×10^{-3}	2.22×10^{-2}
	(11.5%)	(18.5%)	(8.6%)	(20.6%)	(12.8%)

[a] Relative error given in parentheses.

TABLE 2

THE CALCULATED VALUES OF $\rho_0(R^m)$ AND $\rho_i(R^c)$ AT SEVERAL TEMPERATURES

Alkyl group (°C):	250	300	350	400	450
Shift reaction: $\rho_0^s(R^m,T)$					
Me	−3.78	−3.22	−2.84	−2.49	−2.23
	(±2.05)[a]	(±1.49)	(±1.83)	(±1.72)	(±1.23)
Et	−2.28	−1.84	−1.65	−1.27	−1.30
	(±0.48)	(±0.95)	(±0.44)	(±0.49)	(±0.55)
isoPr	−1.28	−1.26	−1.04	−0.75	−0.82
	(±0.89)	(±0.34)	(±0.66)	(±0.36)	(±0.32)
tert-Bu	−0.69	−0.82	0.58	−0.60	−0.67
	—	—	—	—	—
Dealkylation: $\rho_i^c(R^c,T)$					
Me	—	—	—	—	—
Et	−6.94	−5.84	−5.62	−5.11	−5.01
	(±3.63)	(±2.76)	(±1.30)	(±2.61)	(±1.39)
isoPr	−4.65	−4.43	−3.60	−3.65	−3.12
	(±0.86)	(±1.24)	(±1.17)	(±1.52)	(±1.11)
tert-Bu	−3.15	−3.00	−2.57	−2.42	−1.94
	(±1.33)	(±1.72)	(±0.89)	(±0.97)	(±1.21)

[a] Standard error given in parentheses.

k_i^s(*tert*-Bu) and ρ_0^s(*tert*-Bu) were determined from the isomerization data of the *para*- and *meta*-*tert*-butyltoluenes. The values of $k_i^c(\mathrm{R^c}, T)$ and $\rho_i^c(\mathrm{R^c}, T)$ in Eq. (2) ($\mathrm{R^c}$ = Et, isoPr, and *tert*-Bu) were also calculated by means of the nonlinear method of least squares. Tables 1 and 2 summarize the results at several temperatures, together with their relative errors. Equations (1) and (2) are applicable to the isomerization and dealkylation of a dialkylbenzene, respectively, over the temperature range of 200 to 500°C.

Alkyl effects in shift reaction and dealkylation. The logarithms of $k_i^s(\mathrm{R^m}, T)$ and $k_i^c(R^c, T)$ at a given temperature T°K of 473 to 773°K showed a good linear relationship with the enthalpy changes for the hydride abstraction from corresponding paraffins, $\Delta H_{\mathrm{C}}{}^+(R)$, as is shown in Fig. 1.

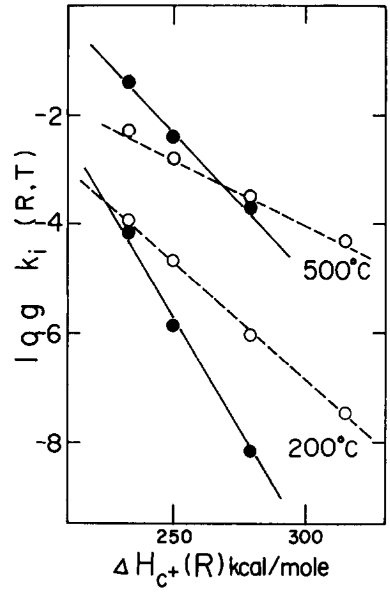


FIG. 1. The logarithms of the rate constants for the shift reaction and the dealkylation of alkyl groups vs enthalpy change, ΔHc+, at 200 and 500°C: (—), the activity for dealkylation; and (---), that for the shift reaction.

Hence, Eqs. (3) and (4) are written for both reactions as follows, for shift reaction

$$\log k_i^s(\mathrm{R^m}, T) = \log k_i^s(0, T) - \gamma_i'^s \Delta H_{\mathrm{C^+}}(\mathrm{R^m})/2.3RT, \quad (3)$$

and for dealkylation

$$\log k_i^c(\mathrm{R^c}, T) = \log k_i^c(0, T) - \gamma_i'^c \Delta H_{\mathrm{C^+}}(\mathrm{R^c})/2.3RT, \quad (4)$$

where $k_i^s(0, T)$ and $k_i^c(0, T)$ are the rate constants at T°K of an imaginary alkyl group whose $\Delta H_{\mathrm{C}}{}^+(R)$ is zero for shift reaction and dealkylation, respectively. The calculated values of $\gamma_i'^s$ and $\gamma_i'^c$, which are constants in Eqs. (5) and (6), are independent of the reaction temperature within error, and $\gamma_i'^s$ is smaller than $\gamma_i'^c$ in magnitude, as shown in Table 3.

TABLE 3
THE CALCULATED VALUES OF γ_i' AT SEVERAL TEMPERATURES

Temp. (°C)	$\gamma_i'^s$	$\gamma_i'^c$
250	0.0920 ± 0.0016	0.184 ± 0.012
300	0.0909 ± 0.0020	0.178 ± 0.014
350	0.0894 ± 0.0019	0.183 ± 0.011
400	0.0880 ± 0.0020	0.190 ± 0.016
450	0.0864 ± 0.0021	0.180 ± 0.011
Av.	0.0890	0.183

As described in a previous paper, the correlation lines of both dealkylation and shift reaction to $\Delta H_{\mathrm{C}}{}^+$ (R) at 400° crossed nearly at the isoPr group and this cross point was presumed to depend on the reaction temperature. As shown in Fig. 1, this cross point was dependent on temperature and approached to ethyl group at 500°C and to *tert*-butyl group at 200°C.

Temperature effects. The rate constants, $k_i^s(0, T)$ and $k_i^c(0, T)$, were described by the following Arrhenius equation, for shift reaction

$$k_i^s(0, T) = k_i^s(0, \infty) \exp\{-E_{A,i}{}^s(0)/RT\}, \quad (5)$$

and for dealkylation

$$k_i^c(0, T) = k_i^c(0, \infty) \exp\{-E_{A,i}{}^c(0)/RT\} \quad (6)$$

where $k_i^s(0, \infty)$ and $k_i^c(0, \infty)$ are preexponential terms, i.e., the rate constants at an infinite temperature; $E_{A,i}(0)$ is the activation energy. By substitution of Eq. (5) into Eq. (3) and that of Eq. (6) into Eq.

TABLE 4
THE EMPIRICAL CONSTANTS CALCULATED FROM EQ. (7) FOR THE SHIFT REACTION AND EQ. (8) FOR DEALKYLATION

	$k_i(0, \infty)$	γ_i'	$E_{A,i}(0)$
Shift reaction	2.70 ± 0.57	0.090 ± 0.0008	-11.4 ± 0.03
Dealkylation	472 ± 179	0.190 ± 0.010	-25.3 ± 3.04

(4), the following Eqs. (7) and (8) are derived, for shift reaction

$$\log k_i^s(\mathrm{R^m}, T) = \log k_i^s(0, \infty) - \{\gamma_i'^s \Delta H_{\mathrm{C^+}}(\mathrm{R^m}) + E_{A,i}^s(0)\}/2.3RT, \quad (7)$$

and for dealkylation

$$\log k_i^c(\mathrm{R^c}, T) = \log k_i^c(0, \infty) - \{\gamma_i'^c \Delta H_{\mathrm{C^+}}(\mathrm{R^c}) + E_{A,i}^c(0)\}/2.3RT. \quad (8)$$

From each of the two sets of rate constants in Table 1, the empirical constants, $k_i(0, \infty)$, γ_i' and $E_{A,i}(0)$, were determined with a fairly good accuracy by means of the nonlinear methods of least squares (Table 4). On the basis of LFER equations for both reactions, Eq. (7) and Eq. (8), we can predict the selectivity of any alkyl groups between two reactions on SA-1-Na-3 catalyst at various temperatures from the empirical constants given in Table 4 and $\Delta H_{\mathrm{C}}{}^{+}(R)$ of an alkyl group. Since the previous studies (*1, 5, 6*) have shown that LFER formulas like these equations can be generally applied to various solid acid catalysts, the conclusion described above may also hold for various solid acid catalysts other than SA-1-Na-3.

The LFER formulas, Eqs. (7) and (8), can be also derived from a different viewpoint in the same manner as that described in the previous paper (*5*). The temperature dependence of $k_i^s(\mathrm{R^m}, \mathrm{T})$ (see Fig. 2) and that of $k_i^c(\mathrm{R^c}, T)$ (see Fig. 3) are expressed as follows, for shift reaction

$$k_i^s(\mathrm{R^m}, T) = k_i^s(\mathrm{R^m}, \infty) \exp\{-E_{A,i}^s(\mathrm{R^m})/RT\}, \quad (9)$$

and for dealkylation

$$k_i^c(\mathrm{R'}, T) = k_i^c(\mathrm{R^c}, \infty) \exp\{-E_{A,i}^c(\mathrm{R^c})/RT\}. \quad (10)$$

The activation energy $E_{A,i}(R)$ and the preexponential term $k_i(R, \infty)$ are given in Table 5. The shift reaction has 6 to 10 kcal/mole lower activation energy than dealkylation. The activation energies for each reaction showed a good linear relationship with $\Delta H_{\mathrm{C}}{}^{+}(R)$, as shown in Fig. 4.

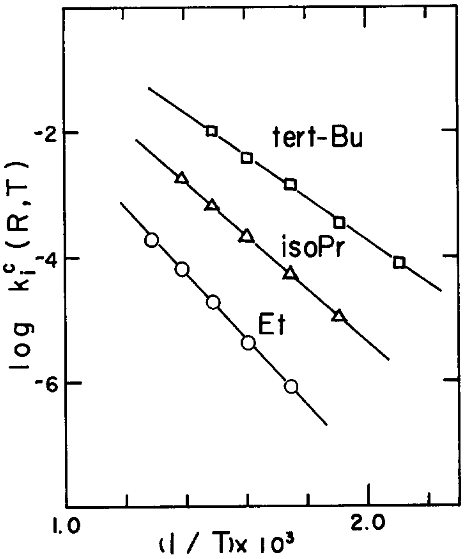


FIG. 2. The Arrhenius plots for dealkylation of Et, isoPr, and *tert*-Bu groups.

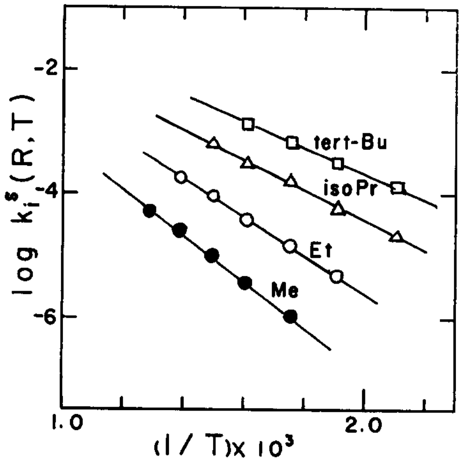


FIG. 3. The Arrhenius plots for the shift reaction of Me, Et, isoPr, and *tert*-Bu groups.

TABLE 5

$E_{A,i}(R)$ AND log $k_i(R,\infty)$

Shift reaction	log $k_i^s(\mathrm{R^m},\infty)^a$	$E_{A,i}^s(\mathrm{R^m})^b$
Me	0.7504 ± 2.48	17.8 ± 2.4
Et	0.5270 ± 0.74	14.1 ± 0.8
isoPr	0.1980 ± 1.37	10.6 ± 1.7
tert-Bu	0.2301 ± 1.82	8.96 ± 2.7
$\gamma_i''^s$		0.109 ± 0.030
Dealkylation	**log $k_i^c(\mathrm{R^c},\infty)^a$**	**$E_{A,i}^c(\mathrm{R^c})^b$**
Me	—	—
Et	3.295 ± 1.49	24.8 ± 2.8
isoPr	3.174 ± 2.51	19.5 ± 1.7
tert-Bu	3.068 ± 1.74	15.6 ± 1.9
$\gamma_i''^c$		0.196 ± 0.013

[a] (moles/g min atm).

[b] (kcal/mole).

Hence, they are expressed as follows, for shift reaction

$$E_{A,i}^s(\mathrm{R^m}) = \gamma_i''^s \Delta H_{\mathrm{C}^+}(\mathrm{R^m}) + E_{A,i}^s(0), \quad (11)$$

and for dealkylation

$$E_{A,i}^c(\mathrm{R^c}) = \gamma_i''^c \Delta H_{\mathrm{C}^+}(\mathrm{R^c}) + E_{A,i}^c(0). \quad (12)$$

The constants γ_i'' were 0.109 ± 0.030 for shift reaction and 0.196 ± 0.013 for dealkylation, which correspond fairly well to the average value of γ_i' in Table 3. The values of the preexponential terms, $k_i^s(\mathrm{R^m},\infty)$ and $k_i^c(\mathrm{R^c},\infty)$, were found to be independent of the alkyl group within error (Table 5). Since any $k_i^s(\mathrm{R^m},\infty)$, therefore, can be replaced by the common term $k_i^s(0,\infty)$, the substitution of Eq. (11) into Eq. (9) gives Eq. (7). A similar treatment for dealkylation yields Eq. (8).

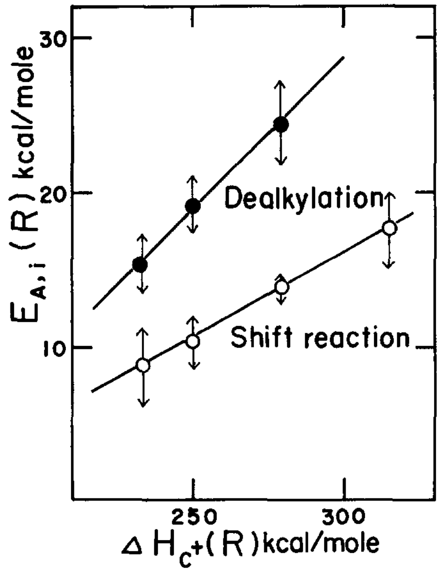


FIG. 4. The activation energies of both reactions vs $\Delta H_{\mathrm{C}^+}(R)$.

The temperature dependence of the Hammett reaction constant ρ has been suggested by Leffler and Grunwald (*7*) and Jaffe (*8*) in the form of

$$\rho(R,T) = \rho(R,\infty)\{1 - \beta(R)/T\}, \quad (13)$$

where $\rho(R,\infty)$ is the ρ values at an infinite temperature and $\beta(R)$ an isokinetic temperature.

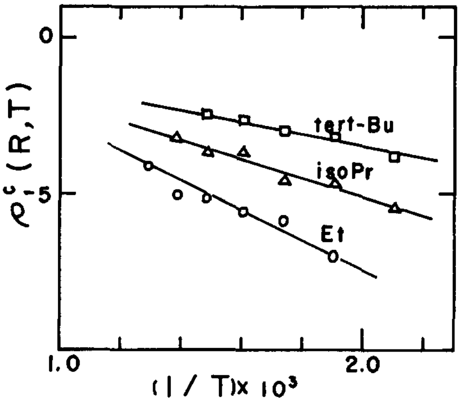


FIG. 5. The temperature dependency of the Hammett ρ values for dealkylation.

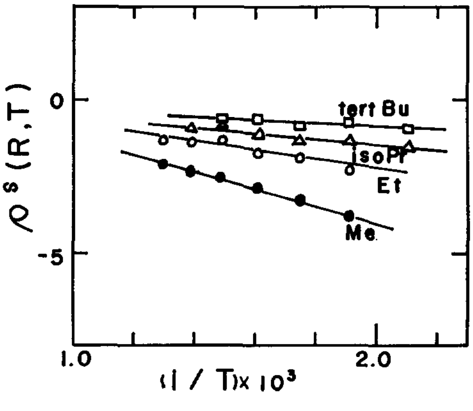


FIG. 6. The temperature dependency of the Hammett ρ values for the shift reaction.

The calculated ρ values decreased with increasing temperature, essentially in accordance with Eq. (13) (see Figs. 5 and 6), although their standard errors were considerably large. Since the values of ρ^s and ρ^c varied little with temperature, less than a factor of two, at the temperature range of 200 to 500°C, they will be considered to be constant practically. Provided that $\rho^s(R, T)$ and $\rho^c(R, T)$ are independent of temperature, the substitutions of Eq. (7) into Eq. (1) and Eq. (8) into Eq. (2), give Eqs. (14) and (15), respectively, for isomerization

$$k_i(R^1, R^2; T)_r = \sum_{\mathrm{R^m}} w(r) k_i{}^s(0, \infty) \exp\left[-\{\gamma_i{}'^s \Delta H_{\mathrm{C^+}}(\mathrm{R^m}) + E_{A,i}{}^s(0)\}/RT + 2.3\rho_0{}^s(\mathrm{R^m})\sigma(\mathrm{R^f})\right], \quad (14)$$

and for dealkylation

$$k_i{}^c(R^1, R^2; T) = \sum_{\mathrm{R^c}} k_i{}^c(0, \infty) \exp\left[-\{\gamma_i{}'^c \Delta H_{\mathrm{C^+}}(\mathrm{R^c}) + E_{A,i}{}^c(0)\}/RT + 2.3\rho_0{}^c(\mathrm{R^c})\sigma(\mathrm{R^f})\right]. \quad (15)$$

By the employment of these equations, the empirical constants $k_i(0, \infty)$, $E_{A,i}(0)$, γ_i' and $\rho(R)$ were comprehensively determined from a set of the overall rate constants for isomerization or for dealkylation of any substrates at five temperatures by means of the nonlinear method of least squares with a computer program named PR1P20-PLG7T4. Table 6 summarizes these calculated results, indicating that Eqs. (14) and (15) apply fairly well to the isomerization and dealkylation of a dialkylbenzene over SA-1-Na-3 in the temperature range from 200 to 500°C. In conclusion, this set of equations is useful in predicting the selectivity between isomerization and dealkylation of a dialkylbenzene on SA-1-Na-3 at various temperatures.

TABLE 6

THE EMPIRICAL CONSTANTS BY EQ. (14) FOR ISOMERIZATION AND EQ. (15) FOR DEALKYLATION

Empirical constants	For isomerization [Eq. (14)]	For dealkylation [Eq. (15)]
$k_i(0, \infty)$	1.03 ± 0.136	448 ± 76
γ_i'	0.099 ± 0.00001	0.179 ± 0.0025
$E_{A,i}(0)$	-14.9 ± 0.149	-27.0 ± 0.65
ρ(Me)	-1.82 ± 0.075	—
ρ(Et)	-1.53 ± 0.248	-4.13 ± 0.99
ρ(isoPr)	-1.28 ± 0.197	-2.81 ± 0.54
ρ(*tert*-Bu)	-0.66 ± 0.119	-0.98 ± 0.28

Furthermore, the reaction scheme proposed in a previous paper (*1*) was refined from LFER described above. According to the reaction mechanism in Fig. 7, the electrophilic attack of protonic acid to a benzene ring in the step of (**I**) to (**II**) is the common step in both dealkylation and isomerization over solid acids. The activated state for dealkylation (**III**) is presumed to have a higher energy than that for isomerization (**IV**) on the basis of the comparison between their activation energies, and it is reasonable since both reactions will be determined by whether or not the alkyl carbonium ion R^+ may be separated far away from a ring. The effects of alkyl groups on isomerization and dealkylation may be explained by the stability of an alkyl carbonium ion in activated complexes, which are likely to be of a transient state of an alkyl carbonium ion interacting with a benzene ring as is drawn in Fig. 7. Dealkylation will be affected by the stability of the alkyl carbonium ion [*tert*-Bu > isoPr > Et > (Me)], but the change in carbonium ion stability should be decreased in the case of isomerization as a result of the interaction of the alkyl carbonium ion with the benzene ring. The

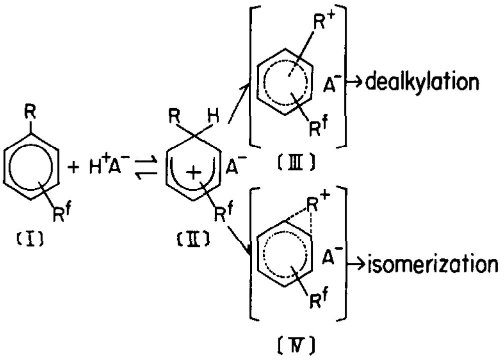


FIG. 7. The reaction scheme refined for isomerization and dealkylation.

values of γ_i' calculated in the present work quantitatively showed the effects of alkyl groups for both reactions and the relative degree of their interaction with the ring in activated states for both reactions. The electron-donating groups substituted on a benzene ring will reduce the activation energies by the stabilization of the alkyl carbonium ions interacted with a ring. In both reactions, the values of ρ were negative as was expected from the above explanation. However, it was difficult to describe further the ρ value because of the insufficient experimental accuracy. Furthermore, we have discussed the overall rate constants which should involve the equilibrium constants between (**I**) and (**II**) (*1*, *2*). In order to discuss the dependency of the ρ values of alkyl groups in detail, the rate constants used in this work must be separated into the equilibrium and the reaction rate constants, as Dunn has pointed out (*9*).

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REFERENCES

1. MATSUMOTO, H., TAKE, J., AND YONEDA, Y., *J. Catal.* **11**, 211 (1968).

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

3. MATSUMOTO, H., TAKE, J., AND YONEDA, Y., to be published.

4. LEWIS, E. S., AND JOHNSON, M. D., *J. Amer. Chem. Soc.* **82**, 5399 (1960).

5. MOCHIDA, I., AND YONEDA, Y., *J. Catal.* **7**, 393 (1967).

6. MOCHIDA, I., AND YONEDA, Y., *J. Catal.* **8**, 223 (1967).

7. LEFFLER, J. E., AND GRUNWALD, E., "Rates and Equilibrium of Organic Reactions." Wiley, New York, 1963.

8. JAFFE, H. H., *Chem. Rev.* **53**, 191 (1953).

9. DUNN, I. J., *J. Catal.* **12**, 335 (1968).