# The Effect of Base Strength on the Catalytic Hydrogenation of Certain Schiff Bases with Pentacyanocobaltate

This work was undertaken to determine quantitatively the effect of ring substituents on the rate of homogeneous catalytic hydrogenation of the carbon–nitrogen double bond of Schiff bases, ArCH=NAr′, where Ar and Ar′ are substituted aryl groups.

Pentacyanocobaltate was chosen for this study as a homogeneous catalyst, and the catalyst solution was prepared by the usual method (*1*) from cobaltous chloride hydrate (0.25 mmole), potassium cyanide (1.25 mmole) and potassium hydroxide (0.75 mmole) in water (20 ml), and the resulting complex was prehydrogenated in a hydrogen atmosphere at 40°. After the absorption of hydrogen by the catalyst solution was complete (about 2 hr), the solution of the reactant Schiff base (1.0 mmole) in ethanol (40 ml) was added. The hydrogen uptake was measured at atmospheric pressure by a gas buret.

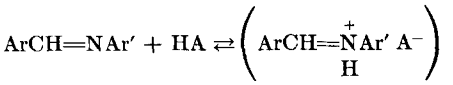
TABLE 1

Initial Rate Constants and Dissociation Constants for Certain Schiff Bases

| Substituent | | | |
|---|---|---|---|
| 4— | 4′— | $k \times 10^{4}$ [a] (mole hr$^{-1}$) | $K \times 10^{-1}$ [b] |
| Br | H | 5.34 | 1.3 |
| Cl | H | 2.80 | 1.4 |
| $CH_3$ | H | 0.57 | 3.1 |
| $CH_3O$ | H | [c] | 4.5 |
| H | H | 1.12 | 1.9 |
| H | Br | 2.04 | 1.3 |
| H | Cl | 4.02 | 1.1 |
| H | $CH_3$ | 0.27 | 3.1 |
| H | $CH_3O$ | [c] | 3.5 |

[a] Reactant 1.0 mmole, catalyst 0.25 mmole.

[b] Dissociation constants at 48°C given by Weinstein and McIninch (*2*) for the following equilibrium:



$$\mathrm{ArCH{=}NAr' + HA \rightleftarrows \left(ArCH{=}\underset{H}{\overset{+}{N}}Ar'\ A^{-}\right)}$$

where HA is *p*-nitrophenol.

[c] Under the reaction condition, no substantial hydrogen uptake was observed.

From the slope of the plot of the hydrogen uptake (corrected to STP and converted to moles) vs time (hr), pseudo zero-order rate constants were calculated for the initial rate process. It may be noted that the hydrogen pressure will affect the results to a slight extent, since the vapor pressure of the solvent would be fairly constant in all processes.

It was found that substituents on the ring of Schiff bases do definitely affect the rate of the hydrogenation. The data show that the hydrogenation is accelerated by electron-withdrawing substituents and retarded by electron-donating substituents (Table 1). The effect of the nitro group could not be determined since it was reduced at a rate comparable to that of the carbon–nitrogen double bond.

On the other hand, Weinstein and McIninch have determined the dissociation constants *K* for the complex formation be-

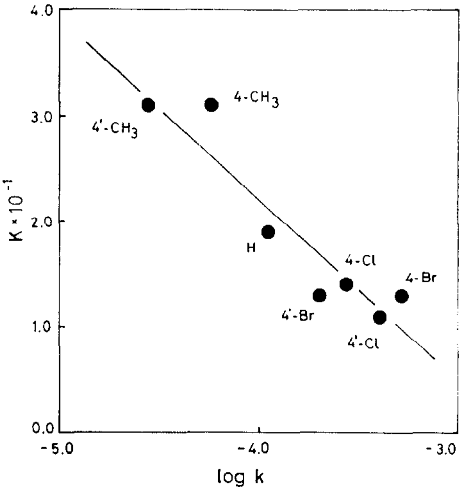


FIG. 1. Correlation between initial rate constants *k* and dissociation constants *K* of substituted Schiff bases.

tween Schiff bases and *p*-nitrophenol using infrared absorbance measurement, and discussed the effect of substituents on the base strength of Schiff bases by means of the Hammett equation (*2*). When these dissociation constants $K$ at 48° were plotted against the logarithm of the rate constants $k$ of the homogeneous catalytic hydrogenation with pentacyanocobaltate, a linear correlation, as shown in Fig. 1, was obtained. The correlation coefficient of the graph was $-0.934$.

A Schiff base of lower base strength is more readily hydrogenated by means of pentacyanocobaltate. This suggests a rate-determining nucleophilic attack by hydridopentacyanocobaltate at the carbon–nitrogen double bond of Schiff bases. Analogous results have been also obtained by the polarographic reduction of substituted Schiff bases (*3*).

## REFERENCES

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