A Kinetic Study of the Simultaneous Dealkylation and Disproportionation of Cumene over Silica-Alumina[1)]

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Cumene has been passed over a silica–alumina bed at low temperature (210 to 254 °C) and at cumene pressures of 0.003 to 0.023 atm. Both dealkylation and disproportionation occurred simultaneously and independently of each other. The disproportionation/dealkylation ratio increased with decrease in temperature and/or an increase in cumene pressure. The dealkylation and disproportionation reactions followed a Langmuir-Hinshelwood model with inhibition by the reactant. The dealkylation has been interpreted in terms of a unimolecular surface reaction, while the disproportionation reaction in terms of a bimolecular surface reaction. The heat of adsorption of cumene and the entropy loss of cumene on adsorption were much larger for the dealkylation sites than for the disproportionation sites. These results indicated that dealkylation was catalyzed by strong acid sites, while disproportionation by weak acid sites. The dealkylation had a much higher activation energy than the disproportionation reaction. The activation energy for dealkylation (33.5 kcal mol^{-1}) was in good agreement with that predicted on the assumption that the previously reported LFER (linear free-energy relationship) in the alcohol dehydration holds for alkylbenzene dealkylation.

The catalytic dealkylation of cumene has been employed as a standard test for characterizing acidic cracking catalysts. The kinetics have been investigated in detail at high temperatures (above 300 °C) by Prater and Lago,[2)] Horton and Maatman,[3)] and Wojciechowski and coworkers.[4,5)] Under the conditions where the reverse reaction is negligible, the accepted kinetic scheme of this reaction is

$$C + S \rightleftarrows CS \longrightarrow \text{products}, \qquad (1)$$

where C represents cumene, S, an active site, and CS, cumene adsorbed on an active site. It has been shown that the bond-breaking step, CS→products, is the rate-determining step.[2,6,7)]

Cumen is known to undergo disproportionation to benzene and diisopropylbenzenes in the presence of a Friedel-Crafts catalyst.[8,9)] Therefore, under favorable conditions, cumene disproportionation may take place on acidic cracking catalysts. However, little attention has been paid hitherto to this reaction over acidic cracking catalysts. The present study intends to obtain kinetic data on the nature of the active sites for cumene dealkylation and disproportionation, as well as about the nature of the two reactions, under the conditions where both reactions take place simultaneously.

Recently, it has been reported that the activation energy for the bond-breaking step in the catalytic dehydration of alkanols (ROH) on silica–alumina has a linear relationship with the heterolytic bond dissociation energy for the C–O bond in alcohols, $D(\mathrm{R^+OH^-})$.[10)] Mochida and Yoneda[7)] reported that the apparent activation energy for the dealkylation of monoalkylbenzenes (RPh, where R=alkyl and Ph=phenyl) over silica–alumina had a linear relationship with the enthalpy change of the hydride abstraction from the corresponding paraffin, $\Delta H_c^+(\mathrm{R})$. This enthalpy change, in its turn, linearly correlates with $D(\mathrm{R^+Ph^-})$ for RPh. Therefore, the present study also intends to establish whether the LFER (linear free-energy relationship) obtained in the alcohol dehydration holds in the catalytic dealkylation of monoalkylbenzenes.

Experimental

Materials. The silica–alumina (SA-1, 13% Al_2O_3) was obtained from the same source.[6,7,10)] Cumene of GR grade from Tokyo Kasei was percolated through two columns packed with silica gel and active alumina, and stored over a mixture of active alumina and Molecular Sieve 4A under nitrogen. Gas-chromatographic analysis of the cumene indicated a purity of 99.2 mol%; the impurities were *m*- and *p*-xylenes which did not affect the reactions to any detectable extent. Hydrogen, used as a diluent gas, was purified by passing it through a Deoxo column and then a Dry Ice–ethanol temperature trap.

Apparatus and Procedures. Experiments were conducted in a continuous flow-type reactor, the details of which have been given in a previous paper.[10)] Catalyst charges of 0.19—0.26 g were used depending mainly on the reaction temperature. The catalyst was activated in a hydrogen stream with a flow rate of 40 STP ml min^{-1} for 2 h at 450 °C. The temperature was then lowered to the reaction temperature (210—254 °C) and additional hydrogen was admitted from another inlet. After the total flow rate of hydrogen had been adjusted to about 300 STP ml min^{-1}, cumene was introduced from a microfeeder. The desired partial pressure was attained about 30 min later.

Subsequently, a portion of the effluent gas was led through a 6-way sampling-valve to a gas-liquid chromatograph with a flame ionizing detector for analysis at intervals of 5—10 min. An analysing column of Silicone DC-11 (2-m long) was used at 140 °C. In some experiments, a column of VZ-7 (6-m long) was also used at 0 °C for analysis of lighter hydrocarbon products.

A total of five kinetic runs were made at 210—254 °C. In each run lasting for 7—8 h at constant temperature, the run was divided into several periods in which the partial pressure of cumene was altered over the range of 0.003—0.023 atm (by changing the feed rate). Each period lasted for 60—80 min, including an initial 30 min period for the attainment of steady-state conditions (no samples taken). In the subsequent period of 30—50 min, the effluent gas was analysed at least four times.

Treatment of Data. A plot of the cumene conversion to each product against the reciprocal space velocity was linear through the origin in the region of total conversion below 8%, indicating that the differential-reactor conditions were met.

Since the total conversion of cumene was kept below this level in all runs, the rate of formation of the i product, v_i, was calculated by

$$v_i = x_i F/W, \tag{2}$$

where x_i is the fractional conversion to the i product, F, the feed rate of cumene (mol min^{-1}) and W, the catalyst weight(g).

Slow catalyst aging occurred during the run, necessitating correction of the data on a common basis. The bracketing sequence of Sinfelt[11] was adopted for this purpose: periods at a chosen standard condition were repeated between periods at other conditions. The rates of formation of the dealkylation and disproportionation products were plotted separately as a function of run time. Smooth curves were drawn through the data of the standard periods to obtain the aging curves. Intermediate run periods were then corrected to a common reference time using the following relationships, since the aging curves were linear as will be stated below:

$$\alpha = (v_r{}^s - v_t{}^s)/v_r{}^s,$$
$$v_r = v_t/(1-\alpha),$$

where α is the degree of catalyst aging, $v_r{}^s$ and $v_t{}^s$, the reaction rates for standard conditions at reference time r and another time t, respectively, and v_r and v_t, the reaction rates for other conditions at times r and t, respectively.

Sample analyses in each period consistently gave the same product composition, implying that the catalyst aging was negligible in that period. Therefore, each period was represented by the reaction rates and run time averaged over that period. Typical plots of the rates of formation as a function of run time are presented in Fig. 1. Other temperature conditions gave a similar catalyst aging pattern, indicating that the catalyst activity declined slowly and linearly with increasing run time. The standard periods were operated at a cumene pressure of 0.003—0.004 atm. The reference time was t/min= 50 in Fig. 1.

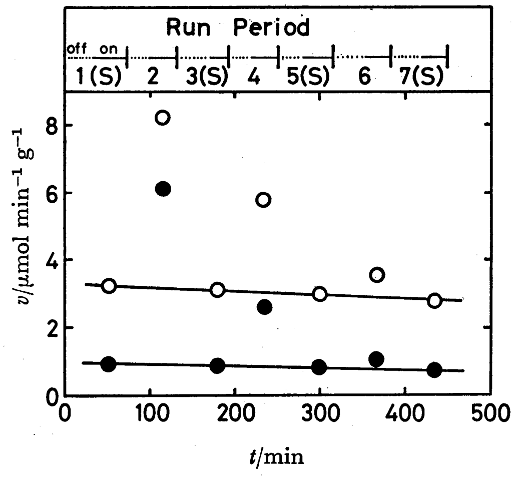

Fig. 1. Catalyst aging for run at 220 °C.
○ and ● denote the rates of dealkylation and disproportionation, respectively, (s), the standard period.

Results

Diffusion Effects. The mass transfer effects were assessed by running at constant partial pressure (0.023 atm) and temperature (250 °C) and by varying the total flow rate of the diluent gas over the range of 100 to 400 STP ml min^{-1}. The reaction rates for dealkylation and disproportionation did not change when the total flow rate was higher than 180 STP ml min^{-1}, indicating that the external diffusion effects were negligible under such conditions. The diluent gas has therefore been passed at a flow rate of about 300 STP ml min^{-1} in all kinetic runs.

The internal diffusion effects have been examined using the Weisz formula,[12]

$$\Phi = \frac{dN}{dt}\frac{1}{C_0}\frac{R^2}{D_{\mathrm{eff}}},$$

where dN/dt is the reaction rate in mol s^{-1} cm^{-3}, C_0, the reactant concentration in mol cm^{-3}, R, the catalyst particle radius in cm, and D_{eff}, the effective diffusion constant in cm^2 s^{-1}. In the present study, the limits for these coefficients are as follows: $dN/dt = 5\times10^{-7}$ mol s^{-1} cm^{-3} as the total reaction rate of cumene, $C_0 = 1\times10^{-7}$ mol cm^{-3}, $R = 5\times10^{-3}$ cm, and $D_{\mathrm{eff}} = 10^{-3}$ cm^2 s^{-1} for the system of silica–alumina and cumene.[12] These values give a Φ of 1.3×10^{-1}, from which the effectiveness factor is evaluated to be very close to 1 for zero- to second-order reactions.[12] Consequently, the internal diffusion effects on the reaction rates have been concluded to be negligible.

TABLE 1. PRODUCT COMPOSITION FROM CUMENE ON SILICA–ALUMINA

t	p a)	Molar ratios of products b),c)				
°C	atm	P	DPB	P+DPB	B	DPB/P
210	0.02	0.59	0.39	0.98	1.00	0.66
230	0.02	0.70	0.33	1.03	1.00	0.47
254	0.02	0.80	0.19	0.99	1.00	0.24
254	0.01	0.85	0.12	0.97	1.00	0.14

a) Cumene partial pressure. b) P=propene, DPB=m- and p-diisopropylbenzenes, B=benzene. c) Normalized to benzene=1.00.

Reaction Products. The reaction products were propene (P), benzene (B), and m- and p-diisopropylbenzenes (DPB); o-diisopropylbenzene was not formed to any detectable extent. Table 1 presents typical data on the product composition. Other temperature and partial pressure conditions gave a similar product composition. On the basis of these data, the following points emerge: (a) propene is consistently smaller in the amount of formation than benzene, indicating reactions other than dealkylation, (b) the amount of propene plus diisopropylbenzenes is equal to that of benzene, (c) the DPB/P ratio changes depending upon the temperature and cumene pressure, *i.e.*, the lower-temperature and/or higher-cumene pressure conditions favor the formation of diisopropylbenzenes.

The formation of propene undoubtedly results from the dealkylation of cumene. The possible reactions which form diisopropylbenzenes are the disproportionation of cumene, the alkylation of cumene with propene, and the alkylation of benzene with propene. The existence of one of the three reactions, in addition to that of dealkylation, accounts for observation (b), P+DPB=B. As mentioned in Experimental, a plot of the cumene conversion to each product against the residence time was linear through the origin, indicating that the two isomers of diisopropylbenzene are primary products. Therefore, the last two of the three reactions are unimportant for the formation of diisopropylbenzenes under these experimental conditions. The rates of formation of diisopropylbenzenes and propene thus give the rates of disproportionation, v_D, and dealkylation, v_C, respectively. In some experiments, the difference in the amounts of benzene and propene was taken as the amount of diisopropylbenzenes formed. The ratio of the meta to the para isomers was 1.3—1.6 for all runs.

Kinetics. The rate data were first subjected to a simple power low rate equation. The plots of log v_C and log v_D *versus* log p(cumene pressure) indicated that the kinetic expressions were more complex than a simple first- or second-order reaction.

Subsequently, the data was analysed using the Langmuir-Hinshelwood theory. Best fits were found when dealkylation was assumed to be controlled by a single-site surface reaction, namely,

$$v_C = \frac{k_C K_C p}{1+K_C p}, \tag{3}$$

and disproportionation by a dual-site surface reaction,

$$v_D = k_D\left(\frac{K_D p}{1+K_D p}\right)^2, \tag{4}$$

where k_C and k_D are the rate constants for dealkylation and disproportionation, respectively, K_C and K_D, the adsorption equilibrium constants of cumene for the dealkylation and disproportionation sites, respectively. Figures 2 and 3 show typical plots for these equations. The proposed fit to the equations is good and the values for the rate and adsorption-equilibrium constants obtained from each plot are given in Table 2. The plots of log k and log K *versus* $1/T$ were ideally linear. The activation energies (E_A), the pre-exponential factors (A), the heats of adsorption (Q_a), and the entropies of adsorption (ΔS_a) were calculated from the plots, the results of which are included in Table 3.

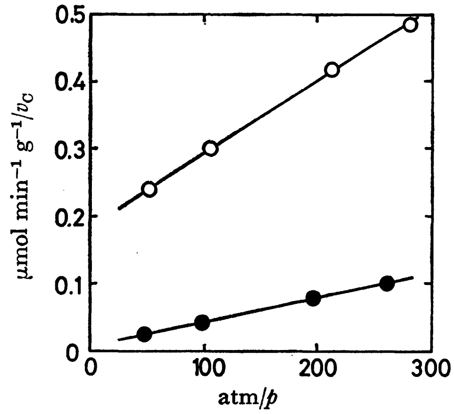

Fig. 2. Correlation of dealkylation rates with Eq. 3.
○: 210 °C, ●: 254 °C.

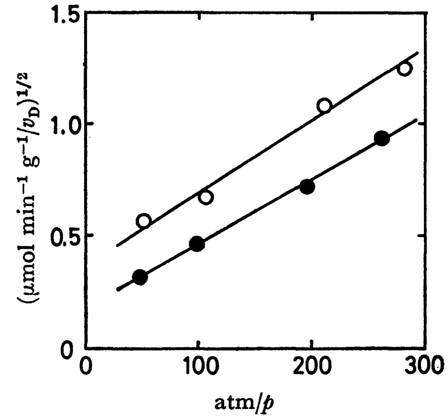

Fig. 3. Correlation of disproportionation rates with Eq. 4.
○: 210 °C, ●: 254 °C.

TABLE 2. RATE AND ADSORPTION-EQUILIBRIUM CONSTANTS FOR CUMENE DEALKYLATION AND DISPROPORTIONATION

t	Dealkylation		Disproportionation	
°C	k_C μmol min^{-1} g^{-1}	K_C atm^{-1}	k_D μmol min^{-1} g^{-1}	K_D atm^{-1}
210	5.33	175	7.31	114
220	12.7	93.5	12.7	88.9
230	20.4	84.0	16.6	79.0
240	40.6	54.0	25.0	71.4
254	105	27.4	39.1	53.3

TABLE 3. ARRHENIUS PARAMETERS, HEATS OF ADSORPTION, AND ENTROPIES OF ADSORPTION FOR CUMENE DEALKYLATION AND DISPROPORTIONATION[a]

	Dealkylation	Disproportionation
E_A/kcal mol^{-1}	33.5	19.4
log (A/μmol min^{-1} g^{-1})	15.9	9.67
Q_a/kcal mol^{-1}	20.1	8.1
ΔS_a/cal K^{-1} mol^{-1}	−31.4	−7.4

a) E_A is the activation energy, A, the pre-exponential factor, Q_a and ΔS_a, the heat and entropy of adsorption, respectively.

Discussion

The Nature of the Dealkylation, Disproportionation, and Active Sites. The kinetic model which best correlates the rate data on the dealkylation at low temperatures is identical with that which has generally been accepted for the same reaction at higher temperatures (Eq. 1). This implies that the low-temperature dealkylation of cumene is rate-determined by a unimolecular surface reaction of cumene adsorbed on an active site. The disproportionation of cumene has kinetically been shown to be rate-determined by a bimolecular surface reaction of the adjacent, absorbed molecules of cumene. The cumene disproportionation is therefore the same in the kinetic model as the disproportionation of toluene[13] and mesitylene[14] over acidic solid catalysts. The reactions are clearly different from each other in the number of cumene molecules which participate in the respective rate-determining steps. This difference gives rise to an increase of the disproportionation/dealkylation ratio with an increase in the partial pressure of cumene. In addition, the dealkylation has a higher activation energy than the disproportionation, as shown in Table 3 and the disproportionation/dealkylation ratio, therefore, decreases steeply with increase in temperature (Table 1).

For the dealkylation, the adsorbed cumene has generally been supposed to be a σ-complex with the proton attached at the substituted position. Accordingly, the rate-determining step in the kinetic model corresponds to a break of the C(phenyl)–C(isopropyl) bond in the σ-complex. Previous LFER studies on the dealkylation of monoalkylbenzenes[6,7] has shown that bond-breaking in the rate-determining step is heterolytic. The alkylbenzene disproportionation in the presence of Friedel-Crafts catalysts has been accepted as rate-determined by the nucleophilic attack of an arene on an arene cation.[8,9,15] The nature of the arene cation does not seem to have been established: a σ-complex[8] of the same type as proposed for the alkylbenzene dealkylation and a π-complex[9] have been suggested; a benzyl cation has also been proposed for the disproportionation of primary alkylbenzenes.[15]

Since the adsorption equilibrium constant measures the strength of the interactions of an adsorbing molecule with an active site, the nature of active sites should be reflected in the constant. If the dealkylation and disproportionation occurred, respectively, *via* a unimolecular and a bimolecular reaction of the surface species present on the same active sites, the same adsorption equilibrium constant would kinetically be observed for the two reactions. The data in Table 2 clearly shows that the adsorption equilibrium constants for the two reactions are different in magnitude. This difference in the adsorption equilibrium constant is emphasized by the data in Table 3, where the Q_a and ΔS_a values are clearly different for the two reactions. The heat of adsorption of cumene is notably smaller for the disproportionation sites than for the dealkylation sites. These results, therefore, indicate that the active sites differ in nature, probably in acidic nature. Dealkylation is catalyzed by strong acid sites, while disproportionation by weak acid sites.

The difference in the heat of adsorption also suggests that the surface species on the disproportionation sites are more mobile than those on the dealkylation sites and this is confirmed by a comparison of the entropy data in Table 3. As shown, cumene in the gas phase has an entropy loss of about 31 cal K^{-1} mol^{-1} when it is adsorbed on the dealkylation sites, while the entropy loss markedly decreases when cumene is adsorbed on the disproportionation sites. An entropy loss of 31 cal K^{-1} mol^{-1} is comparable to that for immobile adsorption, which has been estimated to be 39 cal K^{-1} mol^{-1} under the present experimental conditions.[16] It has therefore been deduced that cumene molecules adsorbed on the disproportionation sites are, probably, relatively free on the surface. This viewpoint is in line with the nature of the disproportionation reaction, since a bimolecular surface reaction necessitates mobile adsorbed molecules.

Finally, it must be said that the correct kinetics for disproportionation were not obtained assuming the following two possible mechanism: a Rediel-type mechanism with the rate-determining step involving reaction between an adsorbed cumene molecule and another cumene molecule in the gas phase, a Langmuir-Hinshelwood mechanism with the rate-determining step in which a cumene molecule chemisorbed on the dealkylation site reacts with another cumene molecule chemisorbed on the adjacent site which differs in nature from the dealkylation sites.

Activation Energy for Dealkylation. Recently, it has been found that, in the catalytic dehydration of alkanols over silica–alumina, the activation energy for the bond-breaking step has a linear relationship with the heterolytic bond dissociation energy for the C–O bond in the alcohols, $D(R^+OH^-)$.[10] The activation energy for the bond-breaking step in the cumene dealkylation has consequently been determined. The silica–alumina catalyst used for both dehydration and dealkylation was from the same batch and was activated in the same way. The alcohol dehydration and the alkylbenzene dealkylation belong to an olefin-forming elimination reaction catalyzed by acids. Therefore, it is necessary to establish whether the LFER obtained in the alcohol dehydration holds in the alkylbenzene dealkylation. The $D(R^+Ph^-)$ value for cumene has been calculated to be 220 kcal mol^{-1} using the reported values for the standard heats of formation of cumene, the isopropyl cation, and the phenyl anion, as shown in Table 4. This $D(R^+Ph^-)$ value is equal in magnitude to the $D(R^+OH^-)$ value for *s*-butyl alcohol. The assumption that the LFER in the alcohol dehydration holds in the alkylbenzene dealkylation predicts an activation energy of 32 kcal mol^{-1} for the bond-breaking step in the cumene dealkylation. The predicted value is very close to the observed one (33.5 kcal mol^{-1}, Table 3).

TABLE 4. HETEROLYTIC BOND DISSOCIATION ENERGY AND RELATED THERMODYNAMIC QUANTITIES[a]

R	$\Delta H^\circ_f(R^+)$[b] / kcal mol^{-1}	$\Delta H^\circ_f(RPh)$[c] / kcal mol^{-1}	$D(R^+Ph^-)$[d] / kcal mol^{-1}
Et	219.0	7.12	241
n-Pr	207.8	1.87	235
i-Pr	191.7	0.94	220
n-Bu	200.7	−3.30	233
i-Bu	198.7	−5.15	233
s-Bu	183.3	−4.17	216
t-Bu	166.6	−5.42	201
	$\Delta H^\circ_f(Ph^-)$[e]/kcal mol^{-1} = 29.0		

a) ΔH°_f is the standard heat of formation, *D*, the heterolytic bond dissociation energy, *EA*, the electron affinity, Et=ethyl; Pr=propyl; Bu=butyl; Ph=phenyl. b) See Ref. 10 and references cited therein. c) D. S. Stull, E. F. Westrum, Jr., and G. C. Sinke, "Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, New York (1969). d) Calculated according to $D(R^+Ph^-) = \Delta H^\circ_f(R^+) + \Delta H^\circ_f(Ph^-) - \Delta H^\circ_f(RPh)$. e) Calculated according to $\Delta H^\circ_f(Ph^-) = \Delta H^\circ_f(Ph) - EA(Ph)$ using $\Delta H^\circ_f(Ph)$/kcal mol^{-1}=80.0[f] and $EA(Ph)$/kcal mol^{-1}=51.0.[g] f) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969). g) A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **59**, 1266 (1963).

The apparent activation energies for the monoalkylbenzene dealkylation have been reported by Mochida and Yoneda,[7] under the conditions where the reaction was nearly first-order in the reactant using silica–alumina taken from the same batch as used in the present work. The numerical values of the apparent activation energies reported in Ref. 7 are as follow (in kcal mol^{-1}): 17±4 (ethylbenzene); 14.5±2 (propylbenzene); 14.5±1.5 (butylbenzene); 11±3.5 (cumene); 11±2 (*s*-butylbenzene); 10±1 (*t*-butylbenzene). The assumption[6] that the heat of adsorption is approximately the same for all the alkylbenzenes used has been used here. Using the observed value for the heat of adsorption of cumene on the dealkylation sites (Table 3), the activation energies for the zero-order dealkylation, namely, for the bond-breaking step in the dealkylation may be calculated as the sum of the apparent activation energies and the heat of adsorption of cumene. The calculated values and the values predicted from the LFER in the alcohol dehydration and the $D(R^+Ph^-)$ values shown in Table 4 are (given in kcal mol^{-1} as the calculated, the predicted): 37±4, 37 (ethylbenzene); 35±2, 35 (propylbenzene); 35±1.5, 35 (butylbenzene); 31±3.5, 32 (cumene); 31±2, 31 (*s*-butylbenzene); 30±1, 28 (*t*-butylbenzene). The activation energy calculated for the cumene dealkylation is in good agreement with that observed in the present study. Also, the agreement between the calculated and the predicted values is excellent for all the alkylbenzenes used, though the equality in the heat of adsorption has been assumed as above. Therefore, it is likely that the LFER observed in the alcohol dehydration holds, at least approximately, in the alkylbenzene dealkylation, as shown in Fig. 4.

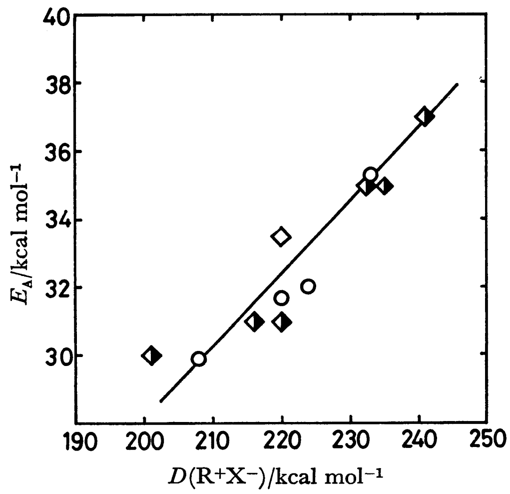

Fig. 4. Correlation of activation energies for alcohol-dehydration and alkylbenzene-dealkylation over silica–alumina with heterolytic bond dissociation energies for the C–X bond. ○: Alcohol-dehydration;[10] ◇ and ⬖: observed and calculated activation energies, respectively, for alkylbenzene-dealkylation (see text).

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