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THE EFFECT OF BASE STRENGTH OF SCHIFF BASES ON THEIR CATALYTIC HYDROGENATION WITH BIS(DIMETHYLGLYOXIMATO)COBALT(II)

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Kinetic measurements were reported for the catalytic hydrogenation of certain Schiff bases with bis(dimethylglyoximato)cobalt(II). The influences of substituents of Schiff bases upon the reactivity were shown to increase with the basicity, which were quite different pattern with that of the hydrogenation with pentacyanocobaltate.

It was pointed out in the preceding paper that the rate of the catalytic hydrogenation of Schiff bases with pentacyanocobaltate is retarded as the base strength of the Schiff base is increased$^{1)}$. Now, we wish to report the effect of the base strength of certain Schiff bases on their catalytic hydrogenation with bis(dimethylglyoximato)cobalt(II) which undergoes some reactions paralleling with those exhibited by pentacyanocobaltate.

Experimental

Bis(dimethylglyoximato)cobalt(II) was prepared according to the method of Schrauzer and Windgassen$^{2)}$ from cobalt(II) acetate and dimethylglyoxime in tetrahydrofuran (THF). The mixture was stirred at 30°C for 8 min. under reduced pressure to complete the complex formation. Then hydrogen was introduced to the system and the solution of the Schiff base (benzalaniline) in THF was added at a time. The hydrogen-uptake was observed after some induction period and the rate was measured at atmospheric pressure by gas-buret and corrected to STP. The reduction product, N-benzylaniline, was analysed by glc, after the reaction was completed.

Results and Discussion

Treatment of the experimental data of the reaction as a simple first-order reaction afforded good agreement. The rate of hydrogen-uptake was almost independent of hydrogen pressure between 760 to 456 mmHg (Table 1). Thus, it appears that the hydrogen-uptake is not diffusion controlled but reaction controlled under the condition employed. Further, it was shown that the reaction rate was enhanced with the increase of the initial concentration of Schiff base up to 30mM, but it was almost constant over 37.5mM (Fig. 1). And the rate was proportional to the concentration of bis(dimethylglyoximato)cobalt(II) (Table 2). Rate measurements over the temperature range 20-35°C for the reaction yielded good Arrhenius plots, from which the activation energy was calculated to be 14.5kcal/mol.

Table 1. Dependence of the rate on the hydrogen pressure. $Co(DMG)_2$: 7.5mM, benzalaniline: 22.5mM, THF: 30ml, 30°C.

H_2 pressure (mmHg)	$-\frac{dH_2}{dt} \cdot 10^5$ (mol/min)
760	9.45
570	11.07
488	9.99
456	10.32

Table 2. Dependence of the rate on the concentration of $Co(DMG)_2$. Benzalaniline: 7.5mM, THF: 40ml, 30°C.

Conc. of $Co(DMG)_2$ (mM)	$-\frac{dH_2}{dt} \cdot 10^5$ (mol/min)
7.5	6.03
15.0	20.56
22.5	31.23

Fig. 1. Dependence of the rate on the initial concentration of benzalaniline[5]. $Co(DMG)_2$: 7.5mM, THF: 40ml, 30°C.

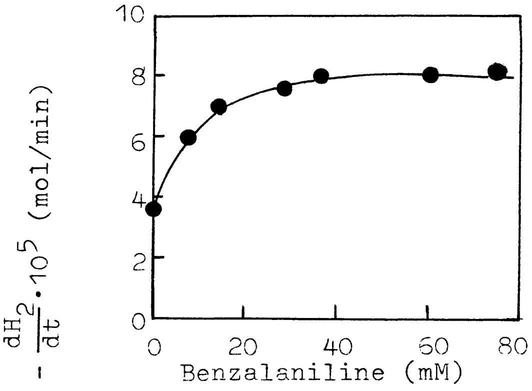
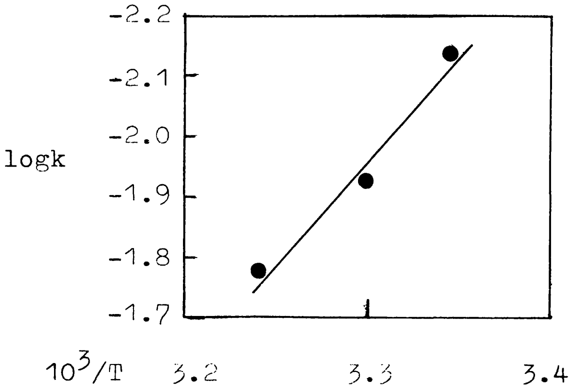


Fig. 2. Arrhenius plots. $Co(DMG)_2$: 7.5mM, benzalaniline: 22.5 mM, THF: 40ml.



As to the substituent effect of 4 and 4' position of Schiff bases, the reaction has shown an opposite reactivity pattern to that of the catalytic hydrogenation with pentacyanocobaltate. The data show that the hydrogenation with bis(dimethylglyoximato)cobalt(II) is accelerated by electron-donation and retarded with electron-withdrawal by substitution. From the slope of the Hammett plot (Fig. 3), the rho value is calculated to be -0.42 for the reaction (correlation coefficient $r=-0.89$, the plot of 4,4'-bis(dimethylamino)benzalaniline was omitted). It should be noted that the rho value for the catalytic hydrogenation of Schiff bases with pentacyanocobaltate has been +2.40 ($r=0.79$), and a rate-determining nucleophilic attack by hydrido pentacyanocobaltate toward Schiff base has been suggested for the hydrogenation[1].

A linear correlation, as shown in Fig. 4, was obtained, when the logarithm of the first-order rate constants k of the catalytic hydrogenation with bis(dimethylglyoximato)cobalt(II) were plotted against the logarithm of dissociation constants K of Schiff bases, which were determined by Weinstein as a measure of basicity for the complex formation between certain Schiff bases and p-nitrophenol using infrared absorbance measurement[3].

Table 3. Substituent constants (σ), first-order rate constants (k) and dissociation constants (K) for 4 and/or 4'-substituted Schiff bases. $Co(DMG)_2$: 7.5mM, Schiff base: 22.5mM, THF: 30ml, 30°C.

No	Substituents		σ^*	$k\cdot10^3$	K **
	4-	4'-		(min^{-1})	
1	H	H	0.00	11.10	39
2	Cl	H	0.23	10.53	29
3	CH_3	H	-0.17	13.40	61
4	CH_3O	H	-0.27	15.40	88
5	$(CH_3)_2N$	H	-0.60	17.70	280
6	H	Cl	0.23	11.30	25
7	H	m-Cl	0.37	8.64	--
8	H	CH_3	-0.17	15.40	61
9	H	CH_3O	-0.27	17.40	63
10	H	$(CH_3)_2N$	-0.60	19.88	140
11	CH_3O	CH_3O	-0.54	16.54	120
12	$(CH_3)_2N$	$(CH_3)_2N$	-1.20	15.19	800

* Jaffe's value; sums of the values are listed in the case of disubstituted Schiff bases.

** Dissociation constants at 27.5°C given by Weinstein[3)] for the following equilibrium:

$$ArCH{=}NAr' + HA \rightleftarrows ArCH{=}\overset{+}{N}HAr'\ A^-$$

where HA is p-nitrophenol.

Bis(dimethylglyoximato)cobalt(II) is known to form 1:1 adducts with a variety of Lewis bases[4)]. Therefore, the first step of this hydrogenation reaction would be the nucleophilic axial coordination of Schiff bases to the planar tetracoordinated cobalt(II) atom of bis(dimethylglyoximato)cobalt(II). In general, it has been accepted that ligands having both electron donor and acceptor property stabilize the metal-hydrogen bond, and so, the stronger the π-basicity of the ligands, the greater will be the ability of the central metal to intact with hydrogen. The enhancement of the rate by electron-donating substituents on the π-electron conjugated Schiff base is consistent with this view. In addition, it has been established in other experiment that the rate of the hydrogen absorption with bis(dimethylglyoximato)cobalt(II) is more enhanced when triarylphosphine with a more electron donating substituent is coordinated to the complex as an axial ligands[5)]. The deviation of the plots of 4-dimethylaminobenzalaniline and 4,4'-bis(dimethylamino) benzalaniline from the line in Fig. 4 might be ascribed to the unparallel between proton-basicity and electron donor-acceptor property. About this point, further investigations are progressing.

Fig. 3. The Hammett relations$^{6)}$.

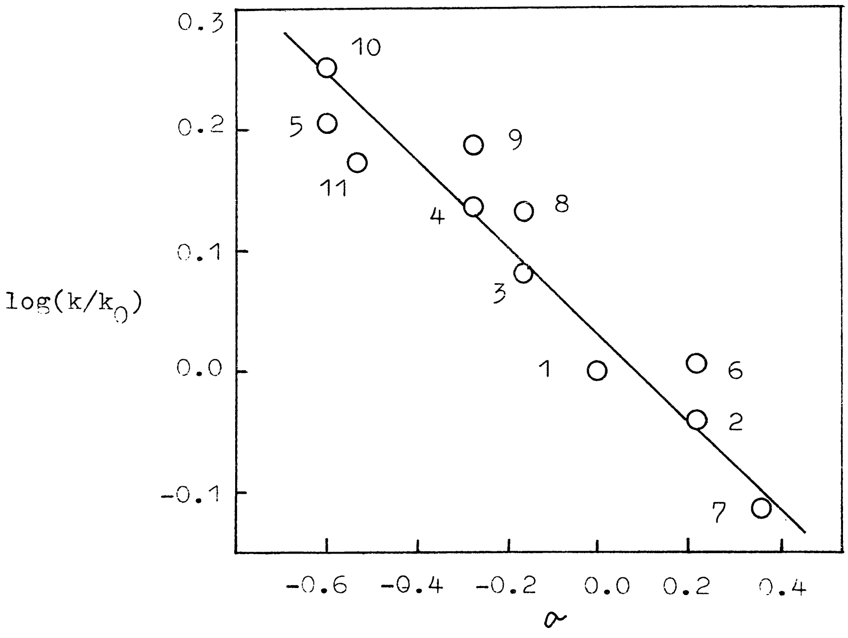
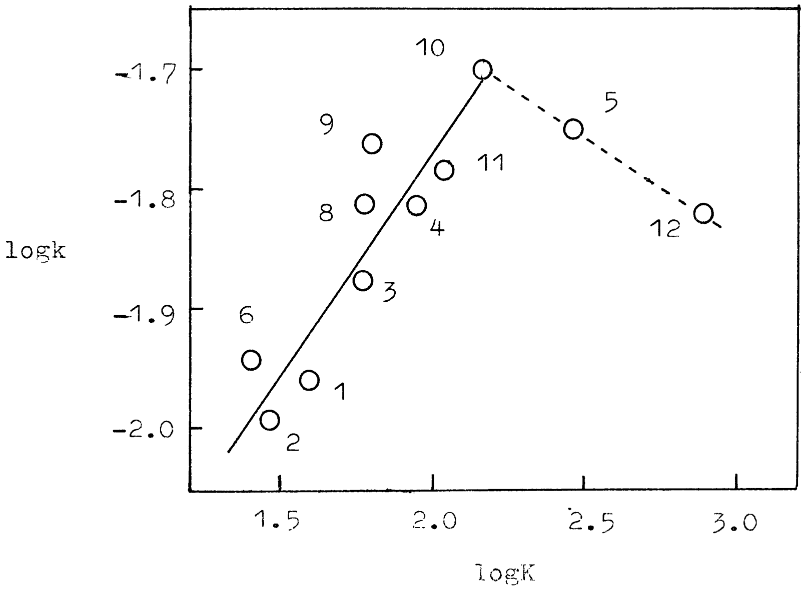


Fig. 4. Correlation between rate constants and dissociation constants (basicity)$^{6)}$.



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2) G. N. Schrauzer and R. J. Windgassen, J. Am. Chem. Soc., 89, 1999 (1967).
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4) G. N. Schrauzer, R. J. Windgassen and J. Kohnle, Chem. Ber., 98, 3324 (1965). J. Halpern and F. Phelan, ibid., 94, 1881 (1972).
5) When any other substrate is absent, bis(dimethylglyoximato)cobalt(II) is hydrogenated to give the reduction product of the ligand. T. Yamaguchi and T. Tsumura, in contribution.
6) Numberings of the plots are listed in Table 3.

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