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# Note on the Use of Linear Free Energy Relationships in Heterogeneously Catalyzed Reactions

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**Synopsis.** A critical examination of the use of linear free energy relationships in the study of the mechanism of heterogeneously catalyzed reactions is presented in the case of the ruthenium catalyzed hydrogenation of monoalkylbenzenes reported in the literature.[5] It is concluded that the use of both electronic and steric substituent parameters leads to a quite different mechanistic interpretation as compared to the statements made before in the literature on the basis of just the electronic substituent parameter.

One of the major purposes in the field of heterogeneous catalysis is a better understanding of the reaction mechanism in order to develop somewhat less empiric approximations towards the choice of the catalyst as well as the reaction conditions.[1-3] The study of a particular reaction with the aid of a series of structurally related compounds on a single catalyst has proved a further suitable tool for mechanistic studies. Thus, a systematic variation of the substrate by the introduction of suitable substituents gives a set of experimental data to be correlated by means of a linear free energy relationship (*e.g.* Hammett and Taft relations), from which conclusions about the reaction mechanism involved can be drawn.[4]

On the other hand, one has to be very cautious in correlating experimental data with structural parameters since the substituent itself will give electronic and/or steric (attractive or repulsive) interactions with the catalyst, *i.e.*, substituent effects are often more complicated than in the case of homogeneously catalyzed reactions. In this respect, the recent investigation of Yoshida[5] concerning the mechanism of the hydrogenation of monoalkylbenzenes over ruthenium metal is an illustrative example of ignoring the above-mentioned interactions between the substituents and the catalyst. As will be outlined below, these "secondary" substituent effects may bring about false conclusions concerning the mechanism and the transition state of the reaction studied.

## Results and Discussion

Yoshida[5] has studied the hydrogenation of monoalkylbenzenes over ruthenium black at 30 °C and 1 atm with ethanol as the solvent and obtained the following data for the reaction rate constants ($k$) and adsorption equilibrium constants ($K$) (Table 1). In addition, both the electronic ($\sigma^*$) and steric ($E_s$) substituent parameters according to Taft[6] have been included in Table 1.

Although the size of the substituents at the aromatic nucleus varies considerably, the data of Table 1 were just correlated[5] with the electronic substituent parameter $\sigma^*$ (Table 2, relations *1* and *4*). On this basis, it was concluded that (i) the initial state of hydrogenation is the adsorption step (in terms of the Horiuti-Polanyi mechanism) and (ii) the rate-determining step involves a nucleophilic attack of a hydride species from the catalyst surface.[5]

Table 1. Hydrogenation of R-substituted benzenes over ruthenium[a]

| Substituent R | log $k$ | log $K$ | $\sigma^*$ | $E_s$ |
|---|---|---|---|---|
| H | −1.85 | 0.30 | 0.49 | 1.24 |
| Me | −2.66 | 0.78 | 0.00 | 0.00 |
| Et | −2.88 | 1.00 | −0.10 | −0.07 |
| Pr | −3.12 | 1.18 | −0.115 | −0.36 |
| *i*-Pr | −3.34 | 0.98 | −0.19 | −0.47 |

a) log $k$ and log $K$ derived from Fig. 2 of Ref. 5.

However, Table 2 shows that the experimental data may also (and even better) be correlated with the steric substituent parameter $E_s$ (*2* and *5*). Correlation of the experimental data by both $\sigma^*$ and $E_s$ shows further that *the reaction rate constant is almost completely determined by steric interactions (3)*, whereas *the adsorption equilibrium constant is influenced by electronic as well as steric effects (6)*.

Table 2. Taft relations[a] for the hydrogenation of R-substituted benzenes over ruthenium[5]

| No. | Reaction rate ($k$) | $\rho_r^*$ | $\delta_r$ | log $k^\circ$ | $R$ |
|---|---|---|---|---|---|
| *1* | $\log k/k^\circ=\rho_r^*\sigma^*$ | 2.05 | — | −2.80 | 0.974 |
| *2* | $\log k/k^\circ=\delta_r E_s$ | — | 0.82 | −2.83 | 0.983 |
| *3* | $\log k/k^\circ=\rho_r^*\sigma^*+\delta_r E_s$ | 0.06 | 0.81 | −2.82 | 0.983 |

| No. | Adsorption equilibrium ($K$) | $\rho_a^*$ | $\delta_a$ | log $K^\circ$ | $R$ |
|---|---|---|---|---|---|
| *4* | $\log K/K^\circ=\rho_a^*\sigma^*$ | −1.16 | — | 0.87 | 0.942 |
| *5* | $\log K/K^\circ=\delta_a E_s$ | — | −0.47 | 0.88 | 0.944 |
| *6* | $\log K/K^\circ=\rho_a^*\sigma^*+\delta_a E_s$ | −0.40 | −0.31 | 0.88 | 0.945 |

a) $\rho^*$ and $\delta$ are the polar and steric reaction parameters,[6] respectively, with r=reaction and a=adsorption; $k^\circ$ and $K^\circ$ are the calculated data for toluene (R=Me); $R$ is the correlation coefficient.

This result leads to the following conclusions: (i) *The reaction rate constant is independent of electronic effects, i.e.*, atomic hydrogen has to be considered as the reducing agent. Increase of the size of the substituent decreases the reaction rate, which implies relatively less disturbance in the initial state of hydrogenation as compared to the transition state, and (ii) *The adsorbed state is stabilized by electron-donating substituents, i.e.*, the higher electron density on the aromatic nucleus will result in a stronger

aryl-ruthenium donor bond by $\pi$-spd overlap. In addition, increase of the size of the substituent enhances the strength of adsorption, which may point to alkyl-ruthenium bond formation in the initially adsorbed state. This result is in agreement with the steric substituent effect on the rate of hydrogenation and may have some resemblance with the homogeneously ruthenium-catalyzed $\alpha$-H/D-exchange of aliphatic alcohols.[7] The picture for the adsorbed state, however, remains somewhat uncertain because of the rather low correlation coefficient of the relations *4—6*.

Summarizing, it is evident that one has to be very cautious in correlating experimental data with structural parameters in the case of heterogeneously catalyzed reactions.

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