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Linear Free Energy Relationships in Heterogeneous Catalysis

VIII. Isomerization of Alkylbenzenes over Solid Acid Catalysts

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An attempt has been made to survey the applicability of linear free energy relationships (LFER) in the heterogeneous isomerization of dialkylbenzenes at high temperatures. The microcatalytic gas chromatographic technique was used to measure reactivities of a set of dialkylbenzenes at 400°C over silica aluminas. The rate of the *shift* reaction, i.e., the migration of alkyl groups in one direction on a monosubstituted ring, increases markedly in the order: Me<Et<iso-Pr<*tert*-Bu. The logarithms of the shift rate constants hold a linear relationship with ΔH_{C^+}, the enthalpy change for the hydride abstraction from the corresponding paraffin. This relationship has been reported to hold also in dealkylation of monoalkylbenzenes. The dependency on ΔH_{C^+} in isomerization was found to be three-fifths of that in dealkylation at 400°C on the same catalyst. Thus, selectivity between both reactions is shown to change according to alkyl groups, and to be nearly unity at an iso-Pr group. On the other hand, the effects of the second substituted groups on isomerization were found to be described by the Hammett law. An agreement between the above-mentioned facts and the proposed reaction scheme is briefly discussed. These successes in LFER will make it possible to estimate the rate constants of isomerization at 400°C.

INTRODUCTION

It is well known that alkylbenzenes react in various ways over solid acid catalysts: dealkylation, isomerization, and disproportionation. Quantitative studies of the dealkylation of alkylbenzenes over solid acids were reported by Mochida and Yoneda (*1–3*); the logarithms of the dealkylation rate constants of monoalkylbenzenes hold a linear relationship with ΔH_{C^+}, the enthalpy change for hydride abstraction from the corresponding paraffin, and the Hammett $\rho\sigma$ relationship holds for dealkylation of di- or trialkylbenzenes. As for the isomerization, however, no quantitative study has been reported on the effect of substituent groups. Only qualitative observations in liquid homogeneous systems were previously reported by Brown and Jungk (*4*), who found that the isomerization rates increased markedly in the following order: *p*-xylene<*p*-ethyltoluene<*p*-isopropyltoluene, and this trend was explained by the stability of alkyl carbonium ions.

In the present work, it was attempted to survey the applicability of LFER (linear free energy relationships) in the heterogeneous isomerization of dialkylbenzenes at high temperatures, and, furthermore, the selectivity between dealkylation and isomerization of alkylbenzenes over solid acid catalysts will be discussed.

EXPERIMENTAL

Catalysts. The catalysts used in this work are listed in Table 1, together with some of their properties. They were calcined at 550°C for 8 hr in the atmosphere.

Reagents. Dialkylbenzenes used in this

TABLE 1
CATALYSTS

No.	Symbol	Surface area[a]	Remarks
1	SA-1	540	Silica-alumina, 13% Al_2O_3, Nippon Cat, a cracking catalyst of the Shokubai Kasei Co.
2	SA-1-Na-1	450	0.048 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
3	SA-1-Na-2	480	0.087 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
4	SA-1-Na-3	480	0.168 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
5	SA-1-Na-HCl-2	—	By treatment of SA-1-Na-4[b] with HCl
6	SA-1-Na-HAcO-2	—	By treatment of SA-1-Na-4 with HAcO
7	A-3	170	Alumina, F-110, an active alumina of the Alcoa Co.

[a] Measured by the BET method with N_2 (m^2/g).
[b] Another lot of SA-1 impregnated with NaOH aq. soln.

work are listed in Table 2, together with their purity, verified by gas chromatography. Most of them were G. R. grade reagents (the Tokyo Kasei Co.) and were used without further purification. Samples of *m*-iso-PrT and *m*-*tert*-BuT were prepared by the Friedel-Crafts isomerization with $AlCl_3$-H_2O from their para isomers; the equilibrated mixture was separated by distillation and gas chromatography, and the purified samples were ensured to be meta isomers by means of infrared spectrometry and nuclear magnetic resonance. Polar impurities such as hydroperoxides in iso-PrB and its derivatives were removed by means of an adsorption column of silica gel and alumina gel.

Apparatus and procedures. The microcatalytic gas chromatographic technique was adopted (*1, 5*). Hydrogen carrier gas from a tank was purified in order to remove oxygen and water by copper on kieselguhr and a Dry Ice–ethanol trap, respectively.

The reactions were divided into two groups according to the reactivities: one group was for X, ET, and DEB and the other for iso-PrT, D-iso-PrB, and *tert*-BuT.*

A weighed amount of a catalyst [20 mg (SA-1) to 500 mg (SA-1-Na-3) according to their activities] was placed at the middle of a glass reactor, and supported by quartz wool. After a 2-hr or longer pretreatment of the catalyst in the hydrogen carrier flow at 470° to 500°C, the reaction was carried out at 400°C at the flow rate of 40 ml/min. The products were analyzed by a gas chromatograph directly connected to the reactor; an analytical column used was 3 m of Bentone 34 (10 wt%) modified with silicone oil (the Ohkura Rikagaku Co.) at 110°C, which could separate the meta and the para isomers of every dialkylbenzene but was unable to do the meta and the ortho isomers. A *round trip* procedure was adopted. Two microliters each of isopropylbenzene, as a standard reactant, and one set of reagents were injected in the sequence given in Table 2 into the gas flow from the top of the reactor through a silicone serum cap with a microsyringe. Then, in the reverse sequence, the same procedure was repeated. The average of these two sets of results was assumed to be the conversion* under the same condition of catalyst fouling. In order to reduce the fouling during runs, 10 μl of benzene was injected before every series of runs.

Analysis of rate constant. The isomerization of *o*-X and *p*-X on silica-alumina (*6*) and alumina-boria (*7*) were reported to be of approximately first order, whereas few kinetic studies on *m*-X have been car-

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* *tert*-BuT was so reactive that the run was carried out only over SA-1-Na-3. In both groups, iso-PrB for cracking was included as a common reagent.

* For example, the conversions of iso-PrB at the first and the last pulse of a round trip were 16.1% and 14.9% on SA-1-Na-3; the average, 15.5%, was assumed to the conversion of iso-PrB.

TABLE 2

REAGENTS AND THEIR REACTIVITIES

Symbol	Name	Purity	Rate constants (moles/g min atm)					
			SA-1	SA-1-Na-1	SA-1-Na-2	SA-1-Na-3	SA-1-Na-HCl-2	SA-1-Na-HAcO-2
p-X	*p*-Xylene	100%	3.87×10^{-3}	1.20×10^{-3}	2.20×10^{-4}	9.68×10^{-5}	1.12×10^{-4}	6.20×10^{-5}
m-X	*m*-Xylene	100%	1.55×10^{-3}	4.27×10^{-4}	7.63×10^{-5}	2.71×10^{-5}	3.60×10^{-5}	2.20×10^{-5}
p-ET	*p*-Ethyltoluene	100%	1.45×10^{-2}	5.56×10^{-3}	1.40×10^{-3}	3.47×10^{-4}	5.45×10^{-4}	2.57×10^{-4}
m-ET	*m*-Ethyltoluene	100%	5.37×10^{-3}	2.17×10^{-3}	3.90×10^{-4}	1.19×10^{-4}	1.56×10^{-4}	8.12×10^{-5}
p-DEB	*p*-Diethylbenzene	99%	2.36×10^{-2}	1.04×10^{-2}	1.96×10^{-3}	5.17×10^{-4}	6.64×10^{-4}	5.12×10^{-4}
m-DEB	*m*-Diethylbenzene	99%	9.98×10^{-3}	4.75×10^{-3}	9.04×10^{-4}	2.19×10^{-4}	3.05×10^{-4}	2.17×10^{-4}
p-iso-PrT	*p*-Isopropyltoluene	99%	—	3.12×10^{-2}	5.60×10^{-3}	1.96×10^{-3}	2.10×10^{-3}	1.35×10^{-3}
m-iso-PrT	*m*-Isopropyltoluene	95%	—	1.48×10^{-2}	2.62×10^{-3}	8.87×10^{-4}	9.98×10^{-4}	6.70×10^{-4}
p-D-iso-PrB	*p*-Diisopropylbenzene	99%	—	4.52×10^{-2}	8.20×10^{-3}	2.50×10^{-3}	2.80×10^{-3}	1.92×10^{-3}
m-D-iso-PrB	*m*-Diisopropylbenzene	99%	—	1.83×10^{-2}	3.35×10^{-3}	1.08×10^{-3}	1.21×10^{-3}	8.18×10^{-4}
p-*tert*-BuT	*p*-*tert*-Butyltoluene	98%	—	—	—	5.23×10^{-3}	—	—
m-*tert*-BuT	*m*-*tert*-Butyltoluene	90%	—	—	—	2.92×10^{-3}	—	—
iso-PrB	Isopropylbenzene	100%	3.55×10^{-2}	1.29×10^{-2}	2.32×10^{-3}	6.76×10^{-4}	7.50×10^{-4}	3.99×10^{-4}

ried out.* The reaction order of *m*-X might be different from the order of *o*-X or *p*-X on solid acid catalysts, since the basicity of *m*-X is reported to be 20 times stronger than that of *p*-X (*8, 9*). The kinetic study of *m*-X was carried out by the present authors (*17*) by means of the conventional flow method over two typical catalysts, SA-1 and SA-1-Na-3, at 400°C under partial pressure from 0.016 to 0.56 atm. The kinetics of *m*-X was found to be nearly the same as those of *o*-X and *p*-X, and was of approximately first order, although all of them obey the Langmuir equation for a monomolecular reaction with a rate-determining step in the surface reaction. Thus the analysis of rate constants by the pulse method, where shape of the injected pulse in the catalyst bed was nearly rectangular, was carried out by assuming the reaction of alkylbenzenes as first order (*10*), and by taking into account the reverse reaction.

The dealkylation was neglected for X, ET, and DEB since it was smaller than one-tenth of isomerization. However, for iso-PrT, D-iso-PrB, and *tert*-Bu-T, the analysis of the rate constant was carried out by taking into account the dealkylation after isomerizing and the reverse isomerization, but by neglecting the reverse reaction of dealkylation; thus the first order rate constant was calculated by the simultaneous differential equations for both isomerizations and dealkylations of meta and para isomers under the same conditions.

RESULTS

The rate constants of the isomerization and the cumene (iso-PrB) cracking at 400°C are listed in Table 2. The trend of the catalytic activity within a series of catalysts for isomerization had a satisfactorily linear correlation with that for cumene cracking under the same conditions, as is shown in Fig. 1. The ordinate, log $k_i(R^1,R^2)_r$, is the logarithm of the rate constant for isomerization r (mp and pm for meta–para and para–meta conversions, respectively) over the *i*th catalyst of a dialkylbenzene with R^1 and R^2 as substituents, and the abscissa, log k_i^c(iso-PrB), is for the *cracking* of cumene over the same *i*th catalyst. On A-3, an alumina catalyst, the isomerization was scarcely observed under this condition.

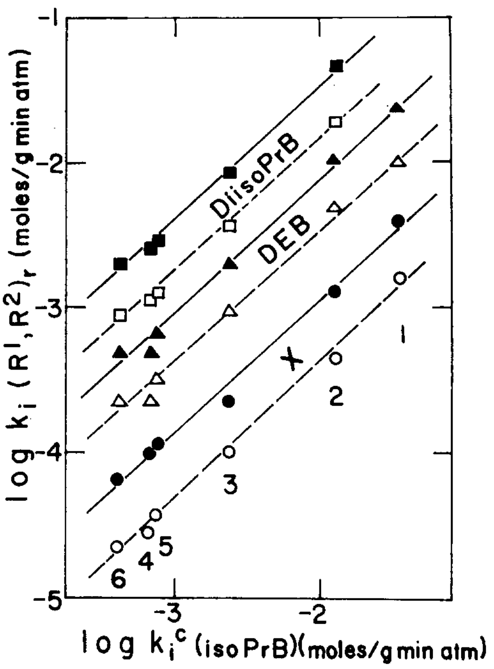

FIG. 1. Rate constants of isomerization of dialkylbenzenes vs. rate constants of cumene cracking over a series of catalysts at 400°C. Numbers refer to Table 1. The solid lines indicate para–meta conversions and the broken lines meta–para conversions.

DISCUSSION

The isomerization of dialkylbenzenes is probably catalyzed also by protons on catalysts, since cumene cracking has generally been believed to occur on the Brönsted or protonic acid sites, whereas it is scarcely catalyzed by alumina, which has a great deal of the Lewis acid sites in place of protonic ones (*11–13*). With respect to the isomerization mechanism, the reaction will take place through an *intra*molecular 1, 2-shift mechanism because the reaction is of essentially first order, and in isomerization starting from a para isomer, the ortho isomer appears only after a significant

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* Recently, K. L. Hanson and A. J. Engel [*AIChE. J.* 13, 260 (1967)] reported that *m*-X isomerization was of first order over silica-alumina.

amount of the meta isomer is produced. This mechanism is in accordance with the prevailing theory of homogeneous isomerization in the liquid phase (*14–16*).

At first the carbonium ion will be produced by addition of a proton staying on the catalyst surface to the carbon atom that has one of the alkyl groups, for instance R^1, as its substituent group [Eq. (1)]. Then, R^1 will move to the adjacent carbon atoms through the 1,2-shift mechanism [Eq. (2)], while R^2 is assumed to be fixed on a ring. Finally the associated carbonium ion will dissociate into an isomer and a proton on the surface. Presumedly the second step [Eq. (2)] will be rate-determining. Then, the overall isomerization rate constant, $k_i(R^1,R^2)_r$, is represented as Eq. (4)

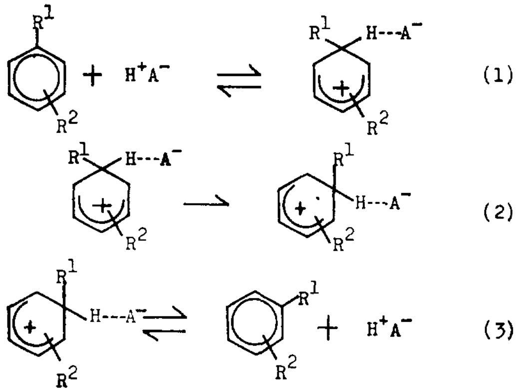

FIG. 2. The mechanism of isomerization of dialkylbenzene by acid catalyst.

$$k_i(R^1,R^2)_r = \sum_{R^m=R^1,R^2} k_i^p(R^m,R^f)_r \qquad (4)$$

where k_i^p is an overall *partial* isomerization rate constant of a group R^m that migrates along the ring and R^f is the second substituent group that is assumed to be fixed on the ring.

The geometric symmetry number, $w(r)$, should be considered. In the case of para–meta conversion, R^m has two adjacent vacant carbon atoms, whereas there is only one in meta–para conversion; hence $w(r) = 2$ for the former and $w(r) = 1$ for the latter. When rate constants of para–meta and meta–para isomerizations are compared with each other, one-half of the former is in general greater than the latter for every dialkylbenzene, as is seen in Table 2. It has already been proved that dealkylation of dialkylbenzenes is well described by the Hammett $\rho\sigma$ rule with a negative value of ρ (*1*). The absolute values of σ for methyl and ethyl groups in the para position are greater than for those in meta position. Thus, the Hammett $\rho\sigma$ rule may reasonably be assumed to hold also in the case of isomerization.

Suppose a hypothetical migration of R^m in *one direction* on a monosubstituted benzene, R^m-Ph, and denote it by a *shift* reaction and its overall rate constant by $k_i^s(R^m)$. Then the partial isomerization rate constant k_i^p will be represented as Eq. (5).

$$k_i^p = w(r)k_i^s(R^m)\exp\{2.3\rho_0(R^m)\sigma(R^f)\} \qquad (5)$$

where $\rho_0(R^m)$ is the Hammett ρ value for the partial isomerization of R^m. The overall rate constant k_i will be deduced from Eqs. (4) and (5).

$$k_i = \sum_{R^m} w(r)k_i^s(R^m)\exp\{2.3\rho_0(R^m)\sigma(R^f)\} \qquad (6)$$

By means of the nonlinear method of least squares with a computer program named PR1P11-PLG7T4, values of k_i^s and ρ_0 were obtained for the *i*th catalyst as given in Table 3, where σ(*m*-iso-Pr) was assumed to be −0.07. The values of k_i^s were found distinctly to depend upon both catalysts and the migrating alkyl groups. However, the values of ρ_0 for overall rate constants should be independent of catalyst from the thermodynamic viewpoint in reversible reactions like isomerization.

The value of k_i^s(*tert*-Bu) was not obtained because of the lack of reactants. However, its value was estimated from k_i(*p*-*tert*-BuT), by assuming ρ_0(*tert*-Bu) $= -0.6$ according to the trend of ρ values. A fine correlation is found between the logarithms of these $k_i^s(R^m)$ and $\Delta H_{C^+}(R^m)$, the enthalpy change for the hydride abstraction from corresponding paraffins (*1*), for about two orders of magnitude in the

TABLE 3

The Calculated Values of k_i^s and ρ_0 [a]

Catalyst	k_i^s(Me)	ρ_0(Me)	k_i^s(Et)	ρ_0(Et)	k_i^s(iso-Pr)	ρ_0(iso-Pr)
SA-1	6.59×10^{-4} (7.1%)	−0.99 (26.1%)	4.01×10^{-3} (5.7%)	−1.13 (18.5%)	—	—
SA-1-Na-1	1.28×10^{-4} (27.6%)	−1.48 (32.6%)	1.98×10^{-3} (33.9%)	−0.63 (51.1%)	1.00×10^{-2} (32.3%)	−0.76 (36.1%)
SA-1-Na-2	2.94×10^{-5} (26.0%)	−1.62 (60.8%)	3.05×10^{-4} (34.2%)	−1.66 (46.3%)	1.82×10^{-3} (32.7%)	−0.75 (37.7%)
SA-1-Na-3	9.21×10^{-6} (11.1%)	−2.49 (69.2%)	8.74×10^{-5} (36.5%)	−1.27 (38.5%)	5.92×10^{-4} (39.6%)	−0.75 (47.7%)
SA-1-Na-HCl-2	1.34×10^{-5} (27.8%)	−1.93 (52.8%)	1.12×10^{-4} (42.0%)	−1.59 (53.9%)	6.84×10^{-4} (34.2%)	−0.62 (53.3%)
SA-1-Na-HAcO-2	8.52×10^{-6} (50.0%)	−1.55 (83.9%)	6.83×10^{-5} (37.9%)	−1.17 (63.2%)	4.68×10^{-4} (35.4%)	−0.53 (73.7%)

[a] (   ), relative error.

shift rate constant, as is given in Fig. 3. Hence, over SA-1-Na-3

$$\log k_i^s(\mathrm{R^m}) = \log k_i^s(0) - \gamma'_i \Delta H_{\mathrm{C^+}}(\mathrm{R^m})/2.3RT \quad (7)$$

where $k_i^s(0)$ is a shift rate constant of a hypothetical group whose $\Delta H_{\mathrm{C^+}}$ is equal to zero, and is dependent upon both the catalyst and the kind of reaction (isomerization in this case) but not upon the alkyl groups; γ'_i is a proportional constant and is 0.085 for SA-1-Na-3 at 400°C.

As regards the dependency of $k_i^s(\mathrm{R^m})$ on catalysts, log k_i^s has a linear correlation with log k_i^c(iso-PrB), which is the *cracking* rate constant of iso-PrB over the *i*th catalyst and is adopted as a tentative expression of a variable that represents the catalytic activity of the *i*th catalyst (Fig. 3). Thus Eq. (8) will be given

$$k_i^s(\mathrm{R^m}) = k_0^s(\mathrm{R^m}) \exp\{2.3\lambda_0(\mathrm{R^m}) \log k_i^c(\text{iso-PrB})\} \quad (8)$$

where k_0^s is an empirical constant equivalent to the value of k_i^s of a catalyst over which k_i^c(iso-PrB) is unity, λ_0 is a proportional constant, and the suffix 0 means that those values do not depend upon catalysts. The generalized Eq. (9) may be deduced from Eqs. (6) and (8)

$$k_i = \sum_{\mathrm{R^m}} w(\mathrm{r}) k_0^s(\mathrm{R^m}) \exp\{2.3\lambda_0(\mathrm{R^m}) \log k_i^c(\text{iso-PrB}) + 2.3\rho_0(\mathrm{R^m})\sigma(\mathrm{R^f})\} \quad (9)$$

Empirical constants, k_0^s, λ_0, and ρ_0 were calculated from rate data of all combinations of reactants and catalysts, again by means of the nonlinear method of least squares. These calculated values are listed in Table 4.

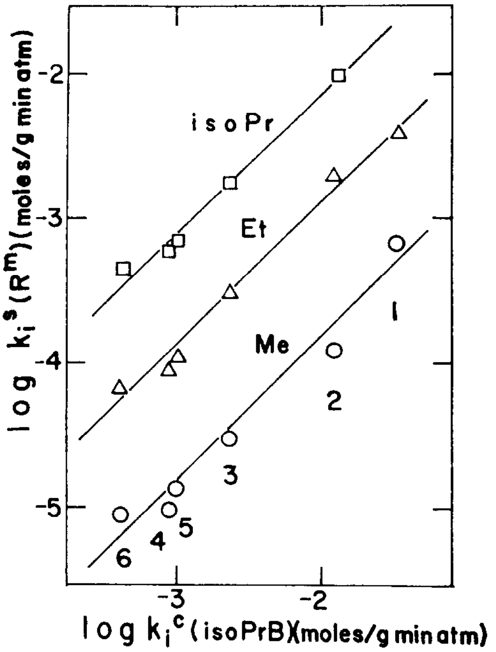

FIG. 3. Shift rate constants of alkyl groups vs. rate constants of cumene cracking over a series of catalysts. Numbers refer to Table 1.

The logarithms of k_0^s given in Table 4 also have a fair correlation with $\Delta H_{\mathrm{C^+}}(\mathrm{R^m})$, as is shown in Fig. 4, although only three values are given, thus

$$\log k_0^s(\mathrm{R^m}) = \log k_0^s(0) - \gamma'_0 \Delta H_{\mathrm{C^+}}(\mathrm{R^m})/2.3RT \quad (10)$$

where $k_0^s(0)$ is a shift rate constant, which is dependent upon only the kind of reaction, but not upon both the alkyl groups and catalysts. The value of γ'_0 is a proportional constant independent of catalysts.

From the above-mentioned analysis, the effects of the second substituted groups on isomerization of dialkylbenzenes were found to be described by the Hammett law over every catalyst used, and the LFER between rate data and $\Delta H_{\mathrm{C^+}}$ of migrating alkyl

TABLE 4

THE CALCULATED VALUES OF THE EMPIRICAL CONSTANTS

$\mathrm{R^m}$	$k_0^s(\mathrm{R^m})$[a]	$\lambda_0(\mathrm{R^m})$	$\rho_0(\mathrm{R^m})$
Me	1.46×10^{-2} (36.7%)[b]	0.97 (5.1%)	−1.72 (28.7%)
Et	1.14×10^{-1} (24.4%)	0.85 (3.5%)	−1.10 (4.7%)
iso-Pr	3.64×10^{-1} (22.7%)	0.80 (3.7%)	−0.80 (1.4%)

[a] Moles/g min atm.

[b] Relative error.

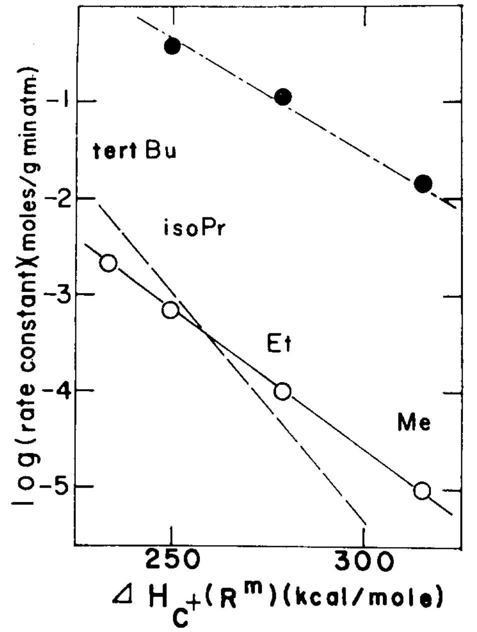

FIG. 4. Rate constants of shift and dealkylation of alkyl groups vs. enthalpy change, ΔH_{C^+}, at 400° C. The solid line indicates the shift rate constant over SA-1-Na-3, the broken line the dealkylation rate constant over SA-1-Na-3, and the chain line $k_0{}^s(R^m)$.

group will be applicable to catalysts other than SA-1-Na-3. Hence, these successes in the LFER will make it possible to estimate the rate constants of isomerization at 400°C from Eq. (9) if some empirical constants and the standard rate constant, k_i(iso-PrB), on a catalyst are known. Furthermore, reactivities of alkyl groups other than those used in the present work may be also predicted by Eqs. (7) or (10) from ΔH_{C^+} values.

In the present work the shift rate of a migrating group R^m was found to have a good correlation with its $\Delta H_{C^+}(R^m)$. The explanation is that the alkyl group will gain a positive charge during the shift and that the ability of the group to stabilize its positive charge may control the shift rate, in agreement with the mechanism suggested by Brown (*4*) in homogeneous reactions.

Both isomerization and dealkylation will have a common preliminary equilibrium ([I] $\rightleftharpoons$ [II]), and the selectivity between them will be determined by whether or not the alkyl carbonium ion R^+ may be separated far away from the ring. In isomerization, the alkyl group migrates along the benzene ring, keeping interaction with the latter. Then the activated complex [VI] should have lower activation energy than [III]. Actually it is roughly proved by comparing the activation energies of dealkylation (*3*) with those of isomerization preliminarily observed by the present authors (*17*). We have been discussing the overall rate constants that have the contribution of the equilibrium constants between [I] and [II]; nevertheless, the variation of the constants among reactants may be neglected, as was discussed in a previous paper (*1*).

For dealkylation of monoalkylbenzenes, a similar equation to Eq. (7) was derived and its γ'_i was 0.148 on the same catalyst, SA-1-Na-3, at the same reaction temper-

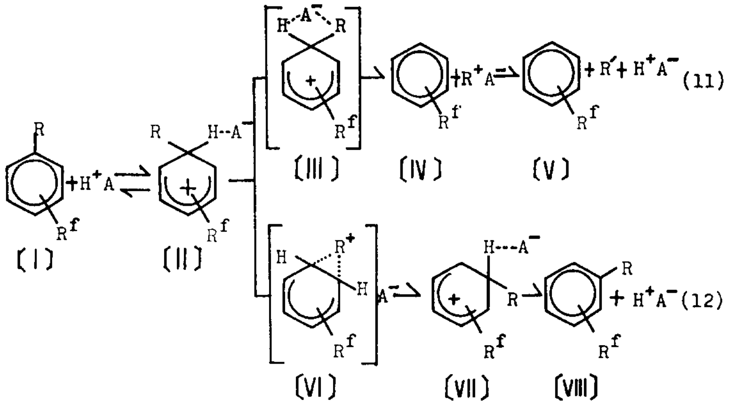

FIG. 5. The reaction schemes of isomerization and dealkylation of dialkylbenzenes.

ature of 400°C. In the case of the isomerization it is 0.085. This trend may reasonably be understood from the above reaction scheme.

The selectivity between both reactions should depend upon the alkyl groups as is shown in Fig. 4 where the rates for the dealkylation are taken from a previous paper (*2*) at the same temperature, 400°C. The reactivities of both reactions cross nearly at the iso-Pr group, but this cross point will be dependent upon temperature because the activation energies of dealkylation were found, in a preliminary experiment, higher than those of isomerization. The dealkylation reaction is favorable at a high temperature from the thermodynamic viewpoint. Thus, the selectivity of alkylbenzenes dependent upon temperature may be quantitatively predicted. The details will be published in the nearest future.

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