

A Comment on the Work by Kraus on, "Linear Correlations of Substrate Reactivity in Heterogeneous Catalytic Reactions"

Recently, linear free energy relationships in heterogeneous catalysis for various substrate have been successfully studied (1, 2).

Kraus (1) discussed the quantitative description of the relations between σ or σ^* and the reactivities of the substrates in various heterogeneous catalytic reactions. He succeeded in obtaining good linear relationships for various kinds of elimination, hydrogenation, and hydrocracking reactions. However, scarce consideration is given to the problems which may be raised when the kinds of substrates are further extended. In the case of hydrogenation of alkylbenzenes on a platinum catalyst, he correlated their reactivities with σ^* of alkyl groups. The linear relation thus obtained

implies the high reactivity of the aromatic ring that is substituted by a group of positive σ^* . Nevertheless, phenylacetic acid is reportedly less reactive than benzene, and phenylmethanes are less reactive than toluene (3), although σ^* of CH_2COOH is larger than that of hydrogen, and σ^* of methyl groups substituted with a phenyl group or groups are larger than σ^* of methyl group (Table 1). All these facts suggest that the nature of factors other than those described by σ^* may be controlling the reactivity of hydrogenation. The steric effect is reportedly more pronounced in the dehydrogenation reaction with a platinum catalyst than with oxide catalysts (4).

The present authors, therefore, proposed

TABLE 1
HYDROGENATION REACTIVITIES OF AROMATICS

| Substrate | σ^*a | E_s^b | $\log k_{obs}^c$ | $\log k_{calc}^d$ | $\log k_{calc}^e$ |
|---------------------------|-------------|---------|------------------|-------------------|-------------------|
| Benzene | 0.49 | 1.24 | 1.46 | 0.828 | 1.35 |
| Toluene | 0.0 | 0.0 | 1.25 | 0.924 | 1.19 |
| Ethylbenzene | -0.10 | -0.07 | 1.114 | 0.944 | 1.18 |
| <i>n</i> -Propylbenzene | -0.115 | -0.36 | 1.068 | 0.947 | 1.08 |
| <i>n</i> -Butylbenzene | -0.130 | -0.39 | 1.034 | 0.950 | 1.07 |
| <i>n</i> -Amylbenzene | -0.130 | -0.40 | 1.068 | 0.950 | 1.07 |
| Isopropylbenzene | -0.190 | -0.47 | 0.982 | 0.961 | 1.04 |
| Isobutylbenzene | -0.125 | -0.93 | 0.826 | 0.949 | 0.860 |
| <i>sec</i> -Butylbenzene | -0.210 | -1.13 | 0.924 | 0.965 | 0.831 |
| <i>tert</i> -Butylbenzene | -0.300 | -1.54 | 0.869 | 0.983 | 0.722 |
| Isoamylbenzene | -0.165 | -0.35 | 1.083 | 0.957 | 1.11 |
| Phenylacetic acid | 1.05 | — | 1.049 | — | — |
| Diphenylmethane | 0.214 | -0.38 | 0.798 | 0.882 | 0.878 |
| 1,1-Diphenylethane | 0.04 | -1.50 | 0.675 | 0.916 | 0.540 |
| Triphenylmethane | 0.405 | -1.76 | 0.130 | 0.845 | 0.224 |
| Phenylcyclohexane | -0.150 | -0.79 | 0.788 | 0.954 | 0.930 |
| Phenylcyclohexylmethane | -0.06 | -0.98 | 0.822 | 0.935 | 0.802 |

^a From ref. (5).

^b From ref. (5a).

^c Observed rate constant from ref. (3).

^d Calculated rate constants with σ^* alone.

^e Calculated rate constant with both σ^* and E_s .

the application of E_s , the steric parameters of substituents (δ), to these hydrogenation reactions. The results are shown in Table 1, where a comparison is given with the case of application of σ^* alone. The dependences of reactivities on these two parameters are -0.584 for σ^* and 0.393 for E_s , respectively. Taking the magnitudes of these parameters into consideration, the contribution of the E_s two to three times larger than that of σ^* . The sign of the dependence of reactivity on σ^* is negative when these two parameters are applied as shown, however, it is positive only with alkylbenzenes.

For the study of linear relationships, various parameters should be applied for the rate data with the substrates of wider range.

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