Linear Free Energy Relationships in Heterogeneous Catalysis

III. Temperature Effects in Dealkylation of Alkylbenzenes on the Cracking Catalysts

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Temperature effects in the Linear Free Energy Relationships (LFER) for dealkylation of monoalkylbenzenes at the temperatures of 300° to 450°C are discussed. The following δ_R LFER equation is proposed with an adequate consideration of the reaction temperature,

$$\log k_i(\mathrm{R_1}, T) = \log k_i(0, \infty) - \{\gamma'_i \Delta H_{C^+}(\mathrm{R_1}) + E_{A,i}(0)\}/2.303RT.$$

The rate constants of dealkylation at any temperature can thus be estimated with the knowledge of $\Delta H_{C^+}(\mathrm{R_1})$, the enthalpy change of hydride abstraction from the corresponding paraffin, and a few empirical constants independent of the reaction temperature. The applicability of the LFER is extended and the constants introduced for the LFER equation are determined more accurately from a set of rate data both at every reaction temperature and of every reactant with the aid of the multiple-variable nonlinear method of least squares. Activation energy is linearly correlated with $\Delta H_{C^+}(\mathrm{R_1})$ and its coefficient coincides with γ'_i of the δ_R LFER equation, whereas the activation entropy of every reactant employed is constant within error. The following linear relationship is obtained among the activity of all catalysts in this work:

$$\log k_i(\mathrm{R_1}, T) = \lambda(\mathrm{R_1}, T) \log k_i(\text{i-Pr}, T) + \kappa(\mathrm{R_1}, T)$$

This relationship, δ_C effects, is derived from the δ_R LFER. The compensation effect is observed among the catalysts, and discussed in connection with the δ_C LFER.

INTRODUCTION

Linear free energy relationships (LFER) in dealkylation of alkylbenzenes on solid acid catalysts at 400°C were discussed in the previous papers (1, 2), where fine linear relationships were observed between the rate constants of monosubstituted alkylbenzenes and the enthalpy change of the hydride abstraction from the corresponding paraffins, $\Delta H_{C^+}(\mathrm{R_1})$, and also between the rate constants of disubstituted ones and the Hammett σ of the second substitution groups.

In this paper, temperature effects in the LFER in dealkylation of alkylbenzenes over cracking catalysts will be reported. The intention is to extend the applicability of the LFER and also to predict the activation energy and the pre-exponential term of a set of a catalyst and a reactant. A method of estimating more accurately the constants introduced in the previous papers (1, 2) will be presented; this method analyzes the rate data both at every reaction temperature and of every reactant with the aid of the multiple-variable nonlinear method of least squares.

Leffler and Grunwald (3) introduced two stabilization operators, i.e., δ_M and δ_R, for the effects due to the media and substituents, respectively. In this work, the catalyst sta-

TABLE 1
CATALYSTS

Catalyst			
No.	Symbol	Name	Composition
1	SA-1	Silica-alumina	13% Al_2O_3
1	SA-1-Na-1	Silica-alumina-NaOH	0.048 meq Na/g
3	SA-1-Na-2	Silica-alumina-NaOH	0.087 meq Na/g
4	SA-1-Na-3	Silica-alumina-NaOH	0.168 meq Na/g
5	SA-Na-HCl	Silica-alumina-NaOH-HCl	0.119 meq Na/g
6	SA-Na-HAcO	Silica-alumina-NaOH-HAcO	0.200 meq Na/g
7	A-B-1	Alumina-boria	10% B_2O_3
8	SM-1	Silica-magnesia	16% MgO

bilization operator, δ_C, is introduced to represent the effects due to the catalysts as one of their modifications.

Temperature effects in the LFER have seldom been discussed even in homogeneous catalysis and quite rarely in heterogeneous catalysis. Cvetanovic reported the regularities in the relative rates of the reaction of olefins with atomic oxygen, and the structure effects were discussed in the light of the electronic theories in organic chemistry (4). Although his work was not concerned with catalytic reactions, valuable information was given about the LFER in gas-phase reactions. Useful suggestions to the present work were inspired also by the monograph of Leffler and Grunwald (3).

EXPERIMENTAL

Catalysts. The catalysts used in this work are given in Table 1. The preparation as well as their physical and chemical properties were described in a previous paper (2).

Reagents. The reagents used in this work are listed in Table 2, although detailed discussion will be made of only six monoalkylbenzenes. The purity and the precautions for these reagents were also described in the previous paper (1).

Apparatus and procedures. The reaction rate constants were measured by the microcatalytic gas chromatographic technique in the same way as was described in the previous paper (1). The reaction temperatures were 300° to 450°C, while the temperature of pretreatment was 450°C. A new portion of a catalyst was used for every run at a different reaction temperature.

RESULTS AND DISCUSSION

Reactant Effects in the Temperature Range of 300° to 450°C

A linear relationship was proposed (1) between the rate constants of the dealkylation reaction of monoalkylbenzenes at 450°C and $\Delta H_{C^+}(R_1)$, as given in Eq. (1),

TABLE 2
REAGENTS EMPLOYED WITH THEIR λ AND κ

Reagent		$\lambda(R_1,666)$	$\lambda(R_1,625)$	$\kappa(R_1,666)$	$\kappa(R_1,625)$
Abbrev.	Name				
Et	Ethylbenzene	1.05	1.03	−1.18	−1.28
n-Pr	n-Propylbenzene	1.02	1.01	−0.84	−0.96
i-Pr	Isopropylbenzene	1.00^a	1.00^a	0.0^a	0.0^a
i-Pr-Me	Isopropyltoluene	0.92	0.90	0.89	0.92
n-Bu	n-Butylbenzene	1.02	1.01	−0.78	−0.88
s-Bu	sec-Butylbenzene	0.95	0.92	0.46	0.52
t-Bu	tert-Butylbenzene	0.83	0.80	1.27	1.39

[a] By definition.

$$\log k_i(\mathrm{R_1}) = \log k_i(0)$$
$$- \gamma'_i \Delta H_{\mathrm{C^+}}(\mathrm{R_1})/2.303RT$$
$$(T = 723°\mathrm{K}) \quad (1)$$

where $k_i(0)$ and γ'_i are constants dependent upon the ith catalyst.

Similar linear relationships were observed at the temperature range of 300° to 450°C, some examples of which are shown in Fig. 1 for the SA-1 catalyst. The ordinate intercept
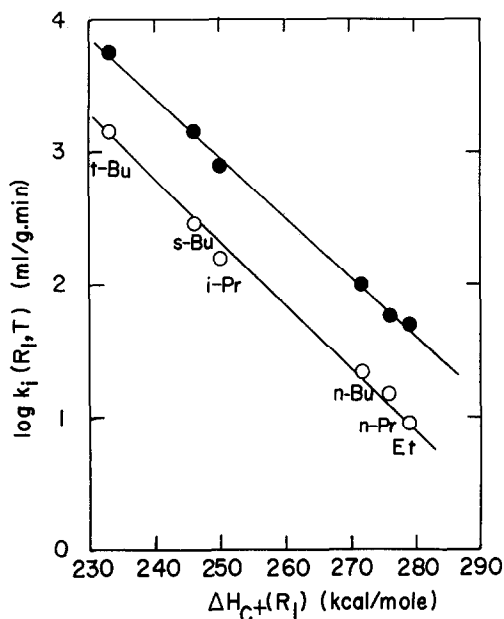

FIG. 1. Rate constants vs. the enthalpy change, $\Delta H_{\mathrm{C^+}}(\mathrm{R_1})$. Catalyst SA-1; ●, 698°K; ○, 615°K.

of Fig. 1, $\log k_i(0)$, and even the slope, $\gamma'_i/2.303RT$ varied with the reaction temperature. Then, Eq. (1) may be converted into the following equation with an adequate consideration of the reaction temperature:

$$\log k_i(\mathrm{R_1},T) = \log k_i(0,T)$$
$$- \gamma'_i \Delta H_{\mathrm{C^+}}(\mathrm{R_1})/2.303RT \quad (2)$$

where $k_i(0,T)$ is the rate constant at $T°\mathrm{K}$ of an imaginary reactant whose $\Delta H_{\mathrm{C^+}}^!(\mathrm{R_1})$ is equal to zero.

The values of $k_i(0,T)$ and γ'_i for every combination of a catalyst and a reaction temperature were calculated by means of the method of least squares. The values of γ'_i at various temperatures for SA-1, as an example, are given in Table 3, together with

TABLE 3
γ'_i OF SA-1 AT VARIOUS REACTION TEMPERATURES

Reaction temp. (°K)	γ'_i	Standard error
698°	0.130	0.005
668°	0.124	0.009
643°	0.128	0.005
635°	0.126	0.005
634°	0.122	0.009
621°	0.118	0.008
615°	0.127	0.005
Average	0.125	

their standard errors. They are approximately constant independent of the reaction temperature. The averaged values of γ'_i are shown in Table 4 with regard to eight catalysts employed in this work. The averaged γ'_i values clearly vary among

TABLE 4
COMPARISON BETWEEN THE AVERAGE γ'_i AND γ''_i

Catalyst	γ'_i	γ''_i
SA-1	0.125	0.124
SA-1-Na-1	0.127	0.144
SA-1-Na-2	0.134	0.202
SA-1-Na-3	0.146	0.196
SA-Na-HCl	0.126	0.186
SA-Na-HAcO	0.134	0.234
A-B-1	0.129	0.140
SM-1	0.155	0.396

catalysts; a catalyst with a higher catalytic activity generally has a smaller value of γ'_i. The averaged values of γ'_i are plotted in Fig. 2 against the logarithms of the rate constants of deisopropylation at 666°K, $\log k_i(\mathrm{i\text{-}Pr},666)$; hence the following linear relationship is obtained except for SA-Na-HCl:

$$\gamma'_i = a_1 \log k_i(\mathrm{i\text{-}Pr},666) + a_2 \quad (3)$$

where a_1 and a_2 are constants. The rate constants at a given temperature, say 666°K, were interpolated from the Arrhenius plots, because the reaction temperatures varied slightly for each catalyst.

Temperature Effects (Activation Energy)

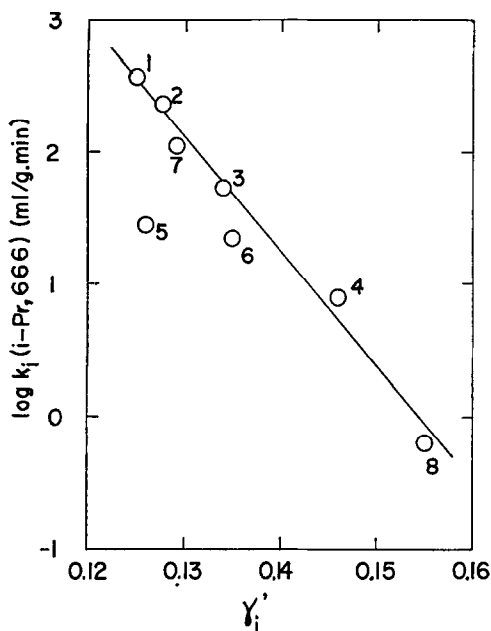The rate constant of the imaginary reactant at $T°\mathrm{K}$, $k_i(0,T)$, can be expressed

FIG. 2. γ'_i vs. the rate constants of deisopropylation of isopropylbenzene at 666°K. Numbers are to be referred to Table 1.

by the following Arrhenius equation with a negative activation energy

$$\log k_i(0,T) = \log k_i(0,\infty) - E_{A,i}(0)/2.303RT \quad (4)$$

where $k_i(0,\infty)$ is the pre-exponential term of the above-defined reactant, i.e., the rate constant at the infinite temperature, and $E_{A,i}(0)$ is its activation energy. Then, Eq. (2) will be transformed into the following equation by the substitution of Eq. (4):

$$\log k_i(R_1,T) = \log k_i(0,\infty) - \{\gamma'_i \Delta H_{C^+}(R_1) + E_{A,i}(0)\}/2.303RT \quad (5)$$

The rate constant on a catalyst would thus be estimated at any temperature for any monoalkylbenzene, provided that $\Delta H_{C^+}(R_1)$ of the reactant and three empirical constants for the catalyst, $k_i(0,\infty)$, γ'_i, and $E_{A,i}(0)$, are known.

The LFER formula, Eq. (5), will be discussed from another viewpoint, i.e., the correlation of the activation energies and pre-exponential terms with $\Delta H_{C^+}(R_1)$ of these alkylbenzenes. The temperature dependency of the rate constants is shown in Fig. 3 for every reactant on SA-1, as an
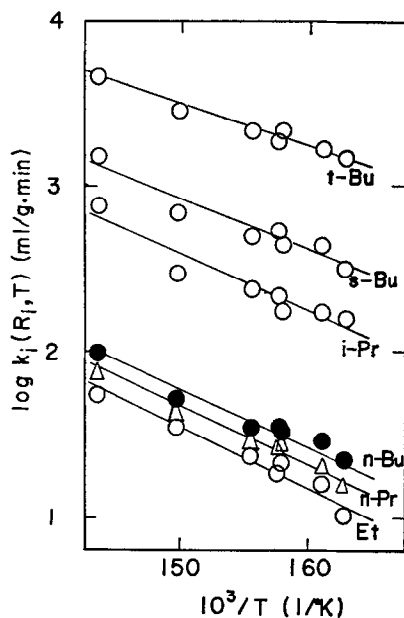

FIG. 3. Arrhenius plots of dealkylation. Catalyst SA-1; ●, n-Bu; △,n-Pr; ○, Et.

example. The rate constant is expressed by the following Arrhenius equation:

$$\log k_i(R_1,T) = \log k_i(R_1,\infty) - E_{A,i}(R_1)/2.303RT \quad (4a)$$

The activation energy, $E_{A,i}(R_1)$, and the pre-exponential term, $k_i(R_1,\infty)$, were calculated by the method of least squares for each catalyst. The values of $E_{A,i}(R_1)$ were
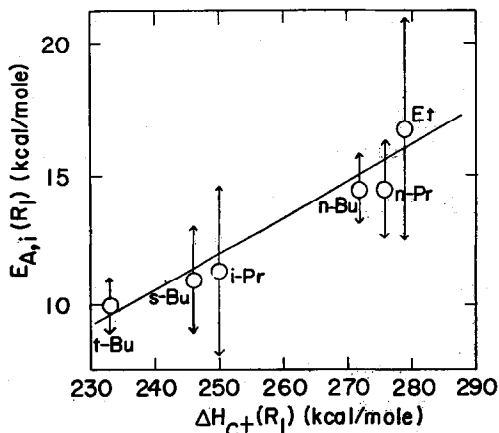

FIG. 4. Activation energy of dealkylation vs. the enthalpy change, $\Delta H_{C^+}(R_1)$. An arrow represents the standard error. Catalyst SA-1.

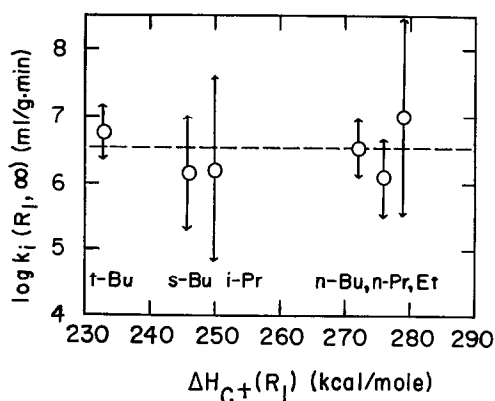FIG. 5. Frequency factor of dealkylation vs. the enthalpy change, $\Delta H_{C^+}(R_1)$. An arrow represents the standard error. Catalyst SA-1.

proved to have linear relationships with $\Delta H_{C^+}(R_1)$, as shown in Fig. 4 for SA-1, as an example. Hence the following equation will be derived:

$$E_{A,i}(R_1) = \gamma''_i \Delta H_{C^+}(R_1) + E_{A,i}(0) \quad (6)$$

The comparison of γ''_i in Eq. (6) with γ'_i is made in Table 4 for each catalyst. The equality of these two values is not good but it is, at worst, bearable.

The values of $\log k_i(R_1, \infty)$ were found constant within error, independent of the reactant, as shown in Fig. 5. In other words, the pre-exponential terms do not vary among the reactants on a particular catalyst. Therefore, every value of $k_i(R_1, \infty)$ is reasonably assumed equal to $k_i(0, \infty)$.

In conclusion, Eq. (5) can be given by the substitution of Eq. (6) and the common pre-exponential term $k_i(0, \infty)$ into Eq. (4a).

Comprehensive Analysis

The validity of Eq. (5) has been discussed with three constants regarding the ith catalyst, $k_i(0, \infty)$, γ'_i, and $E_{A,i}(0)$. However, they were determined by the differential method where either of two variables, T and R_1, was fixed; hence the degree of freedom was small and consequently the accuracy was poor. By employing Eq. (5), three catalyst constants will be determined more accurately from a set of data on the number of monoalkylbenzenes (in this case, 6) times the number of the reaction temperatures (in this case, at least 4) by means of the multiple-variable nonlinear method of least squares. Then, the degree of the freedom in the decision on three catalyst constants will be at least 21. Actually at least 24 simultaneous equations with three unknown parameters were statistically solved for every catalyst with an electronic computation program named DEAL. The results of this calculation are shown in Table 5. These constants are determined with a comparably good accuracy and the relative error is less than 10%. Consequently, Eq. (5) is generally applicable to the dealkylation reaction.

At present, these constants are considered to be characteristic parameters of a particular catalyst, but they will be reduced to more generalized ones which are common among the catalysts, for example, to the acid strength distribution of a catalyst, i.e., the acid strength and the acid content on a catalyst.

The explanation of Eq. (5) based on the reaction mechanism hitherto proposed is essentially the same as was given in a previ-

TABLE 5

LOG $k_i(0, \infty)$, γ'_i AND $E_{A,i}(0)$ DETERMINED BY THE COMPREHENSIVE ANALYSIS

Catalyst	$\log k_i(0, \infty)$	γ'_i	$E_{A,i}(0)$ (kcal/mole)
SA-1	6.53 ± 0.28[a]	0.125 ± 0.002[a]	-20.9 ± 1.00[a]
SA-1-Na-1	6.32 ± 0.34	0.129 ± 0.003	-20.1 ± 1.25
SA-1-Na-2	8.74 ± 0.49	0.134 ± 0.004	-12.8 ± 1.74
SA-1-Na-3	6.84 ± 0.48	0.146 ± 0.003	-19.4 ± 1.70
SA-Na-HCl	7.22 ± 0.71	0.128 ± 0.006	-15.0 ± 2.57
SA-Na-HAcO	7.82 ± 0.82	0.136 ± 0.005	-15.0 ± 2.74
A-B-1	5.71 ± 0.44	0.127 ± 0.004	-20.9 ± 1.60
SM-1	9.73 ± 0.97	0.155 ± 0.007	-6.84 ± 3.62

[a] Standard error.

ous paper (1). The rate-determining step has been considered to be the following one:

$$[R_1 - \phi - H^+] \rightarrow \phi$$
$$+ R_1H^+, \qquad \Delta H_{\ddagger,i}(R_1) \quad (7)$$
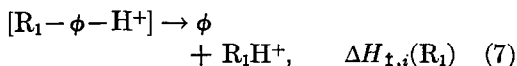
where $R_1 - \phi - H^+$ is the protonated complex of an alkylbenzene and $\Delta H_{\ddagger,i}(R_1)$ is the enthalpy change of the step (7). The value of $\Delta H_{\ddagger,i}(R_1)$ is assumed linear to $\Delta H_{C^+}(R_1)$ because of the resemblance of the two reactions; the activation energy is assumed to be linear to $\Delta H_{\ddagger,i}(R_1)$ based on the Polanyi rule, consequently it is assumed to be linear also to $\Delta H_{C^+}(R_1)$. In this reasoning two constant terms should be introduced, which give $E_{A,i}(0)$ in the activation energy term of Eq. (5).

δ_C Effects (Catalyst Effect)

The rate constants of several reactions at 673°K, $k_i(R_1,673)$, was correlated with those $k_i(\text{i-Pr},673)$ in the previous paper (2). These correlations hold even at other temperatures, as shown in Fig. 6, where those of sec-butylbenzene at 666° and 625°K are given for examples. These correlations are expressed by the following equation:

$$\log k_i(R_1,T) = \lambda(R_1,T) \log k_i(\text{i-Pr},T)$$
$$+ \kappa(R_1,T) \quad (8)$$

where $\lambda(R_1,T)$ is nearly unity, but slightly dependent on R_1 and T, and $\kappa(R_1,T)$ is much dependent on both R_1 and T: These parameters at two temperatures are given in Table 2.

It has already been proved by Leffler (ref. 3, p. 155; 5) that the existence of a precise LFER of the substituent effects in the case of rate constants over a range of temperatures implies the existence of linear activation enthalpy and entropy relationships. Equation (8) implies the existence of such a LFER in catalyst effects; by introducing a modified stabilization operator, δ_C, for the catalyst effects, Eq. (8) will be transformed to Eq. (8a),

$$\delta_C \log k_i(R_1,T)$$
$$= \lambda(R_1,T)\delta_C \log k_i(\text{i-Pr},T) \quad (8a)$$

The difference between Eq. (5) of R_1 and that of isopropylbenzene on the same ith catalyst makes the following equation:

$$\log k_i(R_1,T) - \log k_i(\text{i-Pr},T)$$
$$= (\gamma'_i/2.303RT)\{\Delta H_{C^+}(\text{i-Pr})$$
$$- \Delta H_{C^+}(R_1)\} \quad (9)$$

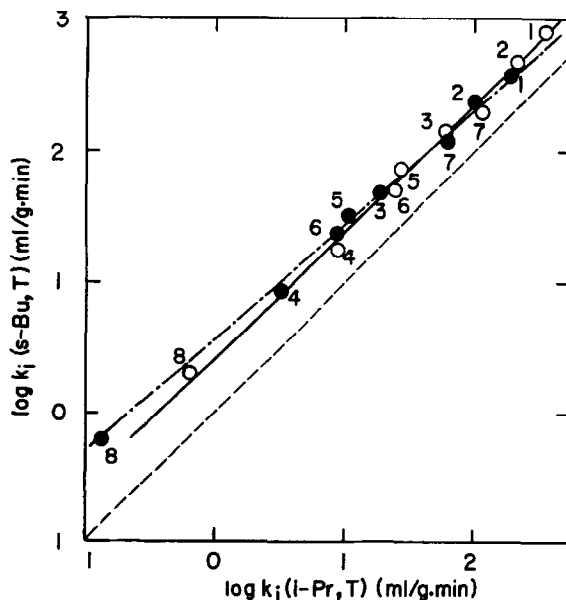Substituting Eq. (3) into Eq. (9), Eq. (8) is easily derived, where

FIG. 6 Correlations between the rate constants of dealkylation of sec-butylbenzene and isopropylbenzene: ○, 666°K; ●, 625°K. Numbers are for the catalysts given in Table 1.

$$\lambda(R_1, T) = 1 - (a_1/2.303RT)\{\Delta H_{C^+}(R_1) \\ - \Delta H_{C^+}(\text{i-Pr})\} \quad (10)$$

$$\kappa(R_1, T) = -(a_2/2.303RT)\{\Delta H_{C^+}(R_1) \\ - \Delta H_{C^+}(\text{i-Pr})\} \quad (11)$$

From Fig. 2, the values of $a_1/2.303RT$ and $a_2/2.303RT$ at $666°K$ are estimated as -3.84×10^{-3} and 5.06×10^{-2}, respectively; within the temperature range employed in the present work, the former has a small negative value and the latter a small positive value regardless of the reaction temperature. Therefore, λ is a little smaller than unity and κ is positive when $\Delta H_{C^+}(R_1)$ is less than $\Delta H_{C^+}(\text{i-Pr})$ as in the case of sec-butylbenzene; λ is a little larger than unity and κ is negative when $\Delta H_{C^+}(R_1)$ is larger than $\Delta H_{C^+}(\text{i-Pr})$ as in the case of ethylbenzene. A comparison between observed and calculated values of λ and κ is made in Table 6.

TABLE 6

COMPARISON BETWEEN CALCULATED AND OBSERVED λ AND κ FOR sec-BUTYLBENZENE

	λ	κ
Obs.	0.95	0.46
Calc.	0.98	0.20

The existence of linear activation enthalpy and entropy relationships, that is, the compensation effects (6), will be proved empirically as follows. Good linear relationships between $E_{A,i}(R_1)$ and $\log \kappa_i(R_1, \infty)$ of alkylbenzenes are observed and those of isopropylbenzene and sec-butylbenzene are shown as examples in Figs. 7 and 8, respectively. They are formulated by the following equations:

$$\delta_C E_{A,i}(\text{i-Pr}) = m' \delta_C \log k_i(\text{i-Pr}, \infty) \quad (12)$$

$$\delta_C E_{A,i}(\text{s-Bu}) = m \delta_C \log k_i(\text{s-Bu}, \infty) \quad (13)$$

A linear relationship also exists between $E_{A,i}(\text{s-Bu})$ and $E_{A,i}(\text{i-Pr})$, as shown in Fig. 9 with the slope of f,

$$f = \delta_C E_{A,i}(\text{s-Bu})/\delta_C E_{A,i}(\text{i-Pr}) \quad (14)$$
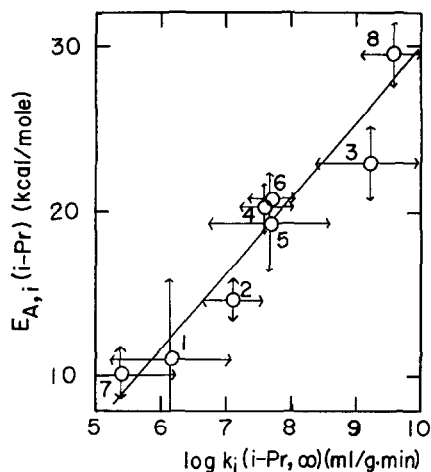

FIG. 7. Compensation effect of deisopropylation of isopropylbenzene. An arrow represents the standard error. Numbers are for the catalysts given in Table 1.

A relation among the coefficient of Eqs. (12), (13), and (14) is obtained from Eq. (8a) at two different temperatures by the application of the Leffler's derivation (6) to the δ_C operation,

$$\lambda_{\text{calc}}(R_1, T) = \frac{2.303RT/m - 1}{2.303RT/m' - 1} f \quad (15)$$

where $\lambda_{\text{calc}}(R_1, T)$ is the theoretical value of λ in Eq. (8) at $T°K$ and can be calculated
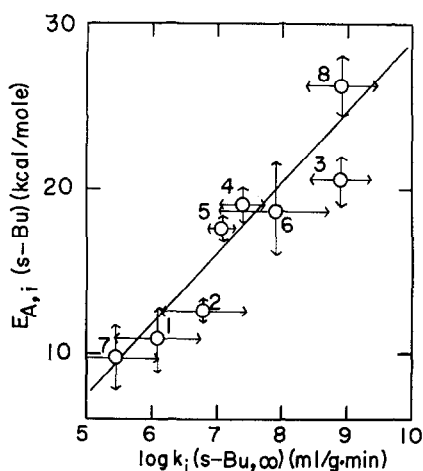

FIG. 8. Compensation effect of dealkylation of sec-butylbenzene. An arrow represents the standard error. Numbers are for the catalysts given in Table 1.
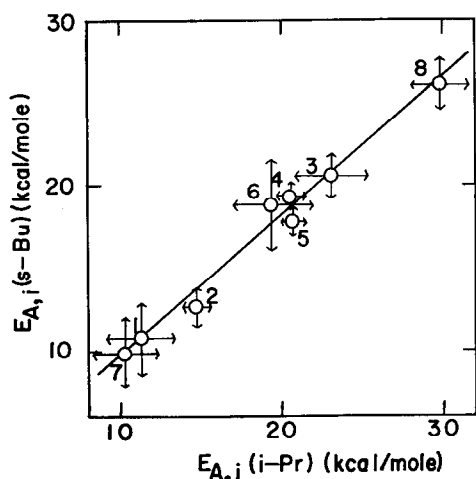
FIG. 9. Correlation between the activation energy of dealkylation of *sec*-butylbenzene and isopropylbenzene. An arrow represents the standard error. Numbers are for the catalysts given in Table 1.

TABLE 7

COMPARISON BETWEEN λ_{obs} AND λ_{calc}

$T°K^a$	m	m'	f	λ_{obs}	λ_{calc}
666°	4.06	4.62	0.84	0.95	0.96
625°	4.06	4.62	0.84	0.92	0.93

^{a} Reaction temperature.

with the values in Figs. 7, 8, and 9. Comparisons between observed and calculated values of λ are shown in Table 7 together with m, m', and f. Thus, the correlations of Eq. (8) or (8a) can be verified without any conflict.

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