NOTES

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Substitution Effect in the Hydrogenation of Monoalkylbenzenes with Ruthenium Catalyst

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Synopsis. The influence of substituents on adsorption coefficients as well as rate constants can be understood from the rules of Horiuti-Polanyi and Taft. It is suggested that a nucleophilic adsorption of alkylbenzene and a nucleophilic surface reaction of the adsorbed alkylbenzene with the metal-hydride occur successively.

Various kinds of linear free energy relationship (LFER), such as the Hammett[1] and the Taft[2] equation, have been given in homogeneous reactions, but only the Horiuti-Polanyi rule[3] has been given in heterogeneous reactions. Recently, Kraus[4] pointed out that the equations of Hammett or Taft could be applied to some heterogeneous reactions over metals. The velocity constants k he used were obtained from experimental rate equations of Langmuir-Hinshelwood type, such as $k\prod_i K_i[A_i]/(1+\sum_j K_j[A_j])$.[5]

The object of the present work is to examine the influence of the substituents on the adsorption coefficients, K_i, as well as on the rate constants, k, in the hydrogenation of monoalkylbenzenes over ruthenium black catalyst.

Experimental

Materials. Alkylbenzenes (purity above 99%, Tokyo Kagaku Seiki Co. Ltd.); Ethanol and other reagents (G.R., Wako Pure Chem. Ind. Ltd.). Ruthenium black was prepared by the reduction of $RuCl_3\cdot 3H_2O$ (Engelhard Ind. Inc.) with formaldehyde. It was washed 10 times with distilled water and stored in ethanol.

Apparatus and Procedure. The reaction vessel: 50 ml flask with cooler and sampling stopcock. After 4.85 mg of ruthenium black had been admitted into the reaction vessel, a given amount of substrate and solvent (ethanol) was added to make the total volume 20 ml under hydrogen atomosphere. Hydrogenation was carried out under a constant (atomospheric) pressure of hydrogen at 10—30 °C. The rate of hydrogenation was determined by measuring either amounts of absorbed hydrogen by a gas-buret or concentrations of the products by gas-liquid chromatography.

Results and Discussion

The initial rates of the benzene hydrogenation with the same catalyst can be expressed by the following rate equation.[6]

$$-\left(\frac{d[X]}{dt}\right)_0=\frac{k_X K_X[X]P_H}{1+K_X[X]} \qquad (1)$$

where [X] is the concentration of benzene and P_H is the pressure of hydrogen. It has been confirmed that the equation can also be applied to the hydrogenation of monoalkylbenzenes ($-CH_3$, $-C_2H_5$, $-n$-C_3H_7 and $-i$-C_3H_7). We can obtain respective values of k and K from the equation. For the competitive hydrogenation of monoalkylbenzenes A and B, we get

$$\frac{d[B]}{d[A]}=\frac{k_B K_B[B]}{k_A K_A[A]} \qquad (2)$$

or

$$\frac{\log(1-X_B)}{\log(1-X_A)}=\frac{k_B K_B}{k_A K_A} \qquad (3)$$

where X_A and X_B are conversions of substrates A and B, respectively. We can obtain respective values of k and K from the hydrogenation of single substrate,

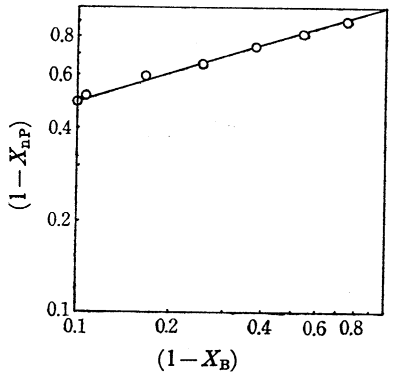


Fig. 1. Competitive hydrogenation between benzene (B) and n-propylbenzene (nP) at 30 °C in ethanol solvent.

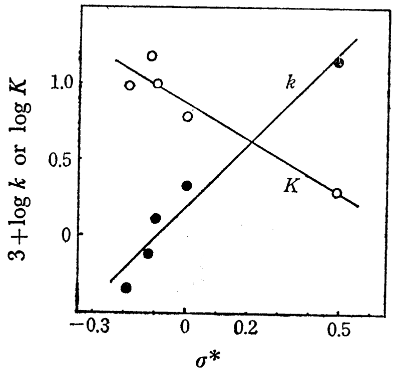
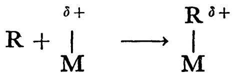


Fig. 2. The relation between substituent parameters (σ^*) and rate constants or adsorption constants at 20 °C in ethanol solvent.

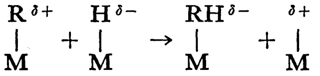
taking the experimental ratios of kK from competitive hydrogenation of two substrates into consideration. The applicability of Eq. (3) in the case of the competitive hydrogenation of benzene and *n*-propylbenzene is shown in Fig. 1 and that of the Taft equation to rate constants k and the adsorption coefficients K in the hydrogenation of alkylbenzenes over ruthenium black in Fig. 2. It should be noted that the slopes of the two lines are opposite each other. That is, the reaction parameter k is positive ($\rho^*=2.05$), while adsorption parameter K is negative ($\rho^*=-1.17$). This can be understood on the basis of the Horiuti-Polanyi rule,[3] provided that the initial state of hydrogenation is the adsorption step of monoalkylbenzenes and that the attack of adsorbed hydrogen as a rate-determining step occurs in succession. The lower the value of σ^*, the higher the electron density in benzene nucleus. Thus, adsorbed alkylbenzene exists stably and surface reaction is retarded.

The negative reaction parameter thus obtained from the Taft plot of adsorption coefficients suggests that a nucleophilic adsorption occurs on the surface of ruthenium, as follows.

Adsorption  (4)

$$\mathrm{R} + \underset{\mathrm{M}}{\overset{\delta+}{|}} \longrightarrow \underset{\mathrm{M}}{\overset{\mathrm{R}^{\delta+}}{|}} \qquad (4)$$

The positive reaction parameter between k and σ^* obtained suggests that a nucleophilic reaction of the adsorbed alkylbenzene complex with a metal-hydride occurs on the surface:

Surface reaction  (5)

$$\underset{\mathrm{M}}{\overset{\mathrm{R}^{\delta+}}{|}} + \underset{\mathrm{M}}{\overset{\mathrm{H}^{\delta-}}{|}} \rightarrow \underset{\mathrm{M}}{\overset{\mathrm{RH}^{\delta-}}{|}} + \underset{\mathrm{M}}{\overset{\delta+}{|}} \qquad (5)$$

The mechanism is similar to the nucleophilic type mechanisms proposed for other reactions; the hydrogenation of alkylbenzene over PtO_2[4,7] ($\rho^*=0.842$), the hydrogenolysis of chlorobenzenes over Pd-carbon[5] ($\rho^*=1.77$) and the homogeneous hydrogenolysis of organic halides with sodium bis(2-methoxyethoxy)aluminium hydride[5,8] ($\rho^*=4.0$).

In this experiment, the Taft plot is more favorable than the Hammett one, as was also pointed out by Kraus[4] who did not deal with adsorption coefficients. Recently, Simonikova *et al.*[9] have reported that the adsorption coefficients showed an opposite trend to the rate constants in heterogeneous hydrogenation of aliphatic ketones, in good agreement with out findings.

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