Studies on the Kinetics and Mechanisms of Reactions of Dimethylglyoxime with Iron(II), Cobalt(II) and Copper(II) Ions in Ethanol-Water Media

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Reactions of dimethylglyoxime with iron(II), cobalt(II) and copper(II) ions in (20%, v/v) ethanol—water media have been studied by stopped-flow spectrophotometry. The results indicate that in all the cases the initial reaction is a rather fast formation of the bis(dimethylglyoximato) complex of M(II) followed by further reaction in a slower step which involves oxidation of the cobalt(II) complex to a cobalt(III) species by the free ligand in solution, transformation of the copper(II) complex to a copper(I) species in an intramolecular process and formation of $Fe(dmgH)_2^-$ from $Fe(dmgH)_2$ respectively. In the case of copper(II), the initial reaction is too fast for the stopped-flow range but in the other two cases rates of formation of the bis-complexes, $M(dmgH)_2$ ($M = Co^{II}$, Fe^{II}), could be studied and results indicated $T_L/k_{obs} = 1/\alpha + [H^+]/\beta \ T_L$, where α and β are constants.

In presence of excess dimethylglyoxime, $Fe(dmgH)_2$ is converted to $Fe(dmgH)_2^-$ in a slow step and the observed pseudo-first order rate constant corresponds to $1/k_{obs} = 1/\alpha' + [H^+]/\beta' \ T_L$. $Cu(dmgH)_2$, formed initially in a fast process transforms intramolecularly to a copper(I) species and the cobalt(II) complex is slowly oxidised to a cobalt(III) complex by excess ligand. The rates of these slow reactions are independent of pH and ligand concentration. Both these reactions have been followed by stopped-flow spectrophotometry.

GENERALLY complex formation reactions involving d^7 metal ion centres are moderately fast[1], but Blackmore and Magee[a] reported the reaction between cobalt(II) and 2-pyridinaldoxime at pH 3–4 to be rather slow. The authors explained this as due to an equilibrium between the *syn-* and *anti-* forms of the ligand. Beck *et al.*[a] repeated the experiments and found that the metal—ligand ratio in the product complex is 1 : 3 instead of 1 : 2 reported previously[a]. Moreover, the slowness of the reaction is merely due to pH effect[a]. Besides formation of the cobalt(II) complex, a redox reaction also takes place in which the ligand oxidises[a] the cobalt(II) to cobalt(III). Lalor[4] similarly demonstrated that parallel to complex formation, the nitrosonaphthol derivatives oxidise cobalt(II) to cobalt(III). Reactions of cobalt(II) with 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN) and their thiazole analogs, TAR and TAN, also show a fast formation of a cobalt(II) complex followed by oxidation[5]. The rate of formation for PAR was found to be of the order of 10^4 $m^{-1} s^{-1}$ but of the order of 10^8 $m^{-1} s^{-1}$ for PAN. The rates of formation of iron(II), cobalt(II) and nickel(II) complexes of acetohydroxamic acid (LH) were found to be of the same order[6]. The rather slow reaction between cobalt(II) and EDTA has also been studied[7].

Experimental

The metal ion solutions were prepared by dissolving cobalt(II) and copper(II) perchlorates and iron(II) sulphate in double-distilled water and were standardised by usual procedures. Recrystallised dimethylglyoxime (E M.) was used to prepare the stock solution of the ligand in 50% aqueous ethanol. Distilled acetic acid was diluted and standardised as usual. Recrystallised sodium acetate was used to prepare its solution which was standardised by conversion to acetic acid by elution through a bed of a strong cation-exchange resin (Dowex-50W-X8 in H⁺-form) and estimating the acid volumetrically as usual. All other reagents used were of analytical grade. Redistilled water was used to prepare all the solutions ; and freshly distilled alcohol was used.

Procedure : A dark-brown complex, presumably $Co(dmgH)_2$, was formed *in situ* when the two components, viz. cobalt(II) salt and dimethylglyoxime ($dmgH_2$) were mixed. This was followed by a relatively slow oxidation of the cobalt(II) to a yellow coloured cobalt(III) species whose spectrum is identical to that of the completely aquated *trans*-$[Co(dmgH)_2Cl_2]^-$ and hence it was *trans*-$[Co(dmgH)_2(H_2O)_2]^+$ species[8]. The rate of complex formation was determined by stopped-flow spectrophotometry at 460 nm where an appreciable change in absorbance was observed within 2–5 s of mixing the reactants. Kinetic runs were made using a Canterbury SF-3A (Hi-Tech, England) stopped-flow spectrophotometer coupled with OS-1000A oscilloscope (Advance Instruments, England) connected to a PL-3 XY/t-recorder (JJ Lloyds, U.S.A.). pH measurements were made with a Systronics 335 pH

meter. From the pH meter readings, [H⁺] values were evaluated from a pH vs [H⁺] calibration curve prepared under identical conditions.

In the pH range 5.4−5.9, iron(II) forms Fe(dmgH)₂ complex in presence of NH₂OH.HCl. The rate of the reaction was measured with a stopped-flow spectrophotometer at 460 nm. Fe(dmgH)₂, in presence of excess dmgH₂, forms Fe(dmgH)₃⁻ in a subsequent slow step. The rate of the reaction was measured using a VSU-2P Carl-Zeiss spectrophotometer at 460 nm.

The rate of formation of the copper(II) complex was too fast to be followed even by stopped-flow spectrophotometry. In a stopped-flow experiment, the reactants on mixing give a very steep signal (absorbance vs time), even in the fastest time scale of the instrument, followed by a decrease in absorbance, the rate of which being independent of ligand concentration over a wide pH range (4−5.2). Observations were made at several wavelengths in the 400−460 nm region.

Ionic strengths of the reacting solutions were adjusted with NaClO₄ in each case and pseudo-first order conditions were maintained in following the reactions. All the solutions were prepared in 20% (v/v) ethanol−water mixture where the reactants and the products formed were soluble at the concentrations used. The data were analysed by usual graphical and least-square procedures.
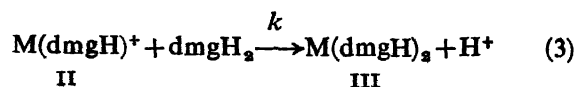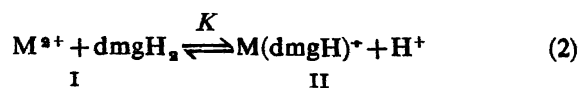
Results and Discussion

The pseudo-first order rate constant for formation of the cobalt(II) complex showed a second order dependence on the ligand concentration. Thus, it may be concluded that in the formation of one mole of the cobalt(II) complex two moles of the ligand are involved. The observed dependence of rate (Table 1) on ligand concentration and pH of the media conform of the following,

$$k_{obs} = \frac{kKT_L^2}{KT_L + [H^+]}$$

which leads to

$$\frac{T_L}{k_{obs}} = \frac{1}{k} + \frac{[H^+]}{kKT_L} \quad (1)$$

Under the experimental conditions the ligand (pKₐ = 11.1 in aqueous media)[9] exists essentially as dmgH₂. Based on these and the observed dependence of rate on total ligand concentration (T_L) and pH of the solution, Scheme 1 appears plausible for formation of the complex.

$$M^{2+} + dmgH_2 \underset{}{\overset{K}{\rightleftharpoons}} M(dmgH)^+ + H^+ \quad (2)$$
$$\text{I} \qquad\qquad\qquad\quad \text{II}$$

$$M(dmgH)^+ + dmgH_2 \overset{k}{\longrightarrow} M(dmgH)_2 + H^+ \quad (3)$$
$$\text{II} \qquad\qquad\qquad\quad \text{III}$$

<center>Scheme 1</center>

The experimentally evaluated k value [(2.03 ± 0.02)×10⁴ mol⁻¹ s⁻¹ at 25°] is much lower than that for the water-exchange process for the Co²⁺ₐq ion which indicates that Eigen's dissociative mechanism is not operating here, and may be that the proton release from the bound ligand to solvent is also a contributing factor in the rate-determining step, examples of which are known[10]. Rate constant of a similar magnitude was also found (3.59×10⁴ mol⁻¹ s⁻¹ at 20°, I=0.1 M) in the reaction between cobalt(II) and acetohydroxamic acid (LH)[6].

TABLE 1—KINETIC PARAMETERS FOR THE FORMATION OF Fe(dmgH)₂ AND Co(dmgH)₂ IN (20%, v/v) ETHANOL − WATER MEDIA

[M²⁺]=0.0005 M, [dmgH₂]=0.005−0.013 M, I=0.1 M (NaClO₄), pH=4.43−4.98 for Co^II and 5.4−5.9 for Fe^II adjusted with HOAc (0 01 M)+NaOAc buffer, NH₂OH.HCl=0 01 M for Fe^II systems only

M(II)	Temp. °C	k ×10⁻³ mol⁻¹ s⁻¹	K ×10⁴
Co^II	25	20.15±0.10	2.96±0.03
	30	28.60±0 30	2.83±0.05
	35	40.10±0.50	2.41±0 02
ΔH≠ (kJ mol⁻¹)		50.65±2.94	
ΔS≠ (JK⁻¹ mol⁻¹)		5.95±0.25	
Fe^II	35	0 46±0.01	0.20±0.01
	40	0.65±0.02	0.17±0 03
	45	0.92±0.01	0.14±0.02
	50	1.30±0.03	0.10±0 01
ΔH≠ (kJ mol⁻¹)		55.2±2.5	
ΔS≠ (JK⁻¹ mol⁻¹)		−16.8±0.6	

The above observation can be rationalised, since k is a composite constant involving the displacement of two water molecules from Co(dmgH)²⁺ in the following series of changes : unidentate binding of dmgH₂ replacing one bound aqua-ligand, proton release from the bound ligand and subsequent chelation replacing the second aqua-ligand and thus forming Co(dmgH)₂⁺. Here, due to the first bound ligand, the remaining water molecules become much more labile.

From the first acid dissociation constant (K'_a) of the ligand and the eqilibrium constant (K) for the formation of the Co(dmgH)⁺ complex, it is possible to evaluate the formation constant β_1 :

$$\beta_1 = K/K'_a \quad (4)$$

Log β_1 has been found to be 8.35 (in aqueous medium)[11] while from the present investigations log $\beta_1 \approx 7.6$ in 20% ethanol−water media.

Formation of Fe(dmgH)₂ complex is appreciable in the pH range 5.4−9.5 in acetic acid-acetate buffer media. The observed pseudo-first order rate constants are similar to those for the cobalt(II) system. The results are given in Table 1.

In presence of excess dmgH₂ in the same range of pH, Fe(dmgH)₂ is converted to Fe(dmgH)₃⁻. This reaction is moderately slow. Based on the experimental results (Table 2) a plausible mechanism

for the formation of tris(dimethylglyoximato)-ferrate(II) from bis(dimethylglyoximato) iron(II) is

TABLE 2—KINETIC PARAMETERS FOR FORMATION OF Fe(dmgH)$_3^-$ FROM Fe(dmgH)$_2$ IN (20%, v/v) ETHANOL—WATER MEDIA

[Complex] = 0.0005 M, [dmgH$_2$] = 0.005 – 0 013 M, I = 0.1 M (NaClO$_4$), NH$_2$OH.HCl = 0.01 M, pH = 5.4 – 5.9 (HOAc 0.01 M + NaOAc)

Temp. °C	k 10^3 s^{-1}	Q ×10^5
40	1.51±0.01	3 64±0.10
45	2.50±0 02	1.50±0.08
50	4 01±0 02	1.45±0.06
$\Delta H^{\neq}$ (kJ mol^{-1})	80 5±4.8	
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	–25.6±2.8	

suggested, which assumes a plausible *trans* structure for Fe(dmgH)$_2$(H$_2$O)$_2$ since Fe(dmgH)$_2$ unit is believed to be planar[12] (Scheme 2), where LLH represents the dimethylglyoxime, dmgH$_2$.
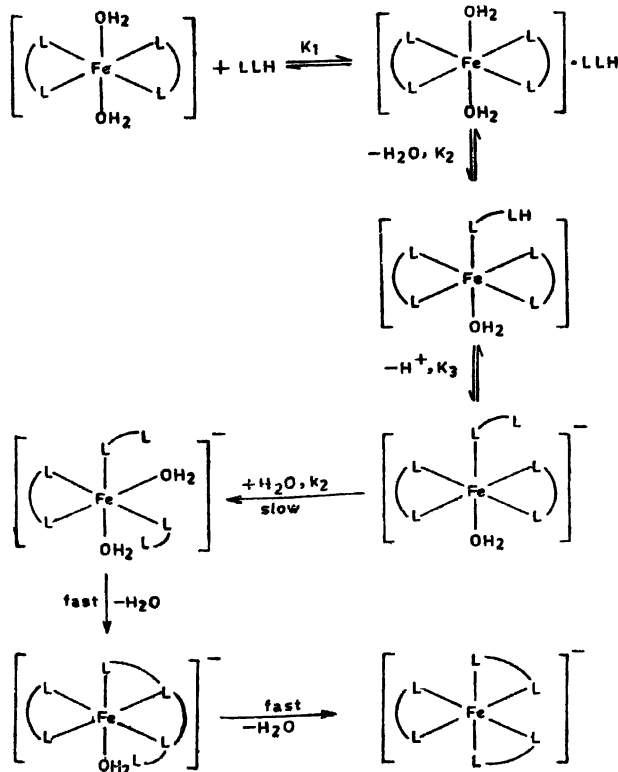
Scheme 2

In Scheme 2, $K_1K_2K_3 = Q$. From the Scheme 2,

$$k_{obs} = \frac{k_2 T_L Q}{T_L Q + [H^+]}, \qquad (5)$$

The rate of formation of the copper(II) complex (presumably Cu(dmgH)$_2^+$) is too fast to be followed

by stopped-flow spectrophotometry. Formation of the complex is followed by a much slower reaction for which the observed pseudo-first order rate constant is independent of pH and ligand concentration (Table 3). Results suggest an intramolecular transformation of the bis(dimethylglyoximato) complex

TABLE 3—INTERACTION OF COPPER(II) AND dmgH$_2$ IN (20%, v/v) ETHANOL—WATER MEDIA

[Cu^{2+}] = 0.0005 M, I = 0.1 M (NaClO$_4$ + NaOAc)

	k_{obs} (s^{-1})		
	20°	25°	30°
(A) Ligand variation at pH = 4.85 ± 0.02 :			
0.007	41.0	46.0	55 0
0.008	40.0	48.0	55.0
0.009	39.0	45.0	53.0
0.010	42.0	47.0	54.0
0.012	42.0	46.0	52.0
0.014	40.0	48.0	56.0
(B) pH variation at 0.01 M dmgH$_2$:			
4 20	39.0	46.0	54.0
4.40	42.0	44.0	56 0
4.63	40 0	44 0	58 0
4.84	41.0	48.0	53.0
5.20	42.0	45.5	55.5

$\Delta H^{\neq}$ = 15.0 ± 0.9 kJ mol^{-1}, $\Delta S^{\neq}$ = –163.7 ± 4.7 JK^{-1} mol^{-1}.

of copper(II) into a copper(I) species in which the bis(dimethylglyoximato) moiety is a radical ion bearing a unit negative charge (Scheme 3).
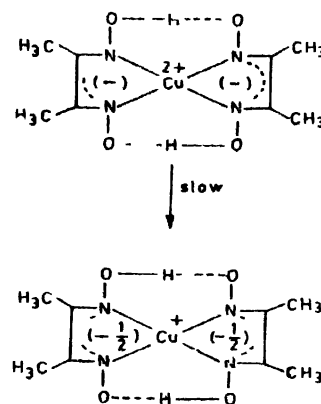
Scheme 3

Such a spontaneous transformation of a copper(II) complex to a copper(I) complex is also known in a few cases such as Cu(dmp)$_2^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline)[13].

References

1. D. BANERJEA, "Fundamental Principles of Inorganic Chemistry", 2nd. ed., Sultan Chand, New Delhi, 1984, Chap. 8.
2. M. W. BLACKMORE and R. J. MAGEE, *J. Inorg. Nucl. Chem.*, 1969, 31, 2859.

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3. G. BAZSA, H G. SHINOUDA and M. T. BECK, *J. Inorg. Nucl. Chem.*, 1978, 40, 1965.

4. G. C LALOR. *J. Inorg. Nucl. Chem.*, 1969, 31, 1783

5. K. MOCHIZUKI, T. IMAMURA, I. ITO and M FUJIMOTO, *Bull. Chem. Soc. Jpn.*, 1978, 51, 1743.

6. L. A. DOMINEY and K. KUSTIN, *Inorg. Chem.*, 1984, 23, 103.

7. K. MOCHIZUKI, T. IMAMURA, I. ITO and M. FUZIMOTO, *Chem. Lett*, 1976, 1207.

8. *Cf.* S. DAS, R. N. BANERJEE, S. G. BHATTACHARYA and D. BANERJEA, *Transition Met. Chem.*, 1983, 8, 241.

9. A. K BABKO and P. B. MIKHELSON, *Zh. Anal. Khim.*, 1951, 6, 267, A similar value has been reported in (20%, v/v) water–ethanol, G. B. PROKHOROVA, L. K. SHPIGUN and E. N. VINOGRADOVA, *Zh. Anal Khim.*, 1972, 27, 780.

10. *Cf.* S. GANGOPADHYAY, R N. BANERJEA and D. BANERJEA, *Transition Met Chem*, 1985, 10, 310, and references cited therein.

11. C. V. BANKS and S. ANDERSON, *Inorg. Chem.*, 1963, 2, 112.

12. *Cf.* B. A. JILLOT and R. J. P. WILLIAMS, *J Chem. Soc*, 1958, 462.

13. J. R. HALL, N. K. MERCHONT and R. A. PLOWMAN, *Aust. J. Chem.*, 1962 15, 480.