

# Linear Free Energy Relationships in Heterogeneous Catalysis

## I. Dealkylation of Alkylbenzenes on Cracking Catalysts

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It was attempted to survey the applicability of LFER (Linear Free Energy Relationships) in heterogeneous catalysis to dealkylation of alkylbenzenes. The principle of LFER in heterogeneous catalysis is to find linear relationships between the rate data and some numerical variables which represent either reactivity of reactants or catalytic activity of heterogeneous catalysts. The microcatalytic gas chromatographic technique was used to measure the reaction rates at 400°C on cracking catalysts. As for monoalkylbenzenes, the logarithms of the rate constants hold a linear relationship with  $\Delta H_{C^+}(R_1)$  for about two and one-half orders of magnitude in the rate constants. This relationship can be formulated by the following equation:

$$\log k_i(R_1) = \log k_i(0) - \gamma'_i \Delta H_{C^+}(R_1)/2.303RT$$

where  $k_i(0)$  is a characteristic value dependent upon both the catalyst  $i$  and the kind of reaction (dealkylation in this case), but not upon the reactants, and  $\Delta H_{C^+}(R_1)$  is the enthalpy change for the hydride abstraction from corresponding paraffins. By this equation it is meant that LFER is applicable to solid acid catalysis. Therefore, the reaction rate constants can be estimated from the values of  $\Delta H_{C^+}(R_1)$  and a few measured values such as  $k_i(0)$  and  $\gamma'_i$ . The effects of the second substituent group on dealkylation rate are also discussed by the Hammett law. Linear relationships between the logarithms of the rate constants and  $\Delta H_{C^+}(R_1)$  or  $\sigma(R_2)$  are applied to the work previously published. In these cases, fine linear relationships are also obtained.

### INTRODUCTION

It should be one of the most important branches of research on catalysis to establish how to estimate the rate of a given reaction of a given reactant on a given catalyst.

The kinetic approach has furnished profound information concerning temperature and pressure dependency of the reaction rates as well as concerning the elucidation of the reaction schemes. This approach, however, pays less attention to the relationship with regard to catalysts or reactants.

In homogeneous systems, however, LFER (Linear Free Energy Relationships) such as the Hammett  $\rho\sigma$  law, the Brönsted catalysis law, or the Polanyi rule, have contributed not only to the estimation of the reaction

rate, but also to the elucidation of the reaction mechanism (1). The principle of LFER in heterogeneous catalysis is to find linear relationships between the rate data and some numerical variables which represent either reactivity of the reactants or catalytic activity of heterogeneous catalysts. As far as numerical variables for reactants are concerned, the thermodynamic values of certain reaction steps including the rate-determining one, empirical reactivity indexes such as the Hammett  $\sigma$ , or some quantum chemical reactivity indexes will be employed.

Greensfelder *et al.* (2) applied this approach for the first time to solid acid catalysis and got success in explaining quantitatively the distribution of the products in

cetane cracking. Franklin and Nicholson (3) correlated the activation energy in the decomposition reaction of various hydrocarbons on silica-alumina with the ionization potential values of the reactants. Recently Emmett *et al.* (4) modified the method of Greensfelder *et al.* (2), and obtained more precise coincidence with the experimental results. Greensfelder *et al.* (2) also suggested qualitatively the correlation between the dealkylation conversion of monoalkylbenzenes and the enthalpy change for the hydride abstraction from corresponding paraffins.

In the present paper, it was attempted to survey the applicability of LFER in heterogeneous catalysis in dealkylation of alkylbenzenes. Rase and Kirk (18) already have published their results for this reaction on silica-alumina; however, the trend of the activation energy in their work differs from that of other work (11). The present authors, therefore, confirmed the rate data by means of a microcatalytic gas chromatographic technique.

#### EXPERIMENTAL

**Reagents.** Alkylbenzenes used in this work are listed in Table 1. Most of them were G. R. or E. P. grade reagents (Tokyo Kasei Co.) and were not purified further. However, polar impurities such as hydroperoxides in isopropylbenzene and its derivatives were removed by means of an adsorption column of silica gel and alumina gel (5).

**Catalysts.** The catalysts used in this work are listed in Table 2, together with some of their properties. They were all calcined at 550°C for 8 hr in the atmosphere.

**Apparatus and procedures.** As numerous

catalysts and reactants were to be tested, a rapid method to get the reaction rates was preferable. The microcatalytic gas chromatographic technique was, therefore, adopted for its convenience (6). Hydrogen carrier gas was purified to remove water and oxygen. The analytical column used was 2.5 m of dioctyl phthalate. The reaction temperature was kept at 400° ± 2°C.

TABLE 1  
REAGENTS

No.	Abbreviation	Reagent
1	Et	Ethylbenzene
2	di-Et	Diethylbenzene
3	<i>n</i> -Pr	<i>n</i> -Propylbenzene
4	iso-Pr	Isopropylbenzene
5	iso-Pr-Me	<i>p</i> -Isopropyltoluene
6	di-iso-Pr	<i>p</i> -Diisopropylbenzene
7	<i>n</i> -Bu	<i>n</i> -Butylbenzene
8	<i>sec</i> -Bu	<i>sec</i> -Butylbenzene
9	<i>tert</i> -Bu	<i>tert</i> -Butylbenzene
10	<i>tert</i> -Bu-Me	<i>p-tert</i> -Butyltoluene

A certain amount of catalyst (e.g., SA-1, about 20 mg; SM-1, about 1 g) was weighed and held at the middle of a glass reactor, 4-mm or 8-mm ID, supported by quartz wool. After a 1- to 3-hr pretreatment of the catalyst in a hydrogen gas flow at 450°C, one set of the reagents in the sequence of Table 1 was injected into the gas flow from the top of the reactor through a silicone serum cap with a microsyringe. The products were analyzed with a gas chromatograph directly connected to the reactor. Then, in the reverse sequence of Table 1, the same procedure was repeated. The average of these two sets of results was assumed to be the conversion under the same condition.

The catalyst was successively poisoned by

TABLE 2  
CATALYSTS

Catalysts		Surface area BET (m <sup>2</sup> /g)	Composition	Remarks
Symbol	Name			
SA-1	Silica-alumina	540	13% Al <sub>2</sub> O <sub>3</sub>	<i>a</i>
SM-1	Silica-magnesia	560	16% MgO	<i>b</i>

<sup>a</sup> "Nippon Cat," cracking catalyst of Shokubai Kasei Co.

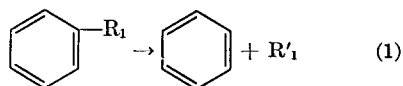
<sup>b</sup> TY-13, cracking catalyst of Nikki Kagaku Co.

every injection but the decline of the activity was so small without depending upon the reactant, that these average values would represent the conversions on the catalyst which was poisoned presumably to the same

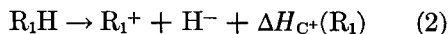
selected so that the conversion would not be saturated for all reagents, except for *p*-tert-butyltoluene, where the conversion was occasionally saturated.

## RESULTS

**Monoalkylbenzenes.** Regarding all reagents listed in Table 1, the apparent rate constant was obtained at 400°C for each catalyst listed in Table 2, with the space velocity varied from  $3.46 \times 10^{-4}$  to  $1.41 \times 10^{-2}$  min g/ml, depending upon the catalytic activity of the catalyst used. The main reaction occurring in this experiment was dealkylation as shown in Eq. (1)



where  $\text{R}_1$  designates an alkyl group and  $\text{R}'_1$ , the corresponding olefin. Other products were not detected by gas chromatography under these conditions. Results are shown in Fig. 1, in which the ordinate is the logarithm of the dealkylation rate constants\* of  $\text{R}_1\text{-C}_6\text{H}_5$  on the  $i$ th catalyst, while the abscissa is the enthalpy change of Eq. (2),  $\Delta H_{C^+}(\text{R}_1)$ ,



where  $\text{R}_1\text{H}$  is a paraffin,  $\text{R}_1^+$  is corresponding alkyl carbonium ion, and  $\Delta H_{C^+}(\text{R}_1)$  is the enthalpy change shown in Table 3, calculated from the standard enthalpy of formation of the corresponding carbonium ion as reported by Olah (?). As for monoalkylbenzenes, the logarithms of the rate constants have a fine linear relationship with  $\Delta H_{C^+}(\text{R}_1)$  over the range of about two and one-half orders of magnitude in the rate constants. This relationship can, therefore, be formulated by the following equation:

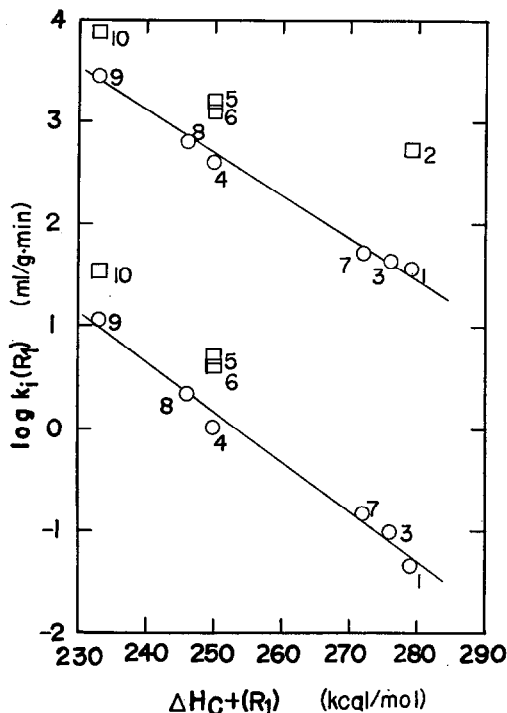


FIG. 1. Rate constants vs. the enthalpy change,  $\Delta H_{C^+}(\text{R}_1)$ . Circles represent monosubstituted alkylbenzenes and squares disubstituted ones. Numbers refer to Table 1.

extent for all the reagents tested. It was also verified experimentally that the conversion of isopropylbenzene was linear to the reciprocal space velocity ( $W/F$ ) up to the 50% conversion level, so that the conversion divided by  $W/F$  was used as the apparent rate constant,  $k_i$ , where suffix  $i$  means  $i$ th catalyst. The space velocity was properly

TABLE 3  
THE ENTHALPY CHANGE FOR THE HYDRIDE ABSTRACTION FROM PARAFFINS

$\Delta H_{C^+}(\text{R}_1)$ (kcal/mole)	Me	Et	<i>n</i> -Pr	iso-Pr	<i>n</i> -Bu	sec-Bu	tert-Bu
This work	315	279	276	250	272	246	233
Greensfelder*	316	281	266	250	268	242	233

\* Previously reported by B. S. Greensfelder, in "The Chemistry of Petroleum Hydrocarbons," Vol. 3 (B. T. Brooks *et al.*, eds.), p. 137, Reinhold, New York, 1955.

$$\log k_i(R_1) = \log k_i(0) - \gamma' \Delta H_{C^+}(R_1)/2.303RT \quad (3)$$

where  $k_i(0)$  is a characteristic value dependent upon both the catalyst  $i$  and the kind of the reaction (dealkylation in this case), but not upon the reactants. The value of  $\gamma'$  depends on the catalyst  $i$  and is found to be 0.12 for SA-1 and 0.16 for SM-1.

A fair correlation is found between the Taft  $\sigma^*(R_1)$  and the reactivity of the reactants, as shown in Fig. 2.† Other reactivity

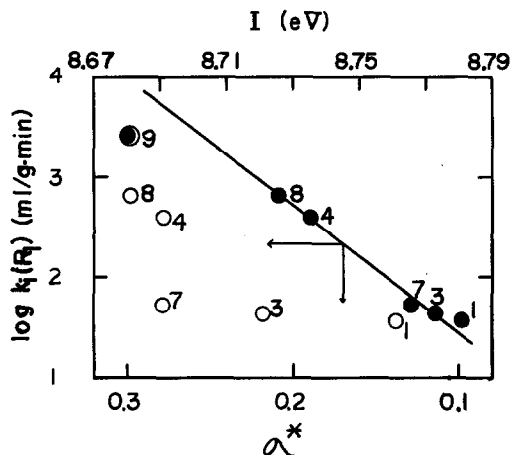


Fig. 2. Rate constants vs.  $\sigma^*(R_1)$  and ionization potential of reactants. Open circles are for ionization potential and solid circles for  $\sigma^*(R_1)$ .

indexes such as  $\sigma(R_1)$  and ionization potential gave poor correlations, some of which are given in Fig. 2 for comparison.

**Polyalkylbenzenes.** The second substituent effects on the dealkylation rate constants of disubstituted benzenes were also studied. Experimental results are plotted in Fig. 1. The electron-donating substituents increased the rate constants in the order  $p$ -isopropyltoluene >  $p$ -diisopropylbenzene > isopropylbenzene. This trend coincides with that of the Hammett  $\sigma$ .

\* In the case of diisopropylbenzene, the rate constants were divided by the appropriate symmetry number, 2.

† According to M. Kraus, Czechoslovak, Institute of Chemical Process Fundamentals, linear correlations are found between rate data and the Taft  $\sigma^*$  in many reactions. His review on this subject will be published in the near future (private communication).

## DISCUSSION

Linear relationships between the logarithm of rate constants and  $\Delta H_{C^+}(R_1)$  represented in Eq. (3) are applicable to research work published previously. Conversion or rate constants of dealkylation of monoalkylbenzenes of Greensfelder *et al.* (2) and those of  $o$ - and  $p$ -monoalkylphenols from Kraus *et al.* (8) are plotted in Figs. 3 and 4, respectively. Both plots exhibit fine linearity, although the slope of the lines differs from

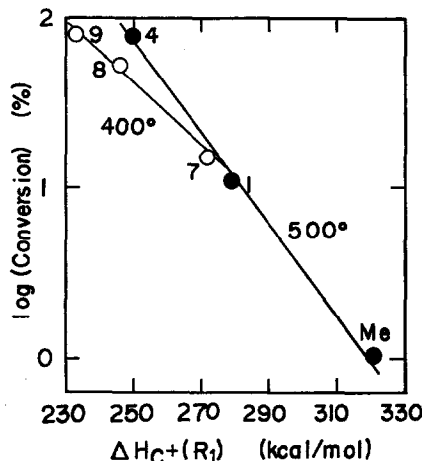


Fig. 3. Conversion of dealkylation of alkylbenzenes vs. the enthalpy change,  $\Delta H_{C^+}(R_1)$ . Conversion data are taken from B. S. Greensfelder *et al.* (2) (silica-alumina-zirconia catalyst).

our results, presumably owing to the catalyst or reaction conditions. However, this application fails in the case of hydrocracking of monoalkylphenols (8).

Now the effects of the second substituent group on dealkylation rate will be discussed. Good and Robert (9) measured dealkylation conversion of isopropylbenzene and its derivatives on silica-alumina-zirconia catalyst at 450°C. They correlated the reactivity qualitatively with the approximate activation energy calculated by means of simple MO theory. Here the reactivity of isopropylbenzene and its derivatives is plotted against the Hammett  $\sigma(R_2)$  of the second substituent and the third one when it is attached. It gives a fine linear relationship between them, as shown in Fig. 5. Very recently Schwab and Mandre (10) measured the conversion values

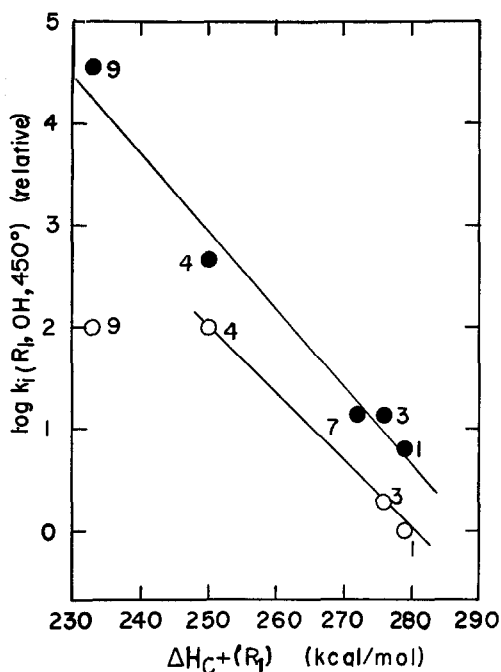


FIG. 4. Rate constants of dealkylation of alkylphenols vs. the enthalpy change,  $\Delta H_{C^+}(R_1)$ . Rate constant data are taken from M. Kraus *et al.* (8) (on aluminum fluoborate catalyst at 450°C). Open circles represent para-substituted phenols and solid circles ortho-substituted phenols.

of deisopropylation of some substituted isopropylbenzenes. Logarithms of the conversion are also correlated to the Hammett

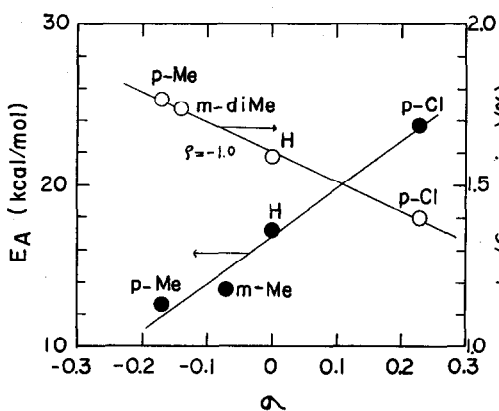


FIG. 5. Conversion and activation energy of deisopropylation of isopropylbenzene derivatives vs. Hammett  $\sigma$ . Conversion data are taken from Good and Robert (9) and activation energy data from Kazanski and Georgiev (11).

$\sigma$  to give a fine linear relationship, as shown in Fig. 6.

The following equation should be derived by adding a term of the Hammett  $\sigma$  to Eq. (3), if the Hammett law holds with other alkylbenzenes than those discussed above.

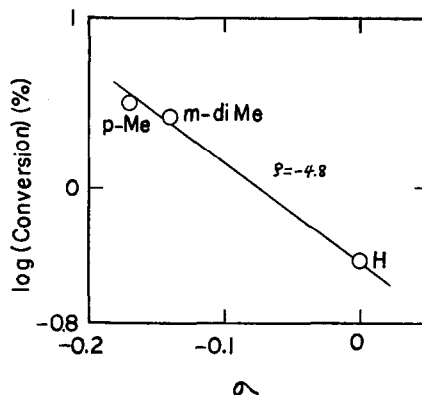


FIG. 6. Conversion of deisopropylation vs. Hammett  $\sigma$ . Conversion data are taken from Schwab and Mandre (10) (Mg-13X catalyst, 26.7% Mg, 414°C).

The dealkylation rate constant of an alkylbenzene,  $R_1-\phi-R_2$  on a certain solid acid catalyst is represented as follows:

$$\log k_i(R_1, R_2) = \log k_i(0) - \gamma'_i \Delta H_{C^+}(R_1) / 2.303RT + \rho_i(R_1) \sigma(R_2) \quad (4)$$

where  $R_1$  is an alkyl group to be cracked and  $R_2$  is the substituent not to be attacked. By Eq. (4), it is meant that LFER is applicable to solid acid catalysis. Therefore, the reaction rate constant can be estimated from the well-known values of  $\Delta H_{C^+}(R_1)$  and  $\sigma(R_2)$  and a few measured values such as  $k_i(0)$ ,  $\gamma'_i$ , and  $\rho_i(R_1)$ . The value of  $k_i(0)$  may be affected by two factors: one, the kind of reaction, and the other, the catalyst. The latter factor may be correlated to acid distributions, e.g., acid strength and acid content of the catalyst, the details of which will be published later.

Even the activation energy of dealkylation is correlated with  $\Delta H_{C^+}(R_1)$  or  $\sigma(R_2)$ . Activation energy of monoalkylbenzenes on silica-alumina in the temperature range from 370° to 490°C (11) holds a fine linear relationship with  $\Delta H_{C^+}(R_1)$  except for ethylbenzene, as

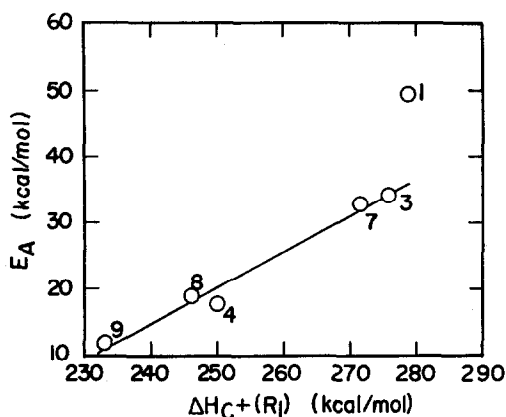


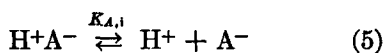
FIG. 7. Activation energy of dealkylation vs. the enthalpy change,  $\Delta H_{C^+}(R_1)$ . Activation energy data are taken from Kazanski and Georgiev (11).

shown in Fig. 7. As for deisopropylation of monosubstituted isopropylbenzenes (11), a fine relationship holds between activation energy and  $\sigma(R_2)$ , as shown in Fig. 5.

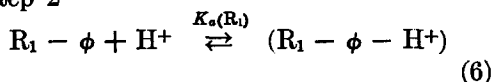
#### Considerations of LFER Based on a Reaction Mechanism

The dealkylation reaction of alkylbenzenes has hitherto been considered to proceed via the following schemes:

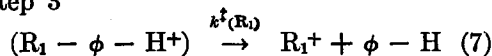
Step 1



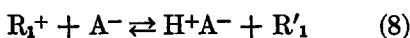
Step 2



Step 3



Step 4



where  $H^+A^-$ ,  $\phi$ , and  $R'_1$  represent solid acid, phenyl group, and olefin, respectively.

When weak adsorption of alkylbenzene is assumed and Step 3 is postulated to be the rate-determining step, then the rate constant will be represented by

$$k_i(R_1) = k^\ddagger(R_1)K_{A,i}K_a(R_1)s_i \quad (9)$$

where  $s_i$  is the total acid content and  $K_{A,i}$  is the average dissociation constant of the  $i$ th solid acid. When only enthalpy factors are

considered for a certain catalyst, Eq. (9) will be converted into Eq. (10).

$$\log k_i(R_1) = -\{E_{A,i}(R_1) + \Delta H_{A,i}(R_1)\}/2.303RT + C'_1 \quad (10)$$

where  $E_{A,i}(R_1)$  is the activation energy of the Step 3,  $\Delta H_{A,i}(R_1)$  is the enthalpy change of Step 2 and  $C'_1$  is the constant term containing the entropy factors. As the reaction of Step 3 resembles reaction (2), the enthalpy change of Step 3,  $\Delta H_{\ddagger,i}(R_1)$  can be assumed to be linear to the enthalpy change of reaction (2),  $\Delta H_{C^+}(R_1)$ ,

$$\Delta H_{\ddagger,i}(R_1) = \epsilon' \Delta H_{C^+}(R_1) + \text{const.} \quad (11)$$

If the Polanyi rule is assumed to hold between  $E_{A,i}$  and  $\Delta H_{\ddagger,i}$ , then,

$$\begin{aligned} E_{A,i}(R_1) &= \epsilon'' \epsilon' \Delta H_{C^+}(R_1) + \text{const.} \\ &= \epsilon_i \Delta H_{C^+}(R_1) + \text{const.} \end{aligned} \quad (12)$$

On the other hand, the heat of adsorption,  $\Delta H_a(R_1)$ , would depend mainly upon the basicity of the reactant as far as the same catalyst is used. It is generally believed, although without direct evidence, that this reaction proceeds through a carbonium ion mechanism and is catalyzed by the Brönsted acid sites. The epitome of dealkylation reaction schemes was given by Johnson (12).

Two types of intermediates may be considered for the dealkylation of alkylbenzenes, i.e.,  $\sigma$  complex and  $\pi$  complex. Thomas (13) postulated, without further confirmation, a protonated  $\sigma$  complex in the dealkylation of isopropylbenzene. Okuda *et al.* (14) assigned the intermediate as a  $\sigma$  complex for the same reaction by means of ultraviolet spectroscopy; however, their identification seems indefinite. The presence of protonated complex in this reaction was also proved by means of isotope tracer technique (15). A  $\sigma$  complex intermediate was proved for electrophilic displacement reactions in homogeneous systems (16). In spite of these discussions, decisive identification of the intermediate of the dealkylation of alkylbenzenes has not been made up to the present.

Brown *et al.* (17) calculated  $\pi$  basicity from the solubility of hydrogen chloride in alkylbenzenes. The electron density of a carbon

atom which has an alkyl group, determined by  $C^{13}$  NMR spectroscopy (19) is postulated to be linear to  $\sigma$  basicity. Both  $\sigma$  basicity and  $\pi$  basicity have a reverse correlation with  $\Delta H_{C^+}(R_1)$  as shown in Fig. 8. Although the

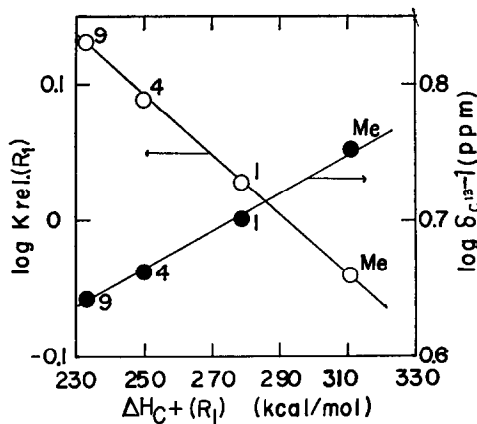


Fig. 8. Basicity of  $\pi$ -complex formation and NMR chemical shift ( $\delta_{C^{13}}$ ) vs. the enthalpy change,  $\Delta H_{C^+}(R_1)$ .  $\pi$ -Basicity data are taken from Brown and Braday (17) and chemical shift from Friedel and Retcofsky (19).

dependence of the heat of adsorption,  $\Delta H_a(R_1)$ , upon  $\Delta H_{C^+}(R_1)$  is difficult to estimate, it seems to be much less than that of  $\log k^{\ddagger}(R_1)$  upon  $\Delta H_{C^+}(R_1)$ . Therefore,  $\Delta H_a(R_1)$  being assumed constant, the following equation will be derived from Eqs. (10) and (12):

$$\log k_i(R_1) = -\{\epsilon_i \Delta H_{C^+}(R_1) + \text{const.}\} / 2.303RT + C'_i \quad (13)$$

Equation (13) coincides with Eq. (3), which is an empirical formulation for monoalkylbenzenes.

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