

Linear Free Energy Relations in Modeling Heterogeneous Catalytic Reactions

IRVING J. DUNN

*From the Chemical Engineering Department, University of Idaho,
Moscow, Idaho 83843*

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Modeling a complex heterogeneous catalytic reaction involves consideration of each elementary rate or equilibrium step. In principle, each step can be modeled with an analog reaction. For example, first order Langmuir-Hinshelwood kinetics can be modeled by combining two analogs, one for adsorption and one for surface rearrangement. The result is the sum of two Hammett-type relations. A linear free energy relation, which must be empirically established, proves the validity of the model and thereby elucidates the details of the catalytic process. The recent work of Mochida and Yoneda is discussed to demonstrate the important utility of linear free energy modeling procedures in the study of heterogeneous catalytic reactions.

INTRODUCTION

Few correlations exist between reactant structure and activity in heterogeneous catalysis, but many catalyst-structure correlations appear in the literature (1). Complex catalyst systems can be understood by comparing them with simpler systems and with systems about which information is available. Modeling is an important scientific technique. Linear free energy relations, so useful in studying structural effects in homogeneous reactions, can find general utility in modeling any chemical reaction system with a simpler analog reaction. The basic empirical principle is that free energy quantities in analogous systems are linearly related. Similarity can indeed be proven by the existence of a linear free energy relation. Once similarity is established comparison of the complex system with the model is valid.

Information can also be obtained through the quantitative parameters which describe the linear correlation. Often physical significance can be assigned to each parameter. For example, Hammett's ρ describes the reaction's electron demand while σ is attributed to the electronic influence of the

side chain substituent. Comparisons of such parameters within a reaction series or from one series to another provide information on the structural and reaction variables. In the case of reactions following the Hammett relation, they are all modeled by the ionization of benzoic acid. Comparisons of ρ constants between reaction series give information on the relative electron demand of each reaction series; while σ comparisons provide information on the relative electron-withdrawing power of different substituents.

Heterogeneous catalytic systems represent a complex sequence of chemical steps which can be elucidated with linear free energy relations. Recently important contributions in this area have appeared in the literature. Kraus (2) has successfully correlated many heterogeneous catalytic reactions of the olefin-forming elimination-type with the Taft relation. Thus, structural effects in a homogeneous reaction system (actually two systems in the Taft relation) appear to model this heterogeneous catalytic series. Dissimilarity between any heterogeneous reaction and a homogeneous model might be expected because of the

free energy changes of chemisorption. Apparently it was not the case here, and the homogeneous model was successful. Mochida and Yoneda (3, 4) used linear free energy relations to test a model of the proposed rate-limiting step in the cracking of alkylbenzenes. Carbonium ion formation was suspected to be rate-limiting. A linear relation between calculated enthalpy changes of this elementary step and the apparent activation energies confirmed this mechanism. This provides a dramatic demonstration of how linear free energy relations can be used to elucidate the details of catalytic processes.

THEORY

The recent work demonstrates the use of linear free energy relations in certain heterogeneous catalytic systems but does not give a clear picture of the general applicability of this technique. For this it is necessary to follow the theoretical foundations of linear free energy relations as formulated for homogeneous systems and apply them to heterogeneous systems to include adsorption effects. It appears sufficient to use the development of Wells (5) rather than the more detailed considerations of Leffler and Grunwald (6). No conflict exists between these views since the difference is one of detail. The independent reaction variables of Wells are regarded by Leffler and Grunwald as dependent variables which can be expressed in terms of independent group variables.

Proceeding according to Wells, any change of free energy, whether free energy of activation or standard free energy change of reaction, can be expressed as a function of independent reaction variables. Thus,

$$\Delta F = f(x, y, \dots)$$

When only one variable changes due to a small change in reactant structure

$$d\Delta F = (\partial\Delta F/\partial x) dx$$

If the change in x is slight the term $\partial\Delta F/\partial x$ remains constant so that

$$\Delta\Delta F = (\partial\Delta F/\partial x) \Delta x$$

In terms of rate constants for the two

structures i and 0 , within a reaction series A,

$$\ln \left(\frac{k_i}{k_0} \right)_A = \left(\frac{\partial\Delta F}{\partial x} \right)_A \frac{(x_0 - x_i)}{RT}$$

If another reaction series B is similar to the extent that changes in structure within the series could lead to the same change in x without affecting other variables then

$$\ln \left(\frac{k_i}{k_0} \right)_B = \frac{(\partial\Delta F/\partial x)_B T_A}{(\partial\Delta F/\partial x)_A T_B} \ln \left(\frac{k_i}{k_0} \right)_A$$

The quantities $(\partial\Delta F/\partial x)$, vary with sensitivity of ΔF to changes in x and thus depend on the nature and conditions of the reaction. The terms T_A and T_B refer to the temperature of reaction for series A and B. The collection of terms,

$$\frac{(\partial\Delta F/\partial x)_B T_A}{(\partial\Delta F/\partial x)_A T_B} \equiv G_x^{AB}$$

will be constant if $(\partial\Delta F/\partial x)_A$ and $(\partial\Delta F/\partial x)_B$ remain constant over the range of structural change. Considering the standard free energy changes of reaction as well as activation energies gives

$$\ln \left(\frac{k_i}{k_0} \right)_B = G_x^{AB} \ln \left(\frac{K_i}{K_0} \right)_A \text{ or } G_x^{AB} \ln \left(\frac{k_i}{k_0} \right)_A$$

The above equation in terms of equilibrium constants is the same as the Hammett relation. Reaction series A in the Hammett relation is the ionization of substituted benzoic acids, and reaction series B involves substituted benzene compounds with a reactive side chain. Reaction A is the model and involves reactants which are very similar in structure to reactants in series B. Strict requirements for structural similarity in the Hammett relation apparently allows considerable freedom in the reaction nature; hundreds of different reaction series have been correlated using the Hammett relation.

The complexity of heterogeneous catalysis is often successfully handled by assuming that adsorption equilibrium of the reactants precedes a rate-limiting, first-order surface rearrangement. This Langmuir-Hinshelwood formulation provides reaction rates in terms of external phase concentrations,

adsorption equilibrium constants, and surface reaction rate constants. For a single adsorbed reactant A with weak adsorption of products or impurities,

$$v = kK_{\text{R}}P_{\text{R}}/(1 + K_{\text{R}}P_{\text{R}})$$

with weak reactant adsorption

$$v = kK_{\text{R}}P_{\text{R}} = k'P_{\text{R}}$$

and for strong reactant adsorption

$$v = k$$

where v is the reaction velocity, k is the surface rate constant, k' is the apparent rate constant, and K_{R} is the adsorption equilibrium constant for reactant R. The general case is more complicated, however, because of a kinetic model involving a sequence of several steps, any of which may be rate-limiting or in equilibrium. Thus the general heterogeneous rate expression involves many rate and equilibrium constants. No method has been found to measure these adsorption constants independently because they apply only to the active sites. This difficulty in separating surface rearrangement rate constants from adsorption equilibrium constants appears unavoidable, and any linear free energy relation or reaction model must take this aspect into account.

Linear free energy relations are applicable to both rate constants and equilibrium constants, and the possibility exists of applying them to each of the constants. For example, considering a unimolecular reaction following Langmuir-Hinshelwood kinetics such that

$$v = kK_{\text{R}}P_{\text{R}}$$

two influences of reactant structure are possible.

(1). The free energy of chemisorption may change.

(2) The free energy of activation of the rate-limiting surface rearrangement may change.

These two effects are quite different and it should be possible to model each of them with a different reaction. Two linear free

energy relations, derived from two models, are required in this case.

No criteria can be given regarding the choice of model reactions. Some general aspects of choosing models can be stated however.

(1) Detailed knowledge of the adsorption and surface rearrangement processes may provide a clue in choosing models.

(2) Proposed mechanisms can be confirmed by obtaining a linear free energy relation using a model reaction which is known to proceed according to the same mechanism. A linear relation serves as a proof of similarity.

(3) Simpler model reactions provide more information than complex model reactions because they are more thoroughly understood.

The second statement follows from Wells' development as outlined previously. Similarity is defined in terms of the common reaction variable x and the constancy of the $\partial\Delta F/\partial x$ terms over a range of x . Ruling out the chance that dissimilar reaction series may display a linear free energy relation over given structural ranges does not appear possible. Thus, absolute proof of similarity can probably not be established without additional evidence.

It follows from the third statement that homogeneous reaction models would provide more information than heterogeneous catalytic reactions. Thus to model the surface rearrangement step with a heterogeneous reaction or even to model one heterogeneous reaction with another will not provide much detailed information. Knowing they are similar may be useful, but the nature of their similarity cannot be extracted without much detailed knowledge of the model reaction.

Consideration of structural effects on adsorption and surface rearrangement leads to some rules in choosing between homogeneous or heterogeneous models to investigate a first order Langmuir-Hinshelwood reaction series.

(1) Adsorption can be modeled by a heterogeneous catalytic reaction if the

structural change affects only the adsorption equilibrium of the model and not the surface rearrangement.

(2) Adsorption can be modeled by a homogeneous reaction if the homogeneous reaction involves a bond similar to the chemisorption bond.

(3) Surface rearrangements can be modeled by similar heterogeneous catalytic reactions if structural changes affect only the surface rearrangement of the model and not the adsorption.

(4) Surface rearrangements can be modeled by homogeneous reactions.

(5) The overall process may be modeled by a single heterogeneous catalytic reaction whenever the structural changes cause similar effects on both adsorption and surface rearrangement processes.

(6) The overall process may be modeled by a single homogeneous reaction if structural changes do not alter the adsorption.

If a single heterogeneous or homogeneous reaction models the entire first order process (rules 5 or 6) a two-parameter, $\rho\sigma$ -type, linear free energy relation results. In terms of Wells' formulation

$$\ln \left(\frac{k'_i}{k'_0} \right)_A = \left[G_x^{AM} \ln \left(\frac{k'_i}{k'_0} \right)_M \right]_{\text{heterogeneous or homogeneous model}}$$

Above, A refers to the reaction series whose reactant structure effects are under investigation; M refers to the model reaction. When separate models are used for the adsorption and surface rearrangement the linear free energy relation takes the form of a summation of two free energy changes. Thus,

$$\Delta\Delta F_{\text{total}} = \Delta\Delta F_{\text{adsorption}} + \Delta\Delta F_{\text{surface rearrangement}}$$

or in terms of Wells' formulation

$$\ln \left(\frac{k'_i}{k'_0} \right)_A = \left[G_x^{AM} \ln \left(\frac{k_i}{k_0} \right)_M \right]_{\text{adsorption model}} + \left[G_x^{AM} \ln \left(\frac{k_i}{k_0} \right)_M \right]_{\text{surface rearrangement model}}$$

Equilibrium constants from model reactions may be used instead of rate constants.

Since linear free energy relations can be written in terms of ratios of rate and equilibrium constants it is sufficient to make measurements of these ratios. In principle reaction rate expressions of considerable complexity can be handled. It should be possible to model any ratio of rate or equilibrium constants. Bimolecular reaction rates which follow the expression

$$v = \frac{kK_1K_2P_1P_2}{1 + K_1P_1 + K_2P_2}$$

can be analyzed by using competitive methods to measure relative rates. For example, if only the structure of reactant 2 is changed from 0 to i the relative rate becomes

$$\frac{v_i}{v_0} = \frac{k'_i}{k'_0} = \frac{k_iK_{2i}}{k_0K_{20}}$$

and the problem thus becomes equivalent to the unimolecular case already discussed. Even reactions which are limited by desorption can be studied by competitive techniques to yield the ratios of individual rate or equilibrium constants (7). Modeling of these ratios using linear free energy relations can then be attempted to learn something about the details of the elementary processes.

DISCUSSION

Mochida and Yoneda (3, 4) have used modeling techniques with linear free energy relations to investigate heterogeneous catalytic dealkylations of alkylbenzenes. It is interesting to see how their work is related to the general considerations discussed here. It involves actually three linear free energy relations:

(1) Modeling an effect of reactant structure with the heats of formation of the rate-determining carbonium ion.

(2) Modeling an effect of reactant structure with the Hammett relation.

(3) Modeling an effect of catalyst structure with a heterogeneous catalytic reaction.

The first relation demonstrated how a proposed reaction mechanism can be verified

using a model reaction. The rate-determining step for this first order dealkylation cracking reaction was thought to be the formation of the alkyl carbonium ion. Heats of formation of these alkyl carbonium ions had already been calculated. Application of the Polanyi relation gave a linear relation between free energies and enthalpies. Overall rate constants for various alkylbenzenes were correlated by the relation

$$\ln \left(\frac{k'_i}{k'_0} \right) = G_x^{\text{AM}} \alpha \left(\frac{\Delta H_0 - \Delta H_i}{RT} \right)$$

where α is the proportionality constant in the Polanyi relation. The correlation was successful and thereby proved almost conclusively that the carbonium ion formation is indeed rate-limiting. Indirectly the correlation also demonstrated that the alkyl group structural changes had essentially no effect on the adsorption equilibrium, since the ratio $(K_i/K_0)_A$ must be unity.

The second relation demonstrated the use of a homogeneous reaction through the Hammett relation in modeling the influence of a second alkyl group on the removal of the first alkyl group. Again the structural change had apparently no influence on the adsorption equilibrium. The third relation involves the use of a heterogeneous catalytic reaction to model the effect of catalyst structure. Thus isopropylbenzene dealkylation is used to characterize the catalyst effect. It is not immediately apparent that Mochida and Yoneda's relation is equivalent to the relations discussed here, but this can be readily seen. The total change in ΔF is written as

$$\Delta \Delta F_{\text{total}} = \Delta \Delta F_{\text{catalyst}} + \Delta \Delta F_{\text{R}}$$

where R refers to the change in alkyl group previously correlated by carbonium ion heat of formation. In terms of rate constants and enthalpy changes

$$\ln \left(\frac{k'_{\text{R}_i, \text{catal}_i}}{k'_{\text{R}_0, \text{catal}_0}} \right) = G_{\text{catal}} \ln \left(\frac{k'_{\text{isoprop}, \text{catal}_i}}{k'_{\text{isoprop}, \text{catal}_0}} \right) + G_{\text{R}} \alpha \left(\frac{\Delta H_{\text{R}_0} - \Delta H_{\text{R}_i}}{RT} \right)$$

This relation should be valid for any cata-

lyst change 0 to i as long as the mechanism does not change. In the form presented by Mochida and Yoneda

$$\ln k'_{\text{R}_i, \text{catal}_i} = G_{\text{catal}} \ln k_{\text{isoprop}, \text{catal}_i} - G_{\text{R}} \alpha \Delta H_i + b$$

where Mochida and Yoneda's constant $K(r)$ is equivalent to the terms $(-G_{\text{R}} \alpha \Delta H_i + b)$. It has been shown in a previous communication (8) that $K(r)$ is indeed linearly related to the carbonium ion heats of formation.

Kraus (2) in his extensive review of published reaction rate data found the Taft equation can be used to correlate those dealkylation reactions which Mochida and Yoneda correlated with carbonium heats of formation. The question arises, which correlation should be used, one based on a proposed rate-limiting step or one of the established correlations? The answer depends on the objective. If the objective is to test a proposed reaction sequence then models of the proposed rate-limiting step should be compared using linear free energy relation techniques. The advantage is clear. Had Mochida and Yoneda used simply the Taft equation little information would have been gained. Even if an excellent correlation were obtained it would have been meaningful only when the Taft parameters σ^* and ρ^* could be compared with those for other reaction series. Instead they modeled the proposed rate-limiting step specifically and thereby verified the mechanism. Linear free energy techniques appear to be powerful tools in discerning the nature of heterogeneous catalysis and it appears fruitful to look beyond the Hammett and Taft equations when using them.

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