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THE EFFECT OF TRIPHENYLPHOSPHINE ON THE HYDROGENATION REACTION OF BIS(DIMETHYLGLYOXIMATO)COBALT(II)

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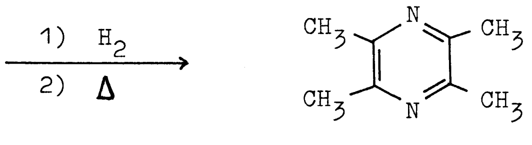
The present study relates to the influence of the axial bases, especially triphenylphosphine, on the catalytic hydrogenation reaction of bis(dimethylglyoximato)cobalt(II). It was established by the kinetical study that an excess triphenylphosphine acts as a poison for this reaction by the formation of 1:2 adduct.

Schrauzer and Windgassen reported that stable metal-alkyl complexes were formed by the reaction of bis(dimethylglyoximato)cobalt(II) and certain olefins under hydrogen atmosphere, and in some cases reduction products were obtained$^{1)}$. It was also reported by Halpern that various bis(dioximato)cobalt(II) complexes reacted with organic halides forming stable organocobalt derivatives. Influences of electronic and steric factors, especially effect of axial bases, upon the reactivity of bis(dioximato)cobalt(II) complexes with organic halides were discussed by the same investigators$^{2,3)}$.

It was now confirmed that when the complex of bis(dimethylglyoximato)cobalt (II) with triphenylphosphine, as an axial base, was treated with hydrogen in tetrahydrofuran without any other substrate to be reduced, an excess hydrogen absorption over the equimolar amount of the complex (about 2.5 times) was observed, and the reduced product of dimethylglyoxime (the ligand), tetramethylpyrazine, was obtained by the sublimation of the reaction mixture in yield of 38-40 %. We wish to report in this communication, the effect of triarylphosphine, axial base, upon the hydrogenation of bis(dimethylglyoximato)cobalt(II) complex.

$$Co(OCOCH_3)_2 \quad + \quad 2\ DH_2 \quad \xrightarrow{Ar_3P} \quad Co(DH)_2{\cdot}PAr_3 \qquad (1)$$



(2)

DH_2 = dimethylglyoxime

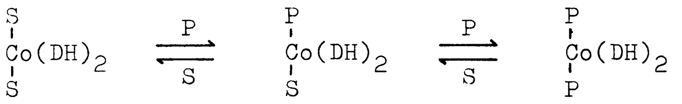
Experimental

The preparation and characterization of the cobalt(II) complex have already been reported by Halpern$^{2)}$. Using essentially the same procedures, cobalt(II) complexes were prepared in situ by addition of triarylphosphines to the solution of cobaltous acetate tetrahydrate and dimethylglyoxime in tetrahydrofuran. The hydrogenation of the complexes were carried out under atmospheric hydrogen pressure at 30°C. The kinetical measurement of the reaction was typically encompassed within the initial concentration of triphenylphosphine 0 to 2.00mM, at 0.5mM cobaltous acetate tetrahydrate and 1.0mM dimethylglyoxime. And initial hydrogen absorption rates were measured by a gas-buret and corrected to STP. Pseudo zero-order rate constants for the initial rate process are listed in Table 1.

For an instance, when a solution of cobaltous acetate tetrahydrate (0.003mol), dimethylglyoxime (0.018 mol) and triphenylphosphine (0.003 mol) in tetrahydrofuran (60 ml) was stirred under atmospheric hydrogen at 30°C, the hydrogen uptake started soon and ceased after 7 hr. The total volume of absorbed hydrogen was about one liter. From the reaction mixture, triphenylphosphine oxide was liberated by the extraction with ether, and after the solvent was removed, tetramethylpyrazine (40%) was obtained from the residue by the sublimation along with a small amount of ammonia.

Results and Discussion

Fig. 1 shows that the addition of triphenylphosphine increases the initial rate but excess of triphenylphosphine retards the rate. This indicates that excess triphenylphosphine acts as a poison for the catalytic hydrogenation of bis(dimethylglyoximato)cobalt(II) by the formation of 1:2 adduct (III) as shown follows$^{4)}$.



$$\overset{\text{S}}{\underset{\text{S}}{\text{Co(DH)}_2}} \underset{\text{S}}{\overset{\text{P}}{\rightleftharpoons}} \overset{\text{P}}{\underset{\text{S}}{\text{Co(DH)}_2}} \underset{\text{S}}{\overset{\text{P}}{\rightleftharpoons}} \overset{\text{P}}{\underset{\text{P}}{\text{Co(DH)}_2}} \qquad (3)$$

(I) (II) (III)

S = solvent (tetrahydrofuran), P = triphenylphosphine

$$K_1 = \frac{(\text{II})}{(\text{I})(\text{P})} \qquad (4) \qquad\qquad K_2 = \frac{(\text{III})}{(\text{II})(\text{P})} \qquad (5)$$

$$k = \frac{k_1 + k_2K_1(\text{P}) + k_3K_1K_2(\text{P})^2}{1 + K_1(\text{P}) + K_1K_2(\text{P})^2} \qquad (6)$$

Table 1. Dependence of the rate constant on the concentration of triphenylphosphine. $Co(OAc)_2$: 0.50mM, dimethylglyoxime: 1.00mM, 30°C.

Ph_3P (mM)	k_{obsd} (mol/hr)	k_{calcd} (mol/hr)
0.00	2.30×10^{-3}	2.30×10^{-3}
0.125	3.76	3.89
0.25	4.44	4.44
0.50	4.88	4.88
0.75	2.77	2.30
1.00	1.88	1.93
1.50	1.22	1.46

$$k_{calcd} = \frac{0.0023+0.00555\times77(P)}{1+77(P)+77\times19(P)^2}$$

Table 2. Reaction rate constants of the complexes with certain tertiary phosphines. $Co(OAc)_2$: 0.50mM, dimethylglyoxime: 1.00mM, phosphines: 0.50mM, 30°C.

Phosphines	$k\times10^3$ (mol/hr)	$\Sigma\sigma$
1. $(CH_3O\text{-}C_6H_4)_3P$	6.92	-0.804
2. $(CH_3\text{-}C_6H_4)_3P$	7.12	-0.510
3. $(C_6H_5)_3P$	4.88	0.000
4. $(ClC_6H_4)_2PC_6H_5$	4.54	+0.454
5. $(Cl\text{-}C_6H_4)_3P$	3.49	+0.681
6. $(n\text{-}C_4H_9)_3P$	8.66	------

Assuming the equilibrium (3) is attained rapidly compared to the hydrogenation of (I), (II) and (III), rate constants (k) of the overall hydrogenation reaction for the initial rate process is given by eq. (6), k_1, k_2 and k_3 are partial rate constants of the hydrogenation of (I), (II) and (III), respectively. The agreement between the observed and calculated rate constants at various concentration of triphenylphosphine is satisfactory assuming that $K_1 = 77$, $K_2 = 19$, $k_1 = 0.0023$ mol/hr, $k_2 = 0.00555$ mol/hr and $k_3 = 0$ mol/hr (Table 1).

Halpern and Phelan have concluded that excess triphenylphosphine does not affect the rate of the alkylation of bis(dimethylglyoximato)cobalt(II), since the 1:2 adduct (III) is completely dissociated in solution into (II) and triphenylphosphine in their condition (0.01-1mM in benzene). However, under our condition (0.5 mM in tetrahydrofuran), the existence of the 1:2 adduct (III) would not be deniable although the spectral titration measurement or others were not achieved.

The contribution of electronic factors to the influence of triphenylphosphine is most clearly revealed by a comparison of complexes of para-substituted triarylphosphines, $(p\text{-}XC_6H_4)_3P$, where differences due to steric factors are presumably unimportant. The Hammett plot of the logarithm of pseudo zero-order initial hydrogen absorption rate and total sigma values, depicted in Fig. 2, showed the enhancement of the rate by electron-donating substituents. However, the plot of tri-p-anisylphosphine, with the most powerful electron-donating substituent, negatively deviated from the line in Fig. 2. This might be ascribed to the formation of inactive 1:2 adduct which should be more serious for the triarylphosphine with the more electron-donating substituent. Further investigation about this point are now progressing with regard to the effect of aniline derivatives as axial bases.

Fig. 1. Correlation between rate constants and Ph_3P-$Co(DH)_2$ ratio

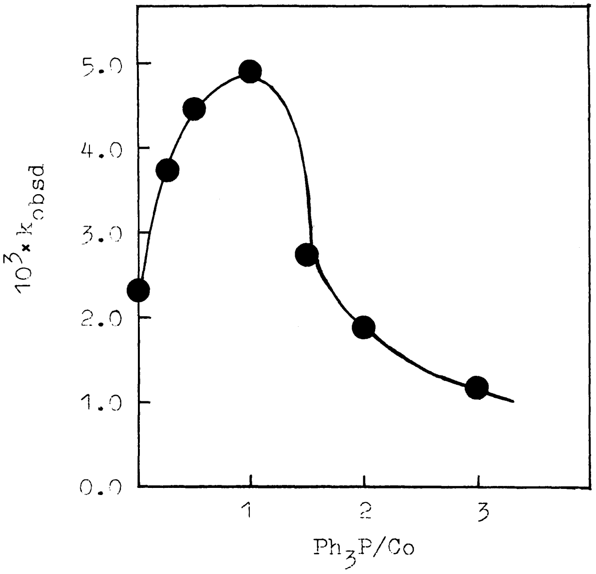
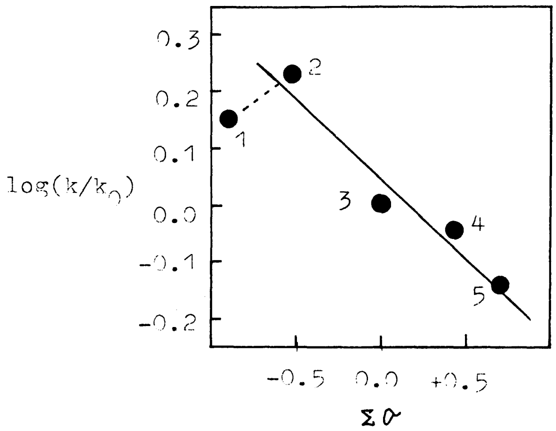


Fig. 2. The Hammett relations[5)]



References

1) G. N. Schrauzer and R. J. Windgassen, J. Am. Chem. Soc., 88, 3738 (1966), 89, 1999 (1967), Schrauzer and E. Deutsch, ibid., 90, 3341 (1968)
2) P. W. Schneider, P. F. Phelan and J. Halpern, ibid., 91, 77 (1969)
3) J. Halpern and P.F. Phelan, ibid., 94, 1881 (1972)
4) Dimeric configurations with Co-Co bond of these intermediates described by Schrauzer et al. (Chem. Ber., 99, 602 (1966)), are omitted here, but their possibility cannot be excluded.
5) Numberings of plots are listed in Table 2.

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