

NOTES

Application of Linear Free Energy Relationships to Heterogeneous Catalysis

Mochida and Yoneda have made an important contribution to the field of heterogeneous catalysis by successfully applying linear free energy relations to the dealkylation of alkylbenzenes. In a recent publication (1) they present data showing how the effect of two structural changes on the reactivity can be modeled. In the second paper (2) they consider the catalyst effect and show empirically that dealkylation reactivity for various alkylbenzenes on different catalysts can be modeled using isopropylbenzene dealkylation rates on the same catalysts.

An empirical linear free energy relation between rate constants on various acid catalysts using the isopropylbenzene cracking as a model is given by Mochida and Yoneda as follows:

$$\log k_i(r) = \lambda(r) \log k_i(\text{iso-Pr}) + \kappa(r) \quad (1)$$

where r refers to a particular dealkylation reaction and i refers to the i th catalyst. The empirical constants $\lambda(r)$ and $\kappa(r)$ are functions of the reactant and reaction only and independent of the catalyst. Their first paper (1) presented a linear relation between dealkylation rate constants of various monoalkylbenzenes and heats of formation of the corresponding carbonium ion. Thus,

$$\log k_i(R_1) = \log k_i(0) - \gamma'_i \Delta H_{C^+}(R_1)/2.303 RT \quad (2)$$

where R_1 refers to a particular alkyl group to be removed and ΔH_{C^+} is the heat of formation of the carbonium ion, R_1^+ . Empirical constant $k_i(0)$ depends on both

the catalyst and the reactant while γ'_i , depends on the catalyst only.

The purpose of this correspondence is to show that Eq. (1) consists of two terms which can be individually related to catalyst and reactant variables. It is further demonstrated that the reactant variable is linearly related to the carbonium ion heats of formation. Proceeding toward these ends, Eqs. (1) and (2) may be equated for cracking reactions which involve the same catalyst, i , and remove the same alkyl group, R_1 . Thus,

$$\ln k_i(0) - [\gamma'_i \Delta H_{C^+}(R_1)/2.303 RT] = [\lambda(r) \ln k_i(\text{iso-Pr})] + \kappa(r) \quad (3)$$

Considering the nature of the terms on the right-hand side, $\kappa(r)$ is a function of reactant and reaction variables only while the group, $[\lambda(r) \ln k_i(\text{iso-Pr})]$, contains reactant and catalyst variables. Mochida and Yoneda have experimentally shown $\lambda(r)$ to be approximately unity for six dealkylations. This can be predicted for first order Langmuir-Hinshelwood kinetics by considering the following:

$$\ln \frac{k'_2}{k'_1} = \ln \frac{k_2}{k_1} + \ln \frac{K_2}{K_1} \quad (4)$$

where k'_1 and k'_2 are the apparent rate constants, k_1 and k_2 are the rate constants for the surface rearrangement, K_1 and K_2 are the adsorption equilibrium constants, and subscripts 1 and 2 refer to different reactant structures. The logarithms of the rate and equilibrium constant ratios can be expressed as free energy changes.

If only one reaction variable, x , is affected by the structural changes and the change is small then

$$\ln \frac{k'_2}{k'_1} = \left[\left(\frac{\partial \Delta F}{\partial x} \right)_{\text{rearrangement}} + \left(\frac{\partial \Delta F}{\partial x} \right)_{\text{adsorption}} \right] (x_2 - x_1) \quad (5)$$

Equation (5) is the same as Eq. (1); the right-hand side of Eq. (5) corresponds to $\kappa(r)$ and k'_1 corresponds to $k_i(\text{iso-Pr})$. Thus the coefficient $\lambda(r)$ should be unity, as Mochida and Yoneda have experimentally shown.

With $\lambda(r)$ unity the first term in brackets on the right side of Eq. (3) contains only the effect of different catalysts as measured by dealkylation of isopropylbenzene. The term $\kappa(r)$ in Eq. (1) must therefore account

for the effect of different alkyl groups in exactly the same way as does the term, $[\gamma'_i \Delta H_{C^+}(R_1)/2.303 RT]$, which appears on the left of Eq. (3). This analysis predicts $\kappa(r)$ should be linearly related to $\Delta H_{C^+}(R_1)$. Mochida and Yoneda have experimentally measured values of $\kappa(r)$ for the dealkylation of six alkyl groups. In Fig. 1 these values are plotted against the corresponding values of $\Delta H_{C^+}(R_1)$. This figure shows the reactant variable, $\kappa(r)$, can be expressed with considerable accuracy as a linear function of $\Delta H_{C^+}(R_1)$.

Equation (1) appears therefore to be considerably more significant and useful than first reported by Mochida and Yoneda. Rewriting the equation in the light of Fig. 1,

$$\ln [k(R_1)/k(\text{iso-Pr})]_{\text{catalyst } i} = m[\Delta H_{C^+}(\text{iso-Pr}) - \Delta H_{C^+}(R_1)] \quad (6)$$

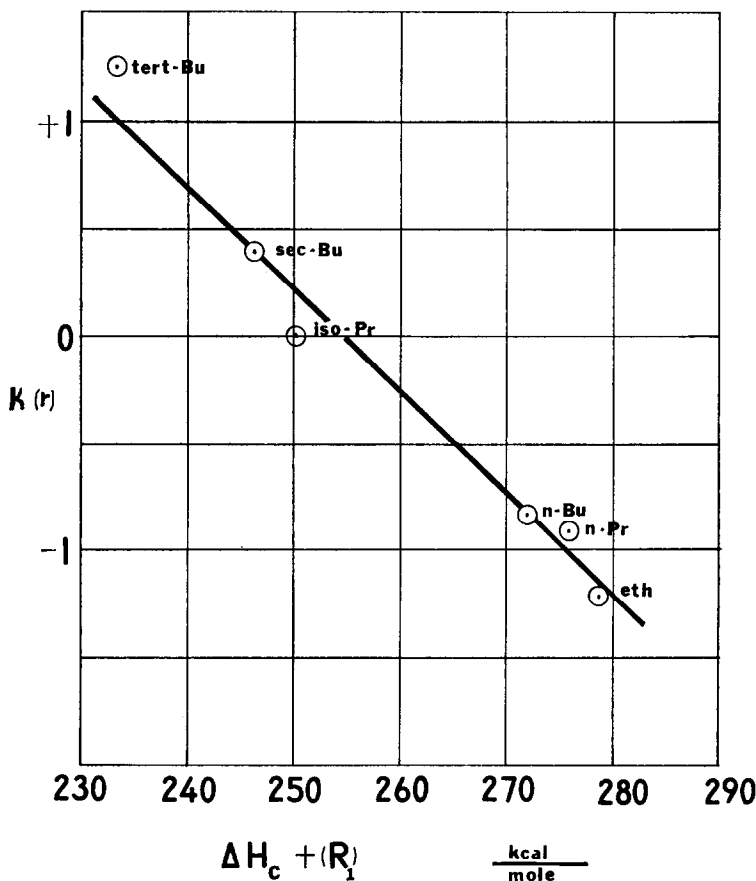


FIG. 1. Reactant variable, $\kappa(r)$, vs. the enthalpy change of carbonium ion formation, $\Delta H_{C^+}(R_1)$.

where m , determined from Fig. 1, has a value of approximately 0.048. In Eq. (6) the effects of changing catalysts is accounted for by using a reference rate measurement on the isopropylbenzene dealkylation. Also the influence of different alkyl groups is now completely separated from the catalyst effects and is linearly related to the heats of formation of the rate-determining carbonium ion.

It is noteworthy and perhaps conspicuous that this successful correlation of reactant structure effects does not require modeling adsorption equilibrium in the same way that surface rearrangement was modeled by the carbonium ion formation. In general, however, the application of linear free energy relations to heterogeneous catalysis may require modeling both adsorption equilibrium and surface rearrangement. For the reaction series considered here Mochida and Yoneda have shown empirically and theoretically, in deriving Eq. (2), that alkyl group changes have no influence on the adsorption equilibrium constants. At the same time they have shown how the surface rearrangement can be modeled. Thus in this case, the use of linear free energy relations has led to detailed knowledge of

both the adsorption and surface rearrangement processes. Because of the complexity of heterogeneous catalytic reactions, linear free energy relations can be expected to be particularly useful in isolating the adsorption, reactant, and catalyst effects. Their utility lies not so much in making predictive correlations but in dissecting the various steps in the catalytic process and testing proposed models for each step. This general problem will be discussed in a later communication.

ACKNOWLEDGMENT

The author is grateful to the National Science Foundation for an Engineering Research Initiation Grant supporting work in this area.

REFERENCES

1. MOCHIDA, I., AND YONEDA, Y., *J. Catalysis* **7**, 386 (1967).
2. MOCHIDA, I., AND YONEDA, Y., *J. Catalysis* **7**, 393 (1967).

IRVING J. DUNN

*Department of Chemical Engineering
University of Idaho
Moscow, Idaho 83843
Received March 12, 1968*

Catalytic Behavior of Organic Semiconductors

1,2-Butene Isomerization of Violanthrene A-Iodine Charge-Transfer Complex

The isomerization of 1-butene to 2-butene has been reported to proceed in the presence of acid-base catalysts. This double-bond shift may be accompanied by the abstraction and the addition of protons from and to butene molecules, and by their migration on the catalyst surface. On the basis of these facts, it can easily be inferred that centers in which electrons are depleted offer sites for isomerization.

From these considerations, it is expected that the charge-transfer complexes in which

electrons transfer from hydrocarbon would be active in the isomerization of 1-butene to 2-butene. In the complexes, violanthrene A ($C_{34}H_{18}$) reacts with arbitrary amounts of iodine to form an amorphous charge-transfer complex (denoted as VEA- I_2) of a different electrical conductivity as a function of the iodine content (1, 2); electrons in violanthrene transfer to iodine.

In this short note, we will present our preliminary results on the double-bond migration of butene on VEA- I_2 ; we under-