Kinetic studies on the homogeneous hydrogenation of fumaric and maleic acies catalysed by bis(dimethylglyoximato)cobalt(II)

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Abstract. The influence of varying concentrations of $Co(DMGH)_2$, NaOH and axial base on the rate of hydrogenation of fumaric and maleic acids has been studied in detail. Intramolecular hydrogen bonding in the monoanion of maleic acid and the *trans* orientation of carboxylic acid groups in fumaric acid are important factors which account for the difference in the rate of hydrogenation of these substrates. Mono-, di- and trialkyl amines as axial bases modify the activity of the catalyst, dialkylamines conferring the maximum activity and trialkylamines the least. Back-strain on nitrogen atom and solvation energy of the amines are responsible for their different behaviours. A rate law has been proposed and verified.

Keywords. Cobaloxime; hydrogenation; axial base; fumaric acid; maleic acid.

1. Introduction

Glyoxime complexes of cobalt(II) accept bases in the axial positions to form cobaloximes (Schrauzer 1968; Schrauzer and Windgassen 1970; Schrauzer and Holland 1971; Belluco 1970). Because of the similarity to Vitamin B_{12} in their reactions they serve as excellent models for Vitamin B_{12} (Schrauzer 1976). During the past decade there has been considerable growth in the studies related to the bioinorganic aspects of Co(II). These studies involve synthesis and reactions of complexes of Co(II) with dimethyl and other glyoximes, Schiff bases and other macrocyclic ligands. The green Co(I) species formed by the reduction of cobaloximes have strong reducing properties and nucleophilic character (Dodd and Johnson 1973; Witman and Weber 1977). As a part of our studies on the activation of molecular hydrogen by complexes (Vancheesan et al 1978; Rajagopal et al 1979; Pillai et al 1980, 1982; Thangaraj et al 1980) we have investigated the hydrogenation of fumaric and maleic acids by cobaloxime. We report here the results of our studies on the role of (i) orientation of functional groups as in fumaric and maleic acids, (ii) the influence of the axial base in the complex and (iii) the concentration of NaOH on the rate of hydrogenation.

2. Experimental

Cobalt chloride hexahydrate and dimethylglyoxime (BDH, AR) were used for the preparation of cobaloxime(III). The catalyst solutions were prepared *in situ* in aqueous

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alkaline medium. All reagents were purified by standard techniques. Extra care was taken to check and remove peroxide impurities from the unsaturated substrates by shaking with a saturated solution of ferrous ammonium sulphate (BDH, AR). Alkaline cobaloxime solutions were saturated with hydrogen at the reaction temperature prior to the addition of substrates by vigorous stirring till no further hydrogen uptake was observed. The hydrogen absorption was followed at regular intervals by means of a gas burette with provision to maintain a constant pressure of hydrogen. Kinetic studies were carried out by changing any one of the following parameters at a time keeping others constant: (i) catalyst concentration, (ii) substrate concentration, (iii) axial base, (iv) concentration of sodium hydroxide and (v) temperature. Reaction mixtures were withdrawn periodically for product analysis. After separation from the catalyst and other reagents, solid products were analysed by TLC technique using alumina. Liquid samples were analysed by GLC using Varian 1800 model with hydrogen as carrier gas.

3. Results and discussion

3.1. Effect of axial base

Co (DMGH)$_2$ forms 1 : 1 and 1 : 2 adducts with a variety of Lewis bases. These adducts are soluble in a number of organic solvents and water. 1 : 2 adducts dissociate in solution as

$$Co(DMGH)_2 2B \rightarrow Co(DMGH)_2 B + B$$
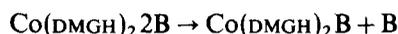
Under hydrogenation conditions hydrido cobaloximes, $HCo(DMG)_2 B$ (DMG = mono-anion of dimethylglyoxime) which are Bronsted acids corresponding to the Co(I) nucleophiles, are formed. This hydrido species is the catalytic intermediate as in other well-known examples of Ru(II), Rh(I), etc. (Hallman et al 1968; Osborn et al 1966). The stability of the hydridocobaloximes is very much influenced by the axial base (Schrauzer and Holland 1971). Predominantly σ donor nitrogen bases form unstable hydrido species that cannot be isolated whereas π-acceptors like triaryl and trialkyl phosphines as axial ligands form stable hydrides (Schrauzer and Holland 1971). If the hydride intermediate is too stable, migration of hydride to coordinated substrate becomes difficult, rendering the complex catalytically inactive. On this account pyridine and other N-donor ligands like various substituted amines are considered better axial bases than phosphines for catalytically active complexes. Among several nitrogen containing compounds (table 1) tried, pyridine was found to be the best. There are several reports of pyridine being a good axial base in cobaloxime catalysis (Simandi et al 1980; Zahonyi et al 1972, 1975).

The catalytic activity of the cobaloxime is attributed to the presence of unpaired d electrons in Co(II) which is extensively delocalised along the z axis as indicated by ESR studies (Simandi et al 1972, 1975). The result of such delocalisation is an increase in the free radical nature of Co(II), facilitating the interaction with hydrogen through a homolytic cleavage of molecular hydrogen. The efficiency of the axial base may be related to the availability of the lone pair. Thus among the mono, di and trialkyl amines the following order of reactivity is expected:

trialkylamine > dialkylamine > monoalkylamine

However, the initial rates of hydrogen absorption and percentage conversion to products indicates that trialkylamines are least reactive, dialkylamines showing the maximum

Table 1. Effect of variation of axial base B^+.

Base	H_2 absorbed (ml/hr)	% conversion to product
n-butylamine	8 1	33
di-n-butylamine	12·0	46
tri-n-butylamine	nil	nil
Triethyl amine	nil	nil
Trimethyl amine	nil	nil
Pyridine	25	98

[+]Concentrations of catalyst, substrate, NaOH, axial base and temperature are maintained constant.

reactivity. This deviation from expected reactivity could be attributed to increased back-strain on the N-atom in trisubstituted amines which increases the p-character on the lone pair. However, in solution the basicity is increased with the extent of solvation and the solvation energies of the conjugate ammonium ions are in the order:
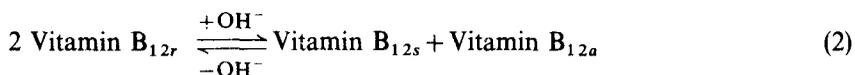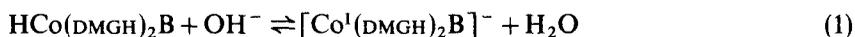
$$RNH_3^+ > R_2NH_2^+ > R_3NH^+$$

Electronic and solvation effects which oppose each other decide the basicity. As a result dilakylamine has maximum basicity. The difference in basicity is reflected in the activity of the complex for hydrogenation which is in the decreasing order:

$$\text{disubstituted} > \text{monosubstituted} > \text{trisubstituted}$$

With trialkylamines as axial base there was no absorption of hydrogen.

3.2 *Effect of alkali concentration*

In a strongly alkaline medium (pH $>$ 9), cobaloxime exists predominantly as Co(I) and Vitamin B_{12} as B_{12s} (equations (1) and (2)) (Schrauzer *et al* 1965; Schrauzer and Windgassen 1966; Hill *et al* 1969).

$$HCo(DMGH)_2B + OH^- \rightleftharpoons [Co^I(DMGH)_2B]^- + H_2O \tag{1}$$

$$2 \text{ Vitamin } B_{12r} \underset{-OH^-}{\overset{+OH^-}{\rightleftharpoons}} \text{Vitamin } B_{12s} + \text{Vitamin } B_{12a} \tag{2}$$

(In (2) subscripts s, r and a indicate the oxidation states of cobalt.) In Co^I the highest occupied orbital is probably a weakly antibonding d_{z^2} orbital which forms the centre of high polarizability and charge density. Since the equilibrium will be shifted to the right in strongly alkaline medium (equations (1) and (2)) the presence of the acid form $HCo^{(III)}$ is unlikely (equation (1)). In the presence of H_2 at 1 atmosphere pressure and pH $>$ 9, $Co^{(I)}$ is a very stable form (Takeuchi and Ohgo 1974). However at pH between 7 and 9, $HCo^{(III)}$ is the predominant species and the hydrogenation occurs essentially through proton transfer, the mode of addition of substrate being *cis*. However if $Co^{(I)}$ species reacts with the substrate forming an unstable σ complex, which is subsequently converted to a stable π complex, its further hydrogenation can be effected only under rigorous conditions. This accounts for the sharp decline in the hydrogen uptake in strongly alkaline medium (pH $>$ 9) (figure 1). This observation confirms that in mild
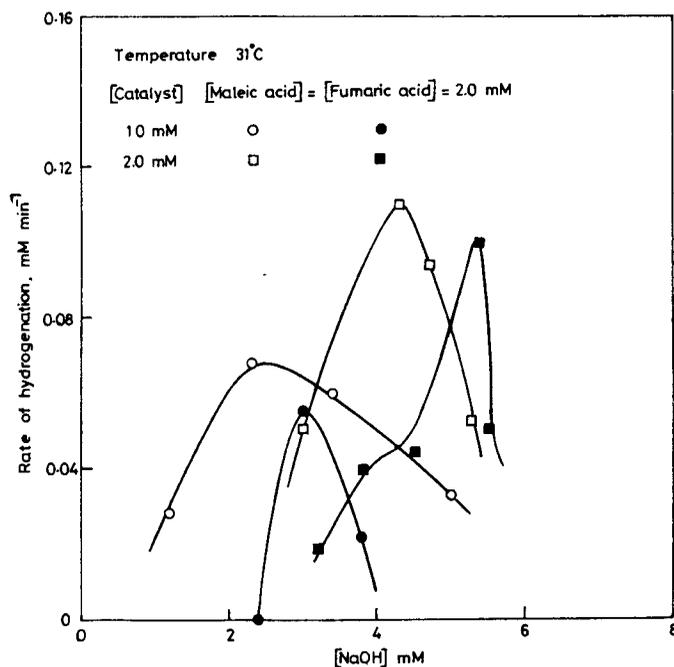
Figure 1. Effect of [NaOH] on the rate of hydrogenation of fumaric acid and maleic acid.

alkaline conditions the active form of cobaloxime is $HCo(DMGH)_2B$. Since the substrates used are carboxylic acids, some amount of alkali is used up for neutralizing the acid. The effective [OH^-] is the excess remaining after neutralisation. On increasing [OH^-] the rate of hydrogenation passes through a maximum (Shanthalakshmy *et al* 1980). This is in agreement with Schrauzer's scheme where cobaloxime(II) is converted into cobaloxime(III) and cobaloxime(I) (Schrauzer *et al* 1965, 1966, 1968).

$$\tfrac{1}{2}H_2 + Co^{(II)} \rightleftharpoons H \underset{-H_2O}{\overset{+OH^-}{\rightleftharpoons}} [Co^{(I)}]^-$$
$$| $$
$$Co^{(III)}$$
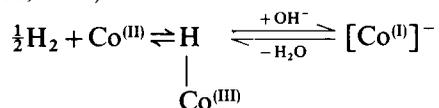
This reaction is complete in the presence of excess alkali which explains the steep fall in the rate as the concentration of alkali is increased. The order with respect to catalyst and the substrate is one each and that with respect to [OH^-] is fractional.

3.3 *Nature of the substrate*

The rate of hydrogenation of maleic acid was found to be higher than that of fumaric acid. On adding OH^-, maleic acid forms the monoanion which enters into hydrogen bonding with the other carboxyl group which is in close proximity to the carboxylate anion. Hence under the experimental conditions further neutralisation of maleic acid to form the dicarboxylate anion is difficult. But in fumaric acid the *trans* orientation of the carboxylic acid groups does not permit the formation of intramolecular hydrogen

bonding. The higher rate of hydrogenation of maleic acid can be attributed to the following: (i) the monoanion of maleic acid with an available H^+ facilitates the formation of hydridocobaloxime(III) which is the active intermediate in the reaction. This is analogous to transfer of hydrogen from a donor solvent to an acceptor *via* hydride intermediate (Pillai *et al* 1980, 1982). The maleate monoanion probably functions as a hydride donor too. This is an additional factor which enhances the rate. In fumaric acid, dianion formation does not leave any scope for the substrate to function as a hydrogen donor. Besides, the *trans* orientation of carboxylate groups is a less favourable geometry for the activation of substrate. This accounts for the difference in the rates of hydrogenation of the two substrates.

3.4 *Rate law*

The following reaction sequence may be considered.

$$Co^{(II)} + B \overset{K_1}{\rightleftharpoons} Co^{(II)}B \tag{3}$$

$$Co^{(II)}B + \tfrac{1}{2}H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCo^{(III)}B \tag{4}$$

$$HCo^{(III)}B + OH^- \overset{K_3}{\rightleftharpoons} Co^{(I)} B^- + H_2O \tag{5}$$

$$USH + OH^- \overset{K_4}{\rightleftharpoons} US^- + H_2O \tag{6}$$

$$HCo^{(III)}B + US^- \overset{k_5}{\rightarrow} HCo^{(III)}B \, US^- + H_2 \rightarrow \text{Products} \tag{7}$$

$$[Co^{(II)}B] = K_1[Co^{(II)}][B] \tag{8}$$

$$[HCo^{(III)}B] = \frac{k_2[Co^{(II)}B][H_2]^{1/2}}{k_{-2} + K_3[OH^-] + k_5[US^-]} \tag{9}$$

$$[US^-] = \frac{K_4[USH][OH^-]}{[H_2O]} \tag{10}$$

Assuming, $\dfrac{K_4}{[H_2O]} = K_4'$, (10) becomes,

$$[US^-] = K_4'[USH][OH^-] \tag{11}$$

$$[HCo^{(III)}B] = \frac{k_2 K_1 [Co^{(II)}][B][H_2]^{1/2}}{k_{-2} + K_3[OH^-] + k_5 K_4'[USH][OH^-]} \tag{12}$$

$$\text{Rate} = k_5 [HCo^{(III)} B][US^-] \tag{13}$$

$$= \frac{k_5 k_2 K_1 K_4' [Co^{(II)}][B][H_2]^{1/2}[USH][OH^-]}{k_{-2} + k_3 [OH^-] + k_5 K_4' [USH][OH^-]} \tag{14}$$

The observed orders with respect to catalyst and substrate are in agreement with the above rate law. The appearance of $[OH^-]$ terms in the denominator of (14) accounts for the decrease in the rate of hydrogenation on increasing $[OH^-]$ (figure 1). At the

initial portions of the curve $[OH^-]$ is negligible and the corresponding terms in the denominator in (14) can be neglected, leaving only k_{-2}. At very high $[OH^-]$, reaction (5) is predominant as discussed earlier. This can be considered to occur *via* formation of $Co^{II}B$ as an intermediate (equation (3)). With increase in $[OH^-]$, $K_3[OH^-]$ and $k_5 K_4'[USH][OH^-]$ increase, since in the denominator of (14), $[OH^-]$ becomes considerable compared to k_{-2}, causing a steep fall in the rate on increasing $[OH^-]$. At low $[OH^-]$, $K_3[OH^-]$ may be small compared to the rest of the terms in the denominator of (14). Neglecting this and rearranging we get

$$\frac{[Co^{II}][B][USH]}{R} = \frac{k_{-2}}{k_5 K_4' k_2 K_1 [H_2]^{1/2} [OH^-]} + \frac{[USH]}{k_2 K_1 [H_2]^{1/2}}$$

A plot of the left side of the above equation against $1/[OH^-]$ is almost parallel to the y axis. Hence the term $K_3[OH^-]$ is included and (14) can be rearranged to give (15)

$$\frac{[USH][Co^{II}][B]}{R} = \frac{k_{-2}}{k_5 k_2 K_1 K_4' [H_2]^{1/2} [OH^-]} + \frac{K_3}{k_5 k_2 K_1 K_4' [H_2]^{1/2}}$$
$$+ \frac{[USH]}{k_2 K_1 [H_2]^{1/2}} \qquad (15)$$

If $k_2[H_2]^{1/2}$ is represented as k_2', $k_5 k_2' K_1 K_4'$ as K and $[Co^{II}][B][USH]/R$ as A, (15) can be rewritten as

$$A = \frac{k_{-2}}{K[OH^-]} + \frac{K_3}{K} + \frac{[USH]}{k_2' K_1} \qquad (16)$$

The variation in A as $[OH^-]$ is changed at constant $[USH]$ is given by

$$\frac{dA}{d[OH^-]} = \frac{-k_{-2}}{K[OH^-]^2}$$

$$\ln \frac{dA}{d[OH]^-} = \ln \frac{-k_{-2}}{K} - 2 \ln[OH^-] \qquad (17)$$

From the intercept of a plot of left side of (17) against $\ln[OH^-]$, k_{-2}/K has been evaluated (table 2, figures 2 and 3). In order to evaluate $k_2' K_1$, (16) is rearranged after substituting for A and written as (18)

$$\left\{ \frac{[Co^{II}][B]}{R} - \frac{1}{k_2' K_1} \right\} [USH] = \frac{k_{-2}}{K[OH^-]} + \frac{K_3}{K} \qquad (18)$$

Table 2. Evaluation of some kinetic parameters.

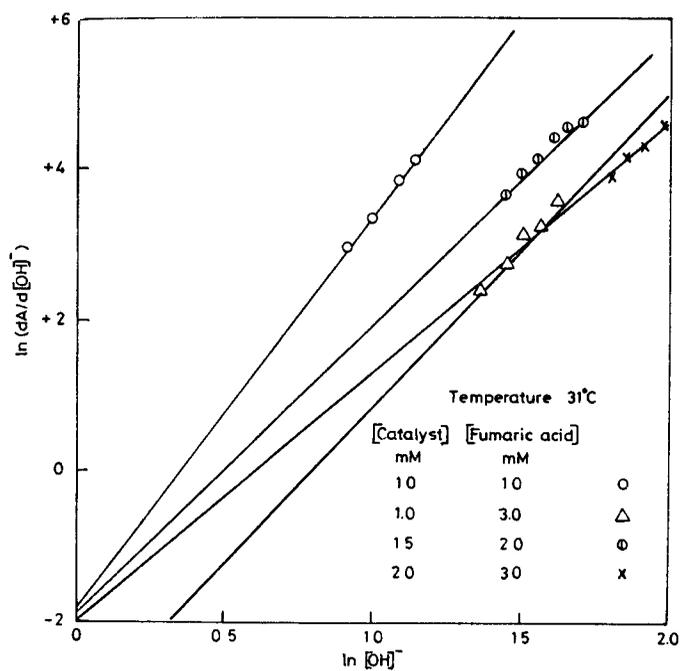|	k_{-2}/K	$k_2' K_1^*$	K_3/K^*	Energy of activation (kcal/mol)
Maleic acid	0·0264	1·19	52·5	17·6
Fumaric acid	0·1114	1·00	100	21·3

Average values, *catalyst = 2 mM.

Figure 2. Plot of $\ln(dA/d[OH]^-)$ *vs* $\ln[OH]^-$ for the evaluation of $-k_{-2}/K_A$ for fumaric acid. Verification of eq. (17).
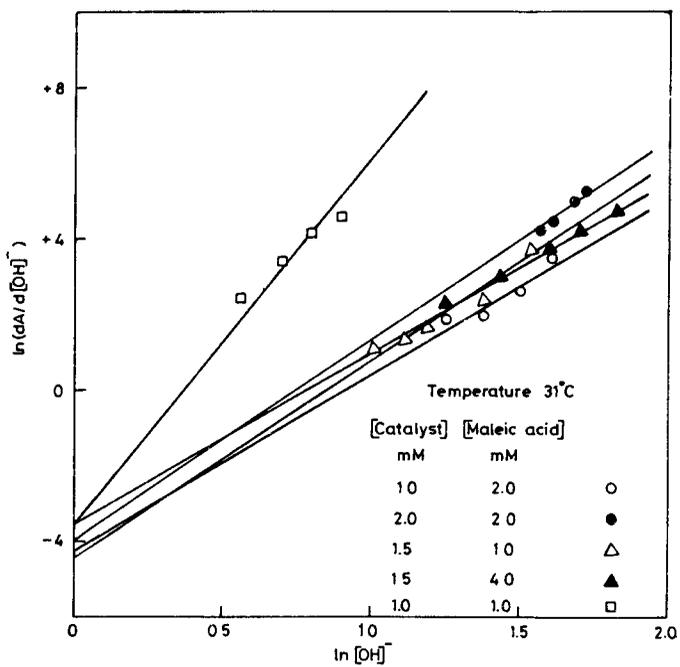

Figure 3. Plot of $\ln(dA/d[OH]^-)$ *vs* $\ln[OH]^-$ for the evaluation of $-k_{-2}/K$ for maleic acid.

Differentiating (18) with respect to $[OH^-]$, we get

$$\left\{ \frac{[CO^{II}][B]}{R} - \frac{1}{k_2' K_1} \right\} \frac{d[USH]}{d[OH^-]} - \left\{ \frac{[Co^{(II)}][B][USH]}{R^2} \right\}$$

$$\frac{dR}{d[OH^-]} = \frac{-k_{-2}}{K[OH^-]^2} \tag{19}$$

Rearranging (19) we get

$$\frac{d[USH]}{d[OH^-]} = K_1 k_2' \left\{ \frac{[Co^{(II)}][B][USH]}{R^2} \frac{dR}{d[OH^-]} - \frac{k_{-2}}{K[OH^-]^2} \right.$$

$$\left. - \frac{[Co^{(II)}][B]}{R} \frac{d[USH]}{d[OH^-]} \right\} = K_1 k_2' Q \tag{20}$$

where Q stands for the quantity in flower bracket { } of (20). Q can be calculated from the known value of k_{-2}/K and other terms. The linear plot of left side of (20) against Q passes through the origin and from the slope of this plot, the $K_1 k_2'$ value has been evaluated (table 2). The $K_1 k_2'$ and k_{-2}/K values are substituted in (18) and the value of K_3/K is obtained from the intercept of a plot of left side of (18) against $1/[OH^-]$. The K_3/K values are given in table 2. The large differences in the k_{-2}/K values and K_3 for the two acids might be due to the differences in K_4' (ionization constants of the two acids) and k_5. The lower rate of hydrogenation of fumaric acid compared to maleic acid suggests that k_5 might be small for fumaric acid. The k_{-2}/K and K_3/K values are thus larger for fumaric acid.

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