Indian Journal of Chemistry
Vol. 37A, November 1998, pp. 947-960

Kinetics and mechanism of the reaction of *trans*-(diaqua)(N,N′ - ethylene bis-(salicylidineiminato)cobalt(III) with ascorbic acid

Anadi C Dash*, Arabinda Das, Gouri S Bramha & Prakash Mohanty
Department of Chemistry, Utkal University, Bhubaneswar 751 004, India

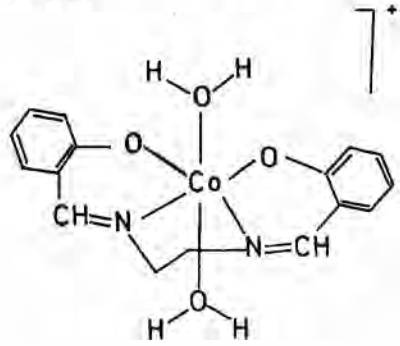
Received 20 May 1998; revised 27 August 1998

The kinetics of the reactions of *trans*-$[Co(Salen)(OH_2)_2]^+$ (Salen = N.N′-ethylene bis (salicylidineiminate) with ascorbic acid (H_2Asc) have been studied under varying conditions of *p*H, [ascorbic acid]$_T$ and temperature at .5 mol dm^{-3} ionic strength. The initial fast reactions observed in the stopped flow time scale are due to the complex formation between the reactants. This occurs in two phases i.e., the formation of the *trans*-[(aqua)(ascorbato)Co^{III}(Salen)] and its transformation to the corresponding ascorbate chelate. The rate constants and the activation parameters for the formation of the monobonded and chelate ascorbate complexes are reported. The low values of $\Delta H^{\ddagger}$ and negative values of $\Delta S^{\ddagger}$ for the complexation reaction favour associative interchange mechanism(I_a). The hydroxide in *trans*-$[Co(Salen)(OH)(OH_2)]$ marginally accelerates substitution of the aqua and by $HAsc^-$ and the *trans*-$[Co(Salen)(OH)(AscH)]^-$ is considered to undergo fast internal proton transfer to generate *trans*-$[Co(Salen)(OH_2)(Asc)]^-$ which undergoes chelation of the Co^{III} centre by the bound ascorbate moiety; the latter reaction is, however, 15 times slower than the corresponding reaction of *trans*-$[Co(Salen)(OH_2)(AscH)]$. The faster complexation reactions are followed by the slow redox reactions. The rate constant for the internal reduction of Co^{III} by the coordinated ascorbate in the chelate $[Co(Salen)(AscH)]$ is 5 - 10 times (25°C - 45°C) faster than the same for $[Co(Salen)(Asc)]^-$. This trend in reactivity is due to the low value of $\Delta H^{\ddagger}$ for the former although the high negative value of $\Delta S^{\ddagger}$ compensates at least partly the overriding effect of the activation enthalpy. The internal redox occurs via innersphere mechanism. We also have observed a redox path involving *trans*-$[Co(Salen)(OH_2)(AscH_2)]^+$ and H_2Asc for which electron transfer most likely involves outersphere mechanism.

L-Ascorbic acid (vitamin C) is believed to be a biological redox agent. As such the study of its chemical redox behaviour has aroused great interest. A number of studies have been devoted to examine its redox activity using several reducible metal ions/ oxidants such as Fe(III)[1-4], Co(III)[5-11], Ni(III/IV)[12,13],Mn(III/IV)[14-18], Ru(III)[2,19,20], Os(III)[2,21], Cr(VI)[22], V(V)[23,24], Cu(II/III)[25-28], Ag(I/III)[29,30], Tl(III)[31] and their complexes and Se(IV)[32]. The reactions involve both inner sphere and outer sphere electron transfer depending on the nature and substitutional lability of the metal ion and its complex. The structural aspect of the oxidation product of ascorbic acid (i.e. monocyclic or bicyclic dehydroascorbic acid)[2,33] is also an important concern of the reaction pathways. Recently Dasgupta *et al* investigated the oxidation of L-ascorbic acid by mononuclear *cis*-(diaqua)cobalt(III)amine[8] and tetranuclear hydroxobridgedcobalt(III)amine (hexol)[9] complexes. There was no evidence of formation of inner sphere complex of ascorbic acid or its anion with these cobalt(III) substrates although outer sphere association between them (Fuoss ion-pair) was considered. These reactions involve outer sphere electron transfer.

The *trans*-$[Co(Salen)(OH_2)_2]^+$ (Salen = N,N'-ethylene bis-(salicylidineiminate)) (**I**), is a suitable cobalt(III) substrate for relatively fast anation (ie replacement of the coordinated aqua ligands)[34-36] unlike several other aqua amine cobalt(III) substrates . Hence there is a possibility of the formation of the ascorbate complex in this case which eventually might undergo reduction by ascorbate/ascorbic acid. The complexation of the diaqua complex might lead to several species such as mono ascorbate, diascorbate (*cis*/*trans*) or ascorbate chelate under varying

conditions of $[H_2Asc]T$ and *p*H (H_2Asc = ascorbic acid). The ascorbate chelate also is likely to be prone to protonation. The questions to be addressed are the following : If complex formation and redox reactions take place, then (i) how does ascorbate/ ascorbic acid substitute the coordinated water molecule(s) ?; and (ii) how does the reduction of cobalt(III) in *trans*-$[Co(Salen)(OH_2)_2]^+$ by this reductant occur? We present here a kinetic investigation to elucidate the mechanism of the reaction of *trans*-$[Co(Salen)(OH_2)_2]^+$ with ascorbic acid which , to the best our knowledge, has not been reported earlier.



I : *trans*-$[Co(Salen)(OH_2)_2]^+$

Materials and Methods

H_2Salen (N,N'-ethylene-bis-salicylidineimine) was prepared by condensing ethylenediamine with salicylaldehyde[37]; IR: ν(cm^{-1}, KBr): ν_s(C=N) 1630, aromatic bands : 1495, 1412, 1283, 1148, 1024 ; $\nu(CH_2)$, 855 . The *trans*-(diaqua)(Salen)cobalt(III) perchlorate was prepared by the published method[38] and stored over fused calcium chloride in a desiccator protected from light. Anal. : Co, 13.2 ; C, 42.0 ; N, 6.83; H, 4.39. Calcd. for $[Co(Salen)(OH_2)_2](ClO_4)$, : Co,12.8 ; C, 41.8; N, 6.10; H, 4.34. {λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 250 (19,940); 378(2940); IR, ν(cm^{-1}, KBr): ν_s(C=N) 1636, ν(HOH): 1719; ν_s(Cl-O), 1086 (ionic ClO_4^-); aromatic bands : 1542, 1449, 1302; $\nu(CH_2)$: 901. Spiser *et al*[38c] reported this complex as a dihydrate. Although the perchlorate complexes are potentially hazardous, we did not notice explosive nature of this complex on storage. A typical cyclic voltamogram of this complex (Ag/ AgCl,Cl$^-$ reference) in N_2 purged aqueous medium ($[Complex]_T$ = 1.0 x 10^{-3}, $[KNO_3]$ = 1.0 mol dm^{-3}, *p*H = 9.01, 25°C) in the voltage span -0.8 - +0.8 volts indicated irreversible redox behaviour (see Fig. 1). L-Ascorbic acid, tris (trishydroxymethyl-aminomethane), $HClO_4$, sodium acetate, acetic acid, cobalt(II) acetate were analytical grade reagents. All other reagents were of extrapure quality. Sodium perchlorate and cobalt(II) perchlorate were prepared by dissolving the corresponding metal carbonates in perchloric acid. The dissolved CO_2 was boiled off from the acidic solutions of the stock metal perchlorate which were evaporated to the point of crystallisation. The *p*H of the stock $NaClO_4$ and $Co(ClO_4)_2$ solutions were adjusted to *ca.* 6 using dilute NaOH solution. The Na^+ in $NaClO_4$ was estimated by a combined ion exchange and alkalimetric procedure. The concentration of Co^{2+} in the $Co(ClO_4)_2$ solution was estimated essentially following the method of Latinen and Burdett[39]. NaClO4 was used for ionic strength adjustment. Sodium acetate/acetic acid (*p*H = 3.7 - 5.8) , Mes (morpholine-N-ethane sulphonic acid, *p*H = 5 - 7) and tris (*p*H 7 - 9) buffers were used to control *p*H. All solutions were prepared in doubly distilled water, the second distillation being made from alkaline $KMnO_4$ in an all glass distillation apparatus. Water was further deareated by nitrogen which was scrubbed through alkaline pyrogallol.

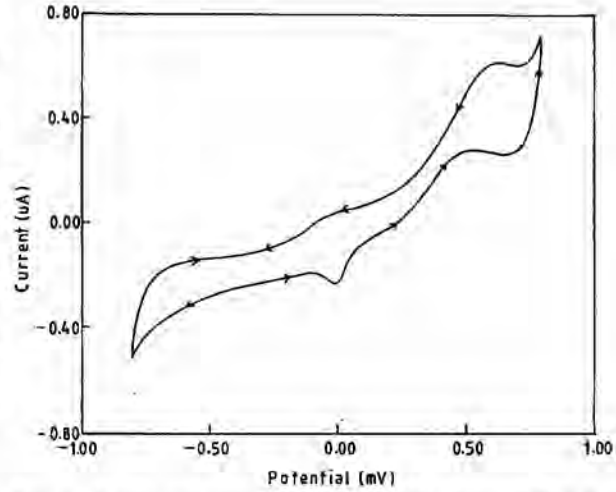


Fig. 1 - Cyclic voltammogram of *trans*-$[Co(Salen)(OH_2)_2]^+$ in aqueous medium at 25°C, $[Complex]_T$ = 1.0 x 10^{-3}, $[KNO_3]$ = 1.0 mol dm^{-3}, *p*H = 9.01; scan rate 20 mV/s.

Instrumentation

The *p*H measurements were made with an Elico digital *p*H meter model LI 120 using a combined glass-Ag/AgCl (2 mol dm^{-3} NaCl) electrode model

Table 1 - Product distribution in the reduction of *trans*-[Co(Salen)(OH2)2]$^+$ by L-ascorbic acid[a]

$10^3[Co^{III}]_T$ (mol dm^{-3})	$10^3[Asc]_T$[b] (mol dm^{-3})	*p*H	$10^3[B]$[c] (mol dm^{-3})	$10^3[Co^{II}]$ (mol dm^{-3})	$10^3[A]$[d] (mol dm^{-3})	$[Co^{II}]/[A]$
2.51	1.00	1.26	0.00 [0.00]	2.03	1.05	1.9
2.51	2.00	1.26	0.75 [0.69]	2.51	1.25	2.0
2.51	4.00	1.26	2.72 [2.71]	2.46	1.25	2.0
2.51	6.00	1.26	4.75 [4.71]	2.51	1.25	2.0
2.51	8.00	1.26	6.75 [6.62]	2.51	1.25	2.0
2.51	10.0	1.26	8.72 [8.47]	2.51	1.25	2.0
0.51	2.00	1.26	1.73 [1.65]	0.51	0.25	2.0
1.01	2.00	1.26	1.50 [1.42]	1.00	0.50	2.0
2.12	2.00	1.26	1.00 [0.82]	2.12	1.05	2.0
4.02	2.00	1.26	0.00 [0.00]	3.97	1.95	2.0
2.60	2.00	5.10	0.73 [0.69]	2.55	1.27	2.0
2.60	4.00	5.16	2.73 [2.67]	2.57	1.27	2.0
2.60	6.00	5.09	4.73 [4.68]	2.59	1.27	2.0
2.60	8.00	5.16	6.70 [6.42]	2.57	1.27	2.0
2.60	2.00	6.32	0.73 [0.69]	2.59	1.27	2.0
2.60	2.00	5.10	0.72 [0.69]	2.59	1.27	2.0
2.60	2.00	3.98	0.71 [0.71]	2.57	1.27	2.0
1.05	4.00	5.09	3.50 [3.33]	1.05	0.50	2.1
2.08	4.00	5.16	2.95 [2.87]	2.06	1.05	1.9
4.16	4.00	5.01	1.98 [1.78]	4.06	2.00	2.0
0.60	4.00	5.12	3.72 [3.43]	0.59	0.27	2.1

[a] 25.0°C. [b] $[Asc]_T$ = total ascorbic acid. [c] $[B]_T$ = unreacted ascorbic acid, unparanthesised values as estimated by oxidising with Fe^{III} and estimating Fe^{II} as $Fe(dipyridyl)_3^{2+}$ (see text), paranthesised values as estimated iodimetrically. [d] A = dehydroascorbic acid.

CL 51. The UV-visible and I R. spectra were recorded by a Perkin Elmer Lambda 20 UV-visible spectrophotometer and Perkin Elmer Paragaon 500 F T I.R. spectrometer respectively. 10 mm matched quartz cells were used for absorbance measurements; all I. R. spectra were recorded in KBr phase. The HITECH (U. K.) stopped flow spectrophotometer SF 51 was used for stopped flow kinetic measurements. The cell block and the flow module was thermostatted to the desired temperature by circulating water from a water thermostat C85 D through a cooler FC 200 (HITECH , U. K.). The stopped flow equipment was automated by an APPLE II GS P. C. Necessary software for fitting the aborbance - time data to single and double exponentials were available from HITECH. Cyclic voltametry was performed using OMNI 90 potentiostat (CYPRESS SYSTEMS INC, U. S. A.) equipped with an on line electronic data acquistion and storage system from CONSERV (India) and automated by an IBM 586 P. C. A standard three electrode configuration, Ag/AgCl, Cl- reference electrode, and bright platinum electrodes as counter and working electrodes were used.

All other calculations were made on an IBM 486 P. C. using nonlinear or linear least squares programs as required.

Stoichiometric measurements

The reaction mixture containing $[Co(Salen)(OH_2)_2]^+$ and ascorbic acid at different *p*H conditions were equilibrated for 48 - 72 h after which cobalt(II) was estimated spectrophotometrically as $[Co(NCS)_4]^{2-}$ (625 nm) as described by Kitson[40]. A calibration curve for cobalt(II) was also constructed using a standardised cobalt(II) perchlorate solution. The unreacted ascorbic acid was estimated iodimetrically as well as by oxidising with Fe(III) and then converting the Fe(II) formed to tris bipyridyliron(II) and measuring absorbance of the latter at 522 nm ($\varepsilon = 8.6 \times 10^3$ dm^3 mol^{-1} cm^{-1} at 522 nm)[17]. The iodine solution was standardised against sodium thiosulphate which was standardised using potassium iodate[41]. Both the methods yielded consistent results (see Table 1).

The redox reaction obeyed 2:1 stoichiometry $\{-\Delta[Co^{III}]/-\Delta[\text{ascorbic acid}] = 2:1\}$ and the relevant data are collected in Table 1. The observed

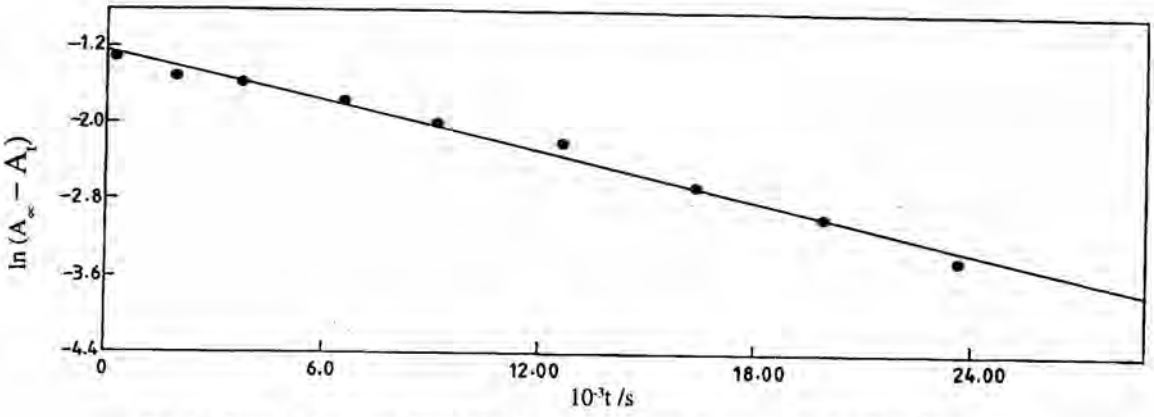


Fig. 2 - ln (A_∞ - A_t) versus $10^{-3}t$/s plot for redox reaction monitored by Co(II) yield at 40°C : $[Co(Salen)(OH_2)_2^+] = 1.0 \times 10^{-3}$, $[H_2Asc]_T = 0.06$, $[HClO_4]_T = 0.02$ mol dm^{-3}.

stoichiometry is consistent with the formation of dehydroascorbic acid as the product of oxidation of ascorbic acid. The dehydroascorbic acid was identified and estimated as its 2,4 dinitrophenyl hydrazone[42].

Kinetic measurements

The fast reactions were studied by the stopped flow spectrophotometer. The measurements were made under pseudo-first order conditions with $[Co^{III}]_T = (1 - 2) \times 10^{-4}$, $[H_2Asc]_T/[Co^{III}] > 10$. The stopped flow traces (380 nm) fitted double exponential equation : $A_\infty - A_t = B \exp(-k_f^{sf}t) + C \exp(-k_s^{sf}t)$, where k_f^{sf} and k_s^{sf} denote the rate constants for the fast and slow phases of the reactions respectively, and all other terms have their usual meaning. At least three replicate measurements were made for each run.

The relatively slower reactions ($t_{1/2} > 15$s) were monitored spectrophotometrically. The absorbance - time data also fitted to a double exponential equation : $A_t - A\infty = B' \exp(-k_f^{sp}t) + C' \exp(-k_s^{sp}t)$. The two rate constants were evaluated using ca. $A\infty = A_t$ at $5t_{1/2}$ for the slower reaction as the absorbance decreased at still longer times due to a very slow reaction. $A\infty$ was varied to get the best fit.

The redox process was also monitored by measuring Co^{II} yield as a function of time as stated above. The reduction of Co^{III} in the presence of excess of H_2Asc was complete. The ln(A_∞ - A_t) versus t(s) plots, where $A\infty$ denotes absorbance due to $Co(NCS)_4^{2-}$ for complete reduction of Co^{III}, were linear (r = corr coeff = 0.995, see Fig. 2) thus establishing the first order kinetics . The rate constants, however, were calculated by fitting the absorbance time data to a single exponential equation characteristic of first order kinetics.

The hydrolysis of Salen under similar conditions (10% MeOH) was also studied spectrophotometrically in order to clarify the complex reaction sequence observed. The experimental details were similar to those involved in the spectrophotometric runs except that a methanolic solution of Salen (0.3 cm^3) was added to the ionic strength adjusted aqueous reaction mixture (2.7 cm^3) containing cobalt(II) acetate, ascorbic acid, ($[Co^{II}] = 1.0 \times 10^{-4}$, $[H_2Salen] = 1.0 \times 10^{-4}$, $[H_2Asc] = 1.0 \times 10^{-3}$ mol dm^{-3}) and $HClO_4$ (0.05 - 0.2 mol dm^{-3}). The decay of absorbance with time followed at 400 nm fitted to a single exponential equation. The rate constants(at 30°C) were comparable with those for the slow phase of the spectrophotometric runs of the Salen complex (see foot note a of Table 3).

Results

Preliminary observations

The UV-visible spectrum of *trans*-$[Co(Salen)_2(OH_2)_2]^+$ displays λ_{max} at 378 nm. It is unaffected by acetate buffer and acidity of the medium (pH = 1 - 6) thus indicating no significant protonation of the complex or its interaction with acetate . However, the successive spectral scans of the mixtures of the diaqua complex and ascorbic acid reveal that λ_{max} at 378 nm first shifted to 375 and 390 nm at $[H^+]$ = 0.2 mol dm^{-3} and pH 5.3

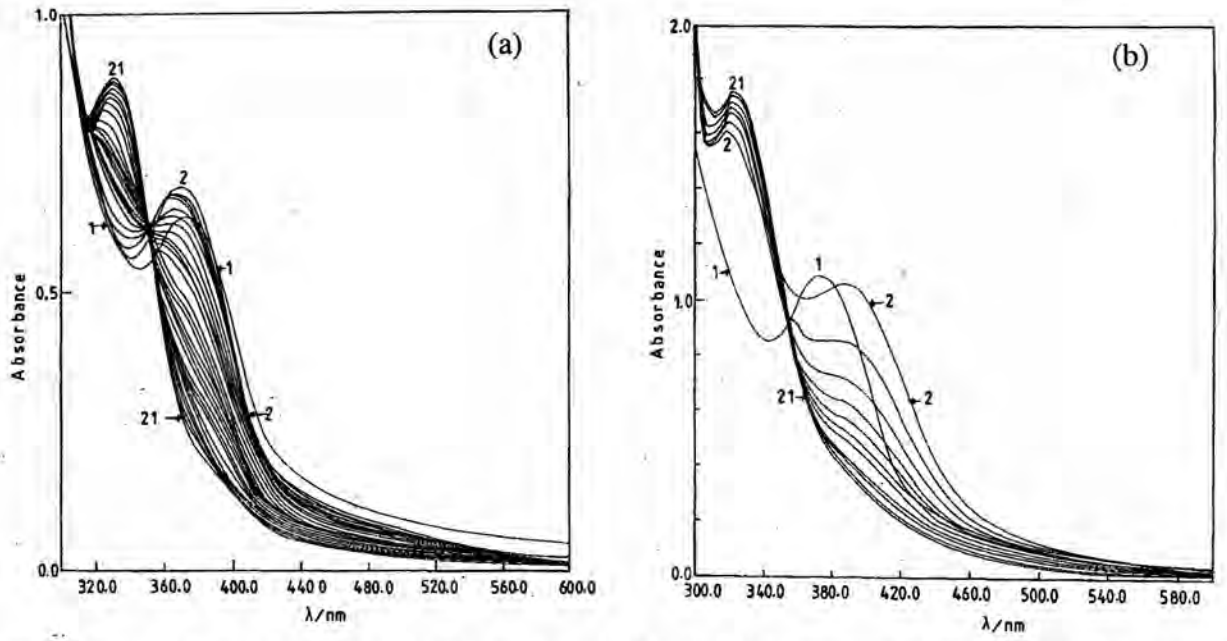
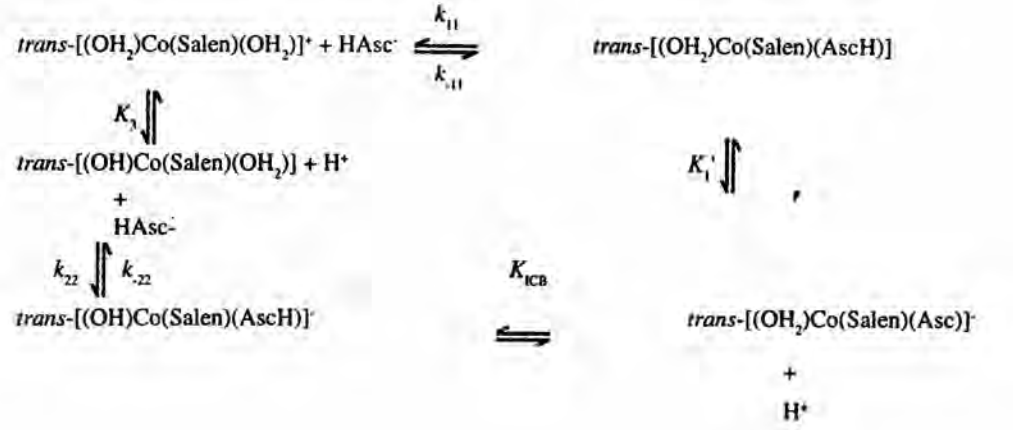


Fig. 3 - Successive spectral scans for the reaction of *trans*-$[Co(Salen)(OH_2)_2]^+$ with ascorbic acid: (a) $[Complex]_T = 2.0 \times 10^{-4}$, $[H_2Asc]_T = 1.0 \times 10^{-3}$, $[HClO_4] = 0.2$ mol dm^{-3}, 25°C; after 15 s of mixing(1); $\Delta t = 30$ s (for 2 - 20); after 48 h (21); (b) $[complex]_T = 3.57 \times 10^{-4}$, $[H_2Asc]_T = 1.0 \times 10^{-3}$ mol dm^{-3}, *p*H = 5.21 (acetate buffer); after 15 s of mixing (1); $\Delta t = 30$ s (for 2 - 20); after 48 h (21).

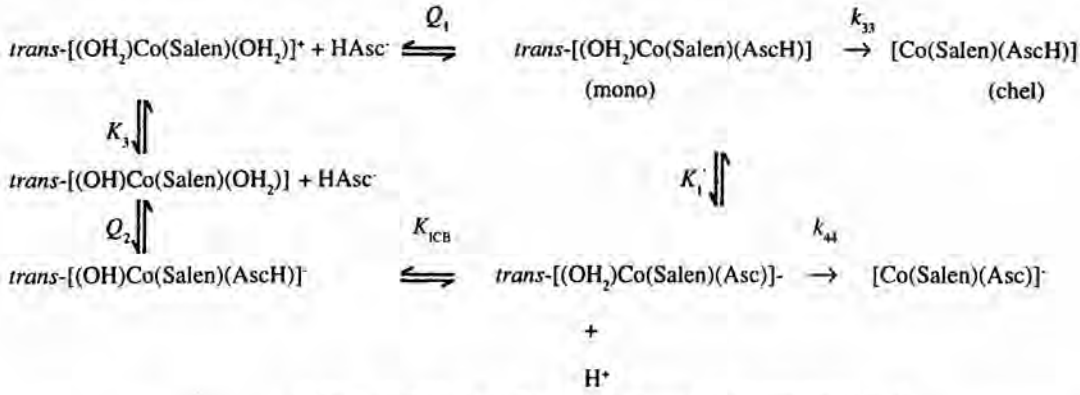
respectively immediately after mixing the reactants (see Fig. 3). The subsequent slow decrease of absorbance at several wave lengths with time displayed isosbestic points points at 354 and 350nm for $[H^+] = 0.2$ mol dm^{-3} and *p*H = 5.3 respectively. The final spectrum, however, agreed with that of the mixture of completely hydrolysed Salen in the presence of cobalt(II) and ascorbic acid under identical condition. Also test of Co^{II} at the end of the reaction indicated quantitative reduction of Co^{III}. Thus it is evident that the relatively slow reduction of cobalt(III) by ascorbic acid is preceded by a fast complex formation reaction between them generating a species (or species) the UV-visible spectrum of which is *p*H sensitive. The latter observation may be reconciled with the protonation equilibrium of the ascorbate complex. The successive spectral scans for a mixture of the diaqua complex (2.0×10^{-4} mol dm^{-3}), ascorbic acid (0.02 mol dm^{-3}) at *p*H = 11.6 (self buffered by Asc^{2-} and $HASc^-$) over extended period of time also displayed a λ_{max} at 390 nm characteristic of the Co(III)(Salen)-ascorbate complex with no evidence of reduction of cobalt(III) (Fig. 4). The formation of ascorbate complexes as intermediates has been observed in the reduction of $Fe(OH_2)_6^{3+}$ (ref.1), V(V) (ref.24) and Mn(Salen)$(OH_2)_2^+$ (ref 14) with characteristic λ_{max} at 550, 425 and 400 nm respectively. Jordan *et. al.* have also reported the formation of a transient complex between Fe(III) and 3-Me-ascorbate (λ_{max} 500 nm)[33].

Reactions at pH 7.0 - 8.9

Tris buffer was used to maintain the *p*H 7.0 - 8.9. Spectrophotometric measurements indicated no interaction of *trans*-$[Co(Salen)(OH_2)_2]^+$ with tris buffer under the conditions of experiments. All of the ascorbic acid will exist exclusively as ascorbate monoanion ($HAsc^-$).The reaction of ascorbate with the cobalt(III) substrate was biphasic and occurred in the stopped flow time scale. Test of cobalt(II) in the reaction mixture after a lapse $10t_{1/2}$ for the slower phase of the reaction was negative. However, at very long time intervals there was indication of reduction of cobalt(III). The initial fast reactions which occurrred in two distinct phases are believed to be due to (i) the substitution of the aqua ligand by ascorbate anion ($HAsc^-$) forming a monodentate complex, *trans*-$[Co(Salen)(OH_2)(AscH)]$, followed by (ii) the transformation of this species to the



Scheme 1 - Formation of the monodentate ascorbate complex



Scheme 2 - The slow phase of the stopped flow runs at *p*H 7 - 9

chelated ascorbate complex. This is detailed in Scheme 1.

Under the pseudo-first order conditions, and using the relationships : $k_{-11} = k_{11}/Q_1$, $k_{-22} = (k_{22}/Q_1K_1')K_3K_{ICB}$, where the rate and equilibrium constants are as defined in Scheme 1, it can be shown that

$$k_f^{sf} = (k_{11} + k_{22}K_3/[H^+])G \quad ...(1)$$

where

$$G = [HAsc^-]/(1.0 + K_3/[H^+]) + Q_1^{-1}/(1.0 + K_1'(app)/[H^+]) \quad ...(2)$$

and

$$K_1'(app) = K_1'(1.0 + K_{ICB}^{-1}) \quad ...(3)$$

The rate constants, k_f^{sf} at 25°C (see Table 2) were iteratively fitted to Eq. (1) using the known value of K_3 ; the values of k_{11}, k_{22} and Q_1^{-1} and K_1'(app) are collected in Table 2. The rate measurements at 20°, 30° and 35°C are reported at constant *p*H (~ 7) at which $K_3/[H^+] << 1$ and $k_{22}K_3/[H^+] << k_{11}(k_{22}/k_{11} = 1.12$ and $K_3/[H^+] = 10^{-2}$ at 25° C, *p*H = 7) conditions are valid. Neglecting $k_{22}K_3/[H^+]$ term and further assuming that K'(app) is temperature independent (20° - 35°C), the values of k_{11} and Q_1^{-1} were calculated . The values of k_{11} and Q_1^{-1} at 20°, 30° and 35° C are quoted in foot note of Table 2. We are, however, aware of the fact that the value of Q_1^{-1} is slightly affected due to the use of a constant value of K_1'(app). The slow phase of the complexation reaction (*p*H 7 - 9) is delineated in Scheme 2.

Accordingly k_s^{sf} is given by Eq. (4):

$$k_s^{sf} = (k_{33} + k_{44}K_1'/[H^+])GG \quad ...(4)$$

where

$$GG = \frac{Q_1[HAsc^-]}{1 + K_3/[H^+] + Q_1[HAsc^-](1 + K_1'(app)/[H^+])} \quad ...(5)$$

$$Q_1 = k_{11}/k_{-11} \quad ...(6)$$

Table 2 - Rate Constants for the complexation of *trans*-$[Co(Salen)(OH_2)_2]^+$ with $HAsc^-$ measured by stopped flow[a]

*p*H[b]	$10^3[HAsc^-]_T$[c] (mol dm^{-3})	k_f^{sf}(s^{-1}) obs,calc[d]	k_s^{sf}(s^{-1}) obs,calc[d]
		20.0 ± 0.1°C	
7.03	2.0	0.96,0.95	0.085,0.058
7.05	4.0	1.10,1.12	0.098,0.098
7.02	6.0	1.30,1.30	0.120,0.129
7.04	8.0	1.48,1.47	0.149,0.150
7.00	10.0	1.65,1.65	0.171,0.172
		25.0 ± 0.1°C	
7.04	2.0	1.07,1.13	0.100,0.062
7.08	4.0	1.29,1.26	0.120,0.106
7.06	6.0	1.50,1.47	0.140,0.140
7.01	8.0	1.71,1.71	0.169,0.170
7.00	10.0	1.95,1.91	0.189,0.193
7.63	2.0	0.62,0.56	0.062,0.059
7.66	4.0	0.79,0.72	0.077,0.088
7.61	6.0	0.93,0.94	0.094,0.108
7.56	8.0	1.03,1.16	0.112,0.125
7.52	10.0	1.29,1.37	0.136,0.139
8.26	2.0	0.34,0.30	0.052,0.054
8.27	4.0	0.53,0.49	0.063,0.066
8.29	6.0	0.72,0.67	0.070,0.071
8.21	8.0	0.93,0.87	0.084,0.078
8.19	10.0	1.12,1.06	0.104,0.082
8.98	2.0	0.22,0.24	0.039,0.050
8.93	4.0	0.43,0.43	0.048,0.055
8.94	6.0	0.62,0.63	0.055,0.057
8.84	8.0	0.79,0.82	0.062,0.060
8.87	10.0	1.00,1.01	0.072,0.060
		30.0 ± 0.1°C	
7.02	2.0	1.24,1.24	0.111,0.075
7.03	4.0	1.48,1.48	0.133,0.126
7.02	6.0	1.72,1.73	0.161,0.163
7.00	8.0	1.95,1.97	0.186,0.194
6.98	10.0	2.21,2.21	0.211,0.219
		35.0 ± 0.1°C	
7.06	2.0	1.26,1.26	0.118,0.082
7.04	4.0	1.59,1.52	0.144,0.137
7.07	6.0	1.73,1.78	0.172,0.172
7.04	8.0	1.96,2.04	0.200,0.204
7.01	10.0	2.38,2.31	0.219,0.232

k_{11}(dm^3 mol^{-1} s^{-1}) [e,f] 91.3 ± 4.6; k_{33}(s^{-1})[g] 0.821 ± 0.034
k_{22}(dm^3 mol^{-1} s^{-1}) [e] 102 ± 9; $k_{44}K_1'$(mol dm^{-3} s^{-1}) (6.52 ± 0.61) x 10^{-9}
Q_1^{-1}(mol dm^{-3}) [e,f] (2.37 ± 0.20) x 10^{-2} k_{44}(s^{-1}) (5.4 ± 0.6) x 10^{-2}
$\Delta H^{\ddagger}$(kJ mol^{-1}) (k_{11} path) 20 ± 5; $\Delta H^{\ddagger}$(kJ mol^{-1}) (k_{33} path) 11.2 ± 1.3
$\Delta S^{\ddagger}$(J K^{-1} mol^{-1}) (k_{11} path) -138 ± 16;$\Delta S^{\ddagger}$(J K^{-1} mol^{-1})(k_{33} path) -209.0 ± 4.3

[a] I = 0.3; $[complex]_T$ = 2.0 x 10^{-4} mol dm^{-3}; 25.0 ± 0.1°C, λ = 380 nm; [b] tris buffer ; [c] total ascorbic acid which exists exclusively as AscH; [d] the calculated values are based on the derived parameters ; [e] based on K_1' (app) = 1.2 x 10^{-7} mol dm^{-3}; F^{43} = 0.050 at 25.0°C; [f] values of k_{11}/dm^3 mol^{-1} s^{-1}(Q_1^{-1}/mol dm^3) are 89.1 ± 2.5 (0.020 ± 0.005); 122± 3 (0.0187 ± 0.0015); 130 ± 12 (0.0180 ±0.003) at 20.0°C (*p*H = 7.03 ± 0.02), 30.0°C (*p*H = 7.02 ± 0.02) and 35.0°C (*p*H = 7.05 ± 0.02) respectively based on a constant value of K_1'(app) = 1.2 x 10^{-7} mol dm^{-3} ; and [g] values of k_{33} (s^{-1}) are 0.73 ± 0.014, 0.88 ± 0.046 , 0.94 ± 0.048 at 20°C (*p*H = 7.03 ± 0.02), 30.0°C (*p*H = 7.02 ± 0.02), and 35.0°C (*p*H = 7.05 ± 0.02) respectively based on the values of Q_1(dm^3 mol^{-1}) : 50.0(20.0°C), 53.5(30.0°C) and 55.4(35.0°C) and neglecting the term $k_{44}K_1'/[H^+]$.

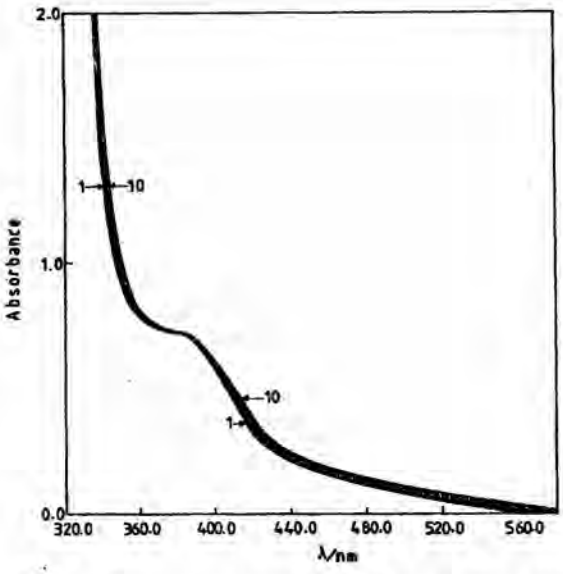


Fig. 4 - Succesive spectral scans for the reaction of *trans*-$[Co(Salen)(OH_2)_2]^+$ with ascorbic acid: [complex] = 2 x 10^{-4}, $[H_2Asc]$ = 0.02 mol dm^{-3}, *p*H = 11.6 (self buffered by Asc^{2-}/$HAsc^-$), 25°C; after 15 s of mixing(1), Δt = 900 s (for 2 - 9); after 48 h (10).

The rate constants at 25°C were fitted to equation (4) iteratively using K' (app) = 1.2 x 10^{-7}mol dm^{-3} (as calculated from the fast phase of the reaction , see Table 2). The calculated values of k_{33}, $k_{44}K_1'$ are given Table 2. The value of k_{44} was calculated assuming that K_{ICB} is much larger than 1 such that the bound hydroxide largely favours intramolecular proton transfer equilibrium in the direction of transformation of *trans*-[Co(Salen)(OH)(AscH)] to *trans*-$[Co(Salen)(OH_2)(Asc)]^-$ (i.e. the coordinated $AscH^-$ is a much stronger acid than the coordinated H_2O in *trans*-$[Co(Salen)(OH_2)(AscH)]$). It may be further noted that k_{33} far exceeds $k_{44}K_1'/[H^+]$ at *p*H 7 (25°C). The rate constants collected at 20°, 30° and 35°C (*p*H 7) were analysed by Eq. (4) neglecting the term $k_{44}K_1'/[H^+]$. The values of k_{33} at these temperatures are quoted in foot note g of Table 2.

Kinetics of the reaction at 0.01 ≤ $[H^+]$/mol dm^{-3} ≤ 0.2 followed spectrophotometrically

The rate constants are collected in Table 3. The k_f^{sp} at $[H^+]$ = 0.1 mol dm^{-3} increased nonlinearly with $[H_2Asc]_T$(see Fig. 5) having little dependence on $[H^+]$.Test for cobalt(II) by Kitson's method in the mixture of cobalt(III) complex (1.0 x 10^{-3} mol dm^{-3}) and ascorbic acid (0.02 - 0.06 mol dm^{-3}) in the presence $HClO_4$ (0.02 - 0.2 mol dm^{-3}) (25°C) after

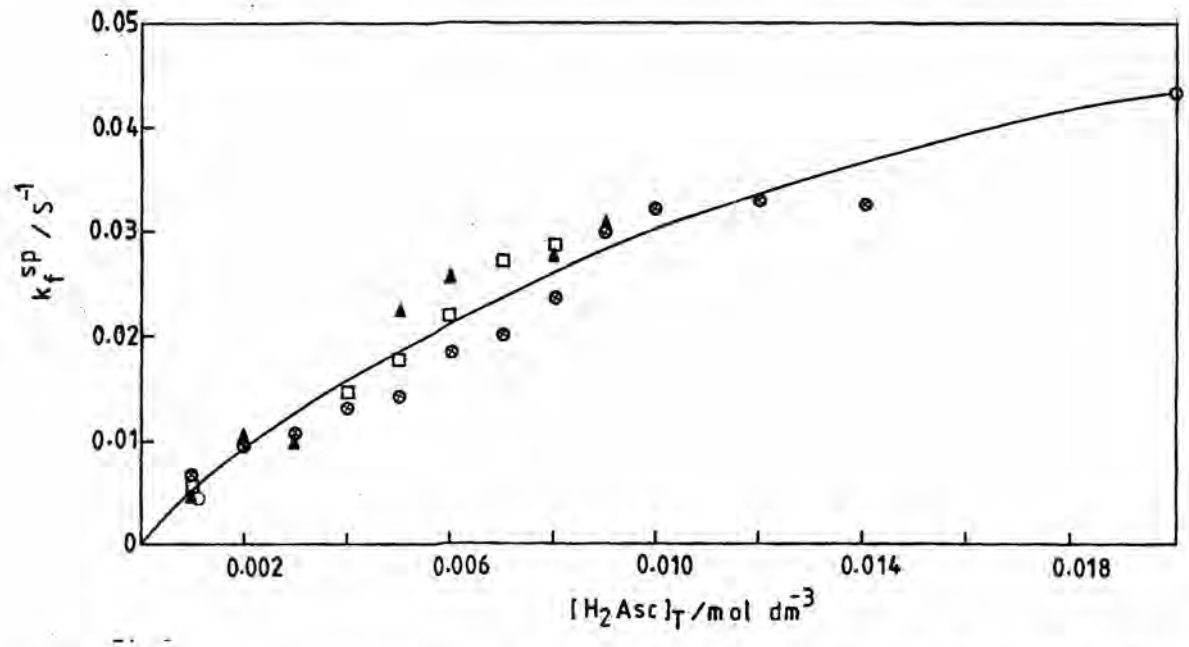


Fig. 5 - k_f^{sp}/s^{-1} versus $[H_2Asc]_T$ /mol dm^{-3} plot at 25°C: $[H^+]$/mol dm^{-3} = 0.01 (O), 0.02(Δ), 0.05 (□), 0.1 (⊗), 0.2 (▲).

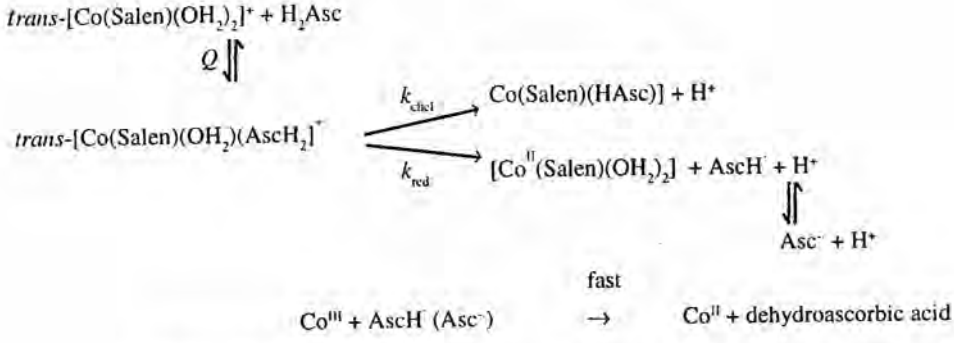
allowing *ca.* $10t_{1/2}$ for the slowest run indicated that less than 20% of reduction of cobalt(III) occurred during this period. Evidently reduction is competitive with complexation. At $[H^+]$ = 0.01 - 0.2 mol dm^{-3}, ascorbic acid will exist predominantly in the unionised form (pK_1 = 4.0, pK_2 = 11.5 for H_2ASc at 25.0°C, I = 0.1 mol dm^{-3} (ref.2); pK = -1.6 for H_3Asc^+ at 3.0 mol dm^{-3}, 25°C)[4a]. The UV- visible spectrum (λ = 250 - 600 nm) of the cobalt(III) substrate was virtually insensitive to $[H^+]$ (= 10^{-6} - 0.5 mol dm^{-3}) indicating that it is not protonated in the range of $[H^+]$ studied. Hence the reaction is represented by Scheme 3.

for which

$$k_f^{sp} = k' Q [H_2Asc]_T/(1 + Q [H_2Asc]) \quad ...(7)$$

where $k' = k_{chel} + 2k_{red}$, the coefficient of k_{red} denotes the stoichiometry of the reaction. Data fitted to Eq. (1) yielded the values of $k' = (4.4 \pm 0.6) \times 10^{-2}$ s^{-1} and $Q = 62 \pm 11$ dm^3 mol^{-1}.

The rate constants for the slow phase of the spectrophometric runs (k_s^{sp}, see Table 3) are virtually insensitive to $[H^+]$. From an independent study of the hydrolysis of Salen under comparable conditions of acidity, $[Co^{II}]$, $[H_2Asc]$ (10% MeOH, 30°C, see foot



Scheme 3 - Reactions of ascorbic acid with *trans*-$[Co(Salen)(OH_2)_2]^+$ at $[H^+]$ = 0.01 - 0.2 mol dm^{-3}.

Table 3 - Spectrophotometrically determined rate constants (k_f^{sp}, k_s^{sp}) for the reactions of *trans*-$[Co(Salen)(OH_2)_2]^{+a}$

$[HClO_4]_T$ (mol dm^{-3})	$10^3[H_2Asc]_T$ (mol dm^{-3})	$10^2k_f^{sp}$(s^{-1})^b	$10^2k_s^{sp}$(s^{-1})
0.10	1.0	0.65 (0.45)	0.13
0.10	2.0	0.90 ± 0.05^b (0.86)	0.15 ± 0.01^b
0.10	3.0	1.07 ± 0.02^b (1.22)	0.15
0.10	4.0	1.30 (1.55)	0.15
0.10	5.0	1.43 (1.85)	0.15
0.10	6.0	1.78 (2.11)	0.17
0.10	7.0	2.0 ± 0.2^b (2.36)	0.28 ± 0.07^b
0.10	8.0	2.35 ± 0.12^b (2.58)	0.25 ± 0.05^b
0.10	9.0	3.00 (2.80)	0.19
0.10	10.0	3.23 (2.99)	0.22
0.10	12.0	3.28 ± 0.29^b(3.33)	0.30 ± 0.02^b
0.10	14.	3.25 (3.63)	0.22
0.10	20.	4.35 (4.33)	0.24
0.20	2.0	0.92± 0.08^b (0.86)	0.13
0.20	3.0	1.03 ± 0.19^b (1.22)	0.12
0.20	4.0	1.37 (1.55)	0.22
0.20	5.0	2.20 ± 0.12^b (1.85)	0.13^b
0.20	6.0	2.50 ± 0.30^b (2.12)	0.16
0.20	8.0	2.71(2.59)	0.17
0.20	9.0	3.06 ± 0.36^b (2.80)	0.19 ± 0.01^b
0.05	1.0	0.58 (0.46)	0.18
0.05	3.0	1.27 (1.22)	0.17
0.05	4.0	1.42 (1.55)	0.13
0.05	5.0	1.83 (1.85)	0.19
0.05	6.0	2.16 (2.12)	0.25
0.05	7.0	2.71 (2.36)	0.29
0.05	8.0	2.84 (2.59)	0.24
0.02	1.0	0.52 (0.46)	0.084
0.01	1.0	0.50 (.46)	0.083

$^a I$ = 0.5, $[complex]_T$(mol dm^{-3}) = (1.0 -2.0) x 10^{-4}, 25.0 ± 0.1°C; λ = 400 nm; values of 10^2k_{obs}(s^{-1}) for the hydrolysis of Salen (see experimental section) are 0.24, 0.69 and 0.76 at $[H^+]$ = 0.05, 0.10 and 0.2 mol dm^{-3} (10% MeOH, 30°C); ^{b} average of triplicate runs; values given under parantheses are calculated using the derived parameters (see text).

note a of Table 3) we are led to believe that the slow phase of the spectrophotometric run is due to the hydrolysis of Salen. It is quite likely that Co^{II}(Salen) generated in the redox path is rapidly hydrolysed and dissociated in the act of electron transfer to yield N-protonated-ethylene-N′-salicylidineimine, $+NH_3CH_2CH_2N{=}CHC_6H_4(o)OH$ which is slowly hydrolysed at the imine function in a subsequent step without H^+-catalysis; the protonated amine function presumably plays the role of H^+ in an intramolecular acid catalysis.

Reduction of trans-$[Co(Salen)(OH_2)_2]^+$ by Ascorbic acid studied by cobalt(II) assay

Preliminary experiments indicated that the Co^{III} substrate is stable to internal reduction in absence of ascorbic acid. The rate constants for the slow reduction of the cobalt(III) substrate by ascorbic acid are collected in Table 4. It is interesting to note that k_{obs} is *p*H indendent at *p*H≤5.1; thereafter it decreases with increasing *p*H tending to attain a limiting value at each temperature. Further k_{obs} is essentially independent of [ascorbic acid]. These facts are consistent with the complete conversion of the cobalt(III) substrate to its ascorbate complex which (in accord with the stopped flow and spectrophotometric runs) we presume to be a chelate species undergoing protonation equilibrium. We propose the following reaction Scheme 4.

$$[Co(Salen)(AScH)]_{(obsd)} \underset{}{\overset{K_1''}{\rightleftharpoons}} [Co(Salen)(Asc)]_{(obsd)} + H^+$$

$$k_0'(red)\downarrow \qquad\qquad k_1'(red)\downarrow$$

$$[Co^{II}(Salen)] + AscH \qquad [Co^{II}(Salen)] + Asc^-$$

$$[Co(Salen)(AscH/Asc]^{\alpha-} + AscH/Asc^- \xrightarrow{fast} Co^{II}(Salen) + \text{dehydroascorbic acid} + H^+$$

Scheme 4 - Internal reduction of the ascorbato complex

for which

$$k_{obs} = (k_0(red) + k_1(red)\,[H^+]/K_1'')\,(1.0 + [H^+]/K_1'') \qquad ...(8)$$

where $k_0(red) = 2k_0'(red)$ and $k_1(red) = 2k_1'(red)$; factor 2 accounts for the stoichiometry of the redox reaction. The k_{obs} versus *p*H plot displays an inflexion point at *p*H = 5 - 8 (see Fig. 6). The mean value of k_{obs} in the $[H^+]$ independent zone (low *p*H) was taken to be $k_1(red)$. The limiting value of k_{obs} at high *p*H was also taken to be $k_0(red)$. The value of pK_1'' was judged from the k_{obs} - *p*H profile corresponding to the mean value of $k_1(red)$ and $k_0(red)$ ($pK_1'' = p$H when $k_{obs} = (k_1(red) + k_0(red))/2$). The rate constants were then fitted to Eq. (8) using these approximate values of $k_0(red)$ and pK_1'' and the mean value of $k_1(red)$. The calculated values of the parameters are quoted in Table 4.

Discussion

Complexation reaction

The $[Co^{III}(Salen)(dik)]$ (dik = β-diketonate) has been reported in which the Salen is believed to adopt non-planar arrangement[44]. The X-ray crystal structure

Table 4 - Reduction of *trans*-$[Co(Salen)_2(OH_2)_2]^+$ by ascorbic acid[a]

$[HClO_4]_T$ (mol dm^{-3})	$[Ascorbic\ acid]_T$ (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})	$[HClO_4]_T$ (mol dm^{-3})	$[Ascorbic\ acid]_T$ (mol dm-3)	$10^5 k_{obs}$ (s^{-1})
			25.0 ± 0.1°C		
0.10	0.020	7.11	0.10	0.020	6.35
0.10	0.060	6.37	0.10	0.060	6.69
0.0050	0.020	6.07	0.0050	0.020	6.22
0.0050	0.060	6.45	0.0050	0.060	6.13
0.010	0.020	6.02	0.010	0.020	7.15
0.010	0.060	7.20	0.010	0.060	5.61
0.020	0.060	5.43	0.050	0.060	6.63
0.15	0.060	7.04	0.20	0.060	6.29
*p*H[b]					
3.89	0.060	6.55	4.53	0.060	6.04
4.95	0.060	6.60	5.23	0.060	5.30
5.95	0.060	4.73	6.39	0.060	3.14
7.10	0.060	1.50	7.53	0.060	1.05
8.99	0.060	0.46			
			35.0 ± 0.1°C		
0.10	0.020	6.75	0.10	0.060	7.65
0.10	0.060	6.69	0.050	0.060	7.47
0.15	0.060	8.08			
*p*H[b]					
3.96	0.060	7.30	4.95	0.060	7.39
5.31	0.060	5.46	5.95	0.060	5.20
6.33	0.060	3.93	7.03	0.060	2.30
7.49	0.060	1.39	8.39	0.060	1.36
8.94	0.060	0.73			
			40.0 ± 0.1°C		
0.10	0.060	8.19	0.10	0.020	8.26
0.10	0.080	8.63	0.020	0.060	8.04
*p*H[b]					
3.81	0.060	9.70	4.12	0.060	8.21
4.51	0.060	8.17	5.08	0.060	8.10
5.69	0.060	7.50	5.95	0.060	6.66
6.31	0.060	5.93	7.08	0.060	3.23
7.68	0.060	2.53	8.58	0.060	1.50
8.98	0.060	1.37			
			45.0 ± 0.1°C		
0.10	0.020	10.1	0.10	0.060	10.1
0.10	0.080	9.87	0.0050	0.060	10.9
0.020	0.060	10.5	0.050	0.060	9.19
0.15	0.060	9.16	0.20	0.060	10.1
*p*H[b]					
3.97	0.060	9.72	4.58	0.060	9.31
5.01	0.060	9.20	5.28	0.060	9.01
5.98	0.060	7.02	6.23	0.060	5.85
7.08	0.060	4.18	7.53	0.060	3.18
8.58	0.060	1.54			
	25.0 ± 0.1[a]	35.0 ± 0.1[a]	40.0 ± 0.1[a]	45.0 ± 0.1°C	
$10^5 k_0$(red)/s^{-1}	0.54 ± 0.21	1.00 ± 0.29	1.98 ± 0.32	2.30 ± 0.39	
$10^5 k_1$(red)/s^{-1}	6.4 ± 0.5	7.3 ± 0.6	8.4 ± 0.3	10.0 ± 0.6	
10^{-6} $K_1''^{-1}$/dm^3 mol^{-1}	2.1 ± 0.3	2.0 ± 0.4	2.0 ± 0.2	2.0 ± 0.4	

$\Delta H^{\ddagger}$(kJ mol^{-1})[c] 57 ± 12 (15 ± 3) ; $\Delta S^{\ddagger}$(J K^{-1} mol^{-1})[c] -59 ± 39 (-276 ± 11)

[a] I = 0.5 mol dm^{-3}; measured by Co(II) assay, $\sigma(k_{obs})/k_{obs} = \pm 0.05$; [b] *p*H adjusted by self buffering with ascorbate (2.93 - 4.51), acetate buffer (5.08 - 6.31), and tris buffer (7.08 - 8.98). [c] values under parantheses are from the temperature dependence of k_1(red) and unparenthesised values are from the values of k_0(red).

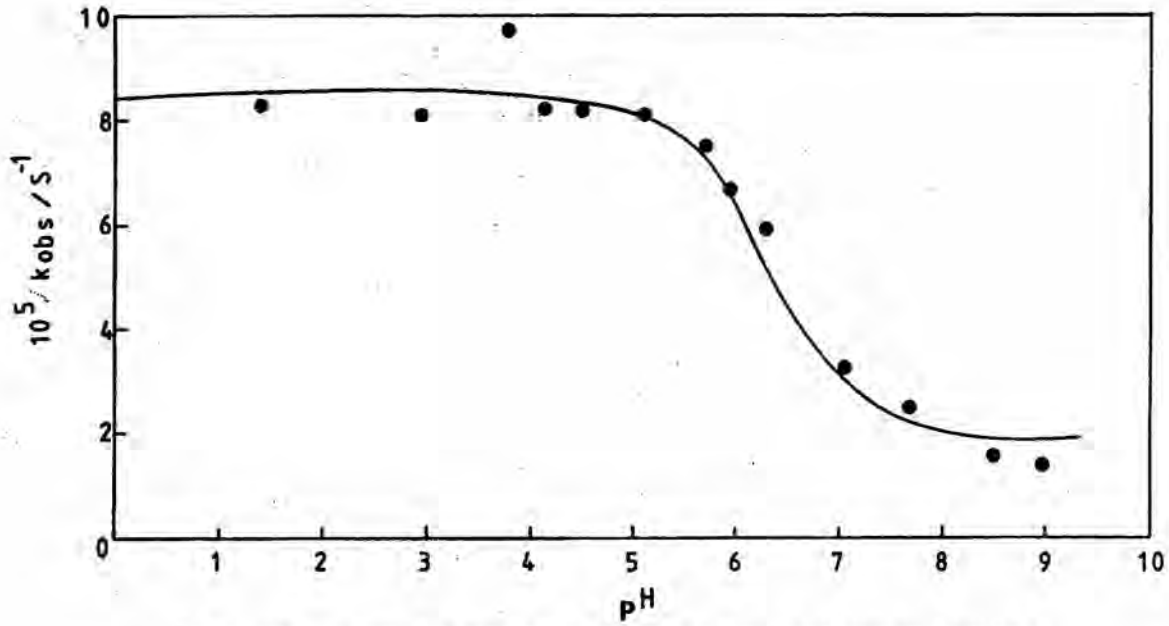
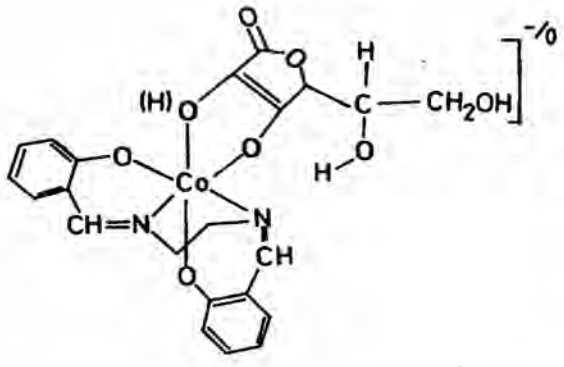


Fig. 6 - $10^5 k_{obs}/s^{-1}$ versus *p*H profile for the reduction of *trans*-$[Co(Salen)(OH_2)_2]^+$ at 40°C.

of $[Co^{III}(Salen)(acac)]$, $0.7H_2O$ (acac = acetylacetonate) reported by Calligaris *et. al.*[45] substantiated this assumption of Poddar *et. al.*[44]. It further showed that the acac acted as a chelating ligand occupying two *cis*-positions of a distorted octahedron around the cobalt atom with one of the O-atoms of *Salen* displaced from the N-Co-N-O plane and the *ethylene* bridge having nearly the *gauche* conformation. We presume nearly similar structure (**II**) for the Co(Salen)(Asc/AscH)]$^{-/0}$ which is also retained in the solution state. Unfortunately all our attempts to isolate the ascorbate complex in the solid state were in vain.

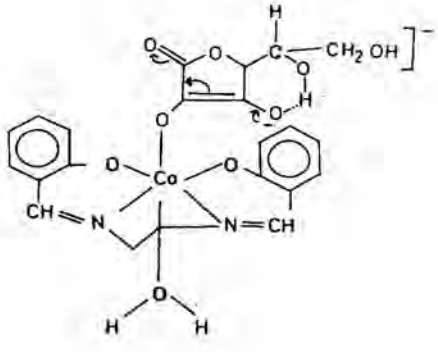


II - Tentative structure of $[Co(Salen)(AscH/Asc)]^{0/-}$

Jordan *et al.*[1] have discussed the structural aspect of iron(III)-ascorbate complex and pointed out that the large bite distance (~ 3 Å) of ascorbate greatly favoured the simultaneous approach of the two oxygen atoms of AscH- towards the centre of the separate octahedral faces for interaction with iron(III) centre. In the present case such a situation might prevail in the complexation reaction. The aqua ligand substitution reaction of *trans*-$[(OH_2)Co(salen)(OH_2/OH)]^{+/0}$ is substantially slower than the same for $[Fe(OH_2)_5(OH_2/OH)]^{3+/2+}$ {$k_{ex}(H_2O) = 1.6 \times 10^2\ s^{-1}$, $1.4 \times 10^5\ s^{-1}$ at 25°C for $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_5(OH)^{2+}$ respectively}[46]. Hence the overall substitution reaction could be observed in distinct two phases i.e. the formation of the monobonded species and its transformation to the chelate form. The second step involves *trans*→*cis* isomerisation at the cobalt(III) centre which most likely occurs in the transition state of the chelation process. It may be further noted that the formation of the (aqua)(ascorbato) complex by the reactions of *trans*-$[Co(Salen)(OH_2)_2]^+$ with $HAsc^-$ (k_{11}) is associated with low value of activation enthalpy ($\Delta H^{\ddagger}$ /kJ mol^{-1} = 20 ± 5) and large negative value of activation entropy ($\Delta S^{\ddagger}$/J K^{-1} mol^{-1} = -138 ± 16). These values ($\Delta S^{\ddagger}$ value in particular) are significantly lower than the same for the complexation of the diaqua complex with $[Fe(CN)_6]^{3-}$

($k_f = 477 \pm 15$ dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 43 \pm 7$ J K^{-1} mol^{-1}, $\Delta S^{\ddagger} = -50 \pm 22$ J K^{-1} mol^{-1}, at 25°C, $I = 0.5$ mol dm^{-3})[34]. We are , therefore, led to believe that the transition state for the formation of the aqua-ascorbate complex involves considerable ordering which is expected in the associative interchange mechanism (Ia). The sequence of reactivities $k_{11} < k_{22}$ ($k_{22}/k_{11} = 1.12$ at 25°C) is in line with the expected electrostatic effects and relatively stronger labilising action of the coordinated hydroxo group. However, it is worth noting that the labilising effect of the coordinated hydroxide in *trans*-[Co(Salen)(OH_2)(OH)] is not substantially large in comparison to the same for several complexes in which (Salen) is replaced by saturated/partially unsaturated ligands containing at least one *NH* function coordinated to cobalt(III).

The mono → chelate rate constant (see k_{33} and k_{44} values in Table 2) follow the trend $k_{33} > k_{44}$ which reflect the greater lability of Co^{III}-bound H_2O in the species, *trans*-[Co(Salen)(OH_2)(AscH)] as compared to the same in *trans*-[Co(Salen)(OH_2)(Asc)]$^-$. The low values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the chelation process ($\Delta H^{\ddagger} = 11.2 \pm 1.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -209 \pm 4.3$ J K^{-1} mol^{-1} for the k_{33} path see Table 2) reveal that this intramolecular process is strongly controlled by the entropy effect and the activation process involves an ordered transition state as expected for the associative interchange mechanism (Ia). However, the observed reactivity trend ($k_{33} >> k_{44}$) may be ascribed to the adverse effect of charge conjugation and internal hydrogen bonding in the (aqua)(ascorbato) complex **(III)**.



III - *H*-bonding and charge conjugation in the *trans*-[Co(Salen)(OH_2)(Asc)]$^-$

Redox reaction

The three slow redox processes identified are the reduction of cobalt(III) in *trans*-[Co(Salen)(OH_2)(H_2Asc)]$^+$ by H_2Asc, and internal reduction of cobalt(III) in [Co(Salen)(HAsc)] and [Co(Salen)(Asc)]$^-$. The internal reduction of the *trans*-{Co(Salen)(OH_2)(AscH)] appears to be too slow to compete with its transformation to the corresponding chelate. The second order path cannot be assessed properly as it is coupled with a chelation process. However, it appears that the reduction of Cobalt(III) in *trans*-[Co(Salen)(OH_2)(H_2ASc)]$^+$ by H_2Asc is faster than the internal redox reactions of the chelate species.

The redox reactions of *trans*-[Co(Salen)(OH_2)$_2$]$^+$ with H_2Asc/HAsc$^-$ may be contrasted with those of the *cis*-[N_4Co(OH_2)$_2$]$^{3+}$ ($N_4 = 4NH_3$, 2en, and tren) recently reported by Dasgupta *et al.*[8]. They reported that only HAsc$^-$ is the reductant for these substrates with no evidence of innershpere complex formation and the electron transfer is outersphere type. The activation enthalpies are reported to be high (> 80 kJ mol^{-1}) and the activation entropies are also positive {46 ± 2, 25 ± 34, 26 ± 6 J K^{-1} mol^{-1} for $(NH_3)_4$, $(en)_2$ and tren complexes}.

It is interesting to note that $k_1(red)/k_0(red) = 12 - 6$ at 25°C - 45°C. This reactivity sequence reflects either greater stabilisation of the +3 oxidation state of cobalt in the ascorbate dianion chelate [Co(Salen)(Asc)]$^-$ as compared to its HAsc$^-$ chelate or the electron transfer from the ascorbate ligand to Co^{III} centre is mediated by intramolecular H^+ catalysis. The values of $k_1(red)$ and $k_0(red)$, however, clearly point out that the reducing power of the ligand is greatly attenuated by complexation. Since the ascorbate dianion is likely to form a stronger complex than its acid form (HAsc$^-$) from the electrostatic ground, the sequence $k_0(red) < k_1(red)$ is very likely. This argument, however, does not completely exclude the possibility of the intramolecular acid catalysis in the internal redox of [Co(Salen)(HAsc)]$^-$. The much greater redox stability of [Co(Salen)(Asc)]$^-$ relative to [Co(Salen)(HAsc)] rests in the enthalpy factor {$\Delta H^{\ddagger}(k_0(red)) = 3\ \Delta H^{\ddagger}(k_1(red))$} and further reflects the relative energy requirements for transferring the electron from the reductant to the acceptor orbital of Co^{III}; substantially low negative value of the

activation entropy ($\Delta S^{\ddagger} = -270 \pm 11$ J K^{-1} mol^{-1}) for the ascorbate dianion complex indicates considerable ordering in the activation process.

Acknowledgement

The authors are thankful to the Department of Science and Technology, New Delhi for financial support and to the U. G. C. for research support through DRS(SAP) programme. A D and G S B are thankful to the DST, New Delhi for the grant of research fellowship.

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