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The Hammett Relationship in the Reduction of Aldehydes with 2-Propanol by Catalysis with Hydrous Zirconium Oxide

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Synopsis. A linear correlation of the Hammett relationship was obtained for a catalytic reduction of substituted benzaldehydes with 2-propanol with hydrous zirconium oxide. The reaction constant ρ was 1.35, indicating that the electronic effect on the reaction is larger than that on the standard one.

In a previous paper, we reported that the reduction of aldehydes and ketones with 2-propanol proceeds efficiently in the presence of hydrous zirconium oxide.[1,2] All the conjugated ketones, as well as sterically hindered ones, could be substantially reduced by this method. The reduction of conjugated, as well as sterically hindered ketones, took a long time. The reduction of ketones with chloride substituted at the α-position was faster. There results suggested that both steric and electronic factors affect the reaction. The Hammett relationship is a useful method for an interpretation of the reaction mechanism, since it indicates the relative electronic effect quantitatively.[3]

In this paper, we report on the relative electronic effect on the reduction by use of the reaction constant (ρ), which was obtained by the Hammett relationship.

Experimental

Catalyst and Materials. Hydrous zirconium oxide was prepared in the manner described in a previous paper.[2] The calcination of the catalyst was performed at 300 °C for 5 h. Commercial reagents were used for the reaction without further purification.

Reduction and Analysis. In a 10 cm³ round-bottom flask equipped with a reflux condenser, 1 mmol of aldehyde, 0.1 mmol of a hydrocarbon as an internal standard, 2 cm³ of 2-propanol, and 0.1 g of hydrous zirconium oxide were placed. The reaction mixture was immersed in an oil bath which was kept at 78±0.1 °C, and 0.1—0.2 µl samples were removed at appropriate time intervals and analyzed by gas chromatography (capilary column PEG 20M 30m).

Results and Discussion

The reduction of substituted benzaldehydes proceeded efficiently to give the corresponding alcohols. No by-products were detected. Exceptionally, *p*-hydroxybenzaldehyde and *p*-(dimethylamino)benzaldehyde were mainly converted to *p*-hydroxybenzyl isopropyl ether and *p*-(dimethylamino)benzyl isopropyl ether, respectively. In all cases, a linear correlation between the natural logarithm of the concentration of aldehyde and reaction time was obtained. It indicated that the reaction rate is of pseudo-first-order in the aldehyde concentration,[2] and the rate constants, k, were calculated from the slope of the line, and are listed in Table 1.

The Hammett relationship for the reduction is illustrated in Fig. 1, and shows $\ln k/k_0$, where k_0 is the rate constant for the reduction of benzaldehyde, plotted against σ, where σ is the substituent constant.[4] A linear correlation was obtained, except for the cases of *p*-hydroxybenzaldehyde and *p*-(dimethylamino)benzaldehyde. This result suggests that a linear free

Table 1. Substituent Effect on the Reduction of Substituted Benzaldehydes[a)]

Entry	Substituent	Rate const.[b)]
1	*m*-NO_2	3.25
2	*p*-CN	2.83
3	*m*-Br	2.68
4	*m*-Cl	2.60
5	*m*-F	2.41
6	*p*-Cl	2.03
7	H	1.41
8	*p*-C_2H_5	1.01
9	*p*-CH_3	1.22
10	*p*-OCH_3	1.02
11	*p*-OH	0.34[c)]
12	*p*-$N(CH_3)_2$	0.30[c)]

a) Aldehyde 1 mmol, 2-propanol 2 cm³, Catalyst 0.2 g, 78.0±0.1 °C. b) $\times 10^{-4}\,s^{-1}$. c) Only isopropyl ether was obtained.

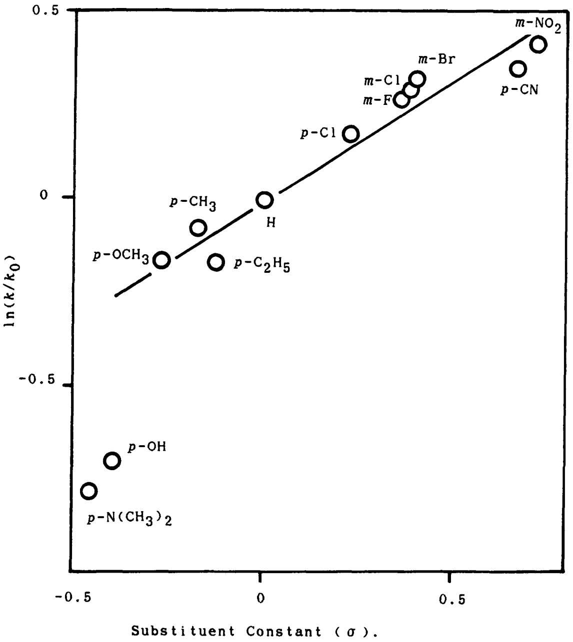

Fig. 1. Correlation between substituent constant, σ, and rate constant of the reduction.
k: Rate constant of substituted benzaldehyde.
k_0: Rate constant of benzaldehyde.

energy relationship exists in the reduction, and that the electronic effect can be directly evaluated.

The reaction constant, ρ, which was obtained from the slope of the line, reflects the sensitivity of the reaction rate to the electronic effect. The value of ρ was 1.35, which indicates that the electronic effect on the reduction was larger than that on the standard reaction (the esterification of substituted benzoic acids).[4]

The reduction of aldehyde with 2-propanol was believed to proceed via the attack on the carbonyl by the hydride from 2-propanol. From this it follows that the electronic deficient aldehyde was reduced faster. This interpretation is supported by the results for the Hammett relationship.

In the case of the reduction of *p*-hydroxybenzaldehyde and *p*-(dimethylamino)benzaldehyde, the rates were too slow and the products were mainly ethers. This is because the affinity of the hydroxyl or dimethylamino group to hydrous zirconium oxide is stronger than that of the carbonyl group.

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