Kinetics and Mechanism of the Reduction of Dodecatungstocobaltate(III) by Iminodiacetate, Nitrilotriacetate, and Ethylenediaminetetraacetate. A Comparative Study of the Reactivity of Different Amine-*N*-carboxylates

Swapan K. Saha, Prabir Bhattacharya, Mahammad Ali, and Pradyot Banerjee*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700032, India

(Received October 19, 1988)

The kinetics of reduction of dodecatungstocobaltate(III) by iminodiacetate (IDA), nitrilotriacetate (NTA), and ethylenediaminetetraacetate (EDTA) have been studied in aqueous solution at 50 °C, 30 °C, and 15 °C respectively. In general, the reactivity of the amine-*N*-carboxylates is in the order EDTA>NTA>IDA. All the anionic species have been found to undergo oxidation via both a spontaneous and an alkali metal ion-catalyzed pathway, while molecular form of the acids are oxidized only via spontaneous pathway. The rate of oxidation is given by a general expression $k_{ox}=k^{\circ}+k[M^+]^n$ where $k_{ox}=k_{obs}/2[L]_T$($[L]_T$=total concentration of a particular amine-*N*-carboxylate) and n may have values 1 or 2 depending on the nature of M^+. The terms k° and k account for the rate constants of the spontaneous and catalyzed paths respectively. A general trend $K^+>Na^+>Li^+$ for the catalyzed path has been observed for the oxidation of these amine-*N*-carboxylates. Reactivities of different species present in the experimental pH range have been evaluated by carrying out experiment at different pH and using these data in appropriate rate expressions. The reactivities (50 °C) of $Hida^-$ are $k^{\circ}=4.70\times10^{-5}\,dm^3\,mol^{-1}\,s^{-1}$ and $k_1=3.44\times10^{-4}\,dm^6\,mol^{-2}\,s^{-1}$ for the spontaneous and Na^+ catalyzed paths respectively. For NTA oxidation (30 °C), rates are $k^{\circ}_{10}(H_3nta)=1.11\times10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$, $k^{\circ}_{11}(H_2nta^-$, spontaneous)$=7.00\times10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$, $k_{11}(H_2nta^-$, Na^+ catalyzed)$=3.50\times10^{-2}\,dm^6\,mol^{-2}\,s^{-1}$, $k^{\circ}_{12}(Hnta^{2-}$, spontaneous)$=7.20\times10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$, $k_{12}(Hnta^{2-}$, Na^+ catalyzed)$=4.01\times10^{-2}\,dm^6\,mol^{-2}\,s^{-1}$. The corresponding reactivities (15 °C) for EDTA oxidation are $k^{\circ}_{20}(H_4edta$, spontaneous)$=6.80\times10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$, $k^{\circ}_{21}(H_3edta^-$, spontaneous)$=4.80\times10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$, $k_{21}(H_3edta^-$, Na^+catalyzed)$=0.48\,dm^9\,mol^{-3}\,s^{-1}$, $k^{\circ}_{22}(H_2edta^{2-}$, spontaneous)$=0.21\,dm^3\,mol^{-1}\,s^{-1}$,$k_{22}(H_2edta^{2-}$, Na^+ catalyzed)$=1.70\,dm^6\,mol^{-2}\,s^{-1}$, $k^{\circ}_{23}(Hedta^{3-}$, spontaneous)$=1.71\,dm^3\,mol^{-1}\,s^{-1}$, $k_{23}(Hedta^{3-}$, Na^+ catalyzed)$=30.00\,dm^6\,mol^{-2}\,s^{-1}$. A plausible mechanism considering an outer-sphere association between the complex and reductant has been suggested where the alkali metal ions are assumed to act as a bridge between the reactants.

The fascinating redox property of the cage molecule, dodecatungstocobaltate(III) has been considered by several groups$^{1-9)}$ in the past. In recent years, we have shown that alkali metal ions play significant role in the electron-transfer reactions between this heteropolyanion and a series of carboxylates e.g., formate,$^{10)}$ oxalate,$^{11)}$ malonate,$^{12)}$ and citrate.$^{13)}$

We now report here another family of carboxylates e.g., iminodiacetate, nitrilotriacetate, and ethylenediaminetetraacetate that give promise of a similarly rich redox chemistry. Previous studies on the oxidation reactions of some of the amine-*N*-carboxylates by cerium(IV) have been carried out$^{14)}$ at high acidity where the unique species present was in the molecular form. We have paid a particular attention to explore the reactivity of the individual amine-*N*-carboxylate species present under varying pH and obtain a possible relationship in the light of their behavior toward cation catalysis phenomenon leading to the redox process.

Experimental

Materials and Reagents. Potassium salts of dodecatungstocobaltate(III), $[CoW_{12}O_{40}]^{5-}$ and dodecatungstocobaltate(II) $[CoW_{12}O_{40}]^{6-}$, hereafter designated as $Co^{III}W$ and $Co^{II}W$ respectively, have been prepared, characterized and standardised in the same way as reported earlier.$^{2,15)}$ Doubly recrystallized disodium salt of iminodiacetic acid, Na_2ida (Fluka AG), nitrilotriacetic acid, H_3nta (Fluka AG), and disodium salt of ethylenediaminetetraacetic acid, Na_2H_2edta (BDH AnalaR) have been used to prepare stock solutions.$^{16)}$ Cation variation studies have been performed using doubly recrystallized sodium perchlorate, sodium nitrate, sodium sulfate, potassium nitrate, and lithium perchlorate. The pH adjustment has been done with the respective acids (perchloric, nitric, and sulfuric) and carbonate free alkali solutions (sodium, potassium, or lithium hydroxide). All solutions have been prepared using doubly distilled water.

Kinetic Studies. A Pye-Unicam SP8-150 spectrophotometer, equipped with a thermostated cell compartment has been used to monitor the reactions by observing the decrease in absorbance at the absorption maximum 388 nm of $Co^{III}W$ ($\varepsilon_{max}=1155\pm5\,dm^3\,mol^{-1}\,cm^{-1}$).$^{2)}$ Identical kinetic results have been obtained when experiments are carried out at 625 nm, the absorption maximum of $Co^{II}W$.$^{2)}$ Dissolved oxygen has not shown any observable kinetic effect. pH measurements are done with a Systronics (model 335, India) digital pH meter. Temperature has been controlled using a Haake F3 thermostat.

Polymerization Studies. The generation of free radicals during the course of reaction has been tested by the polymerization of acrylonitrile.$^{10-13)}$ In three separate vials solutions of IDA, NTA, and EDTA (ca. 0.1 mol dm^{-3}) are taken, and the pH of these solutions are adjusted to 4.45, 3.50, and 4.50 respectively. These solutions are then degassed with dinitrogen and acrylonitrile (5 ml 20% v/v) is added to each reaction mixture at room temperature. When the degassed solution of the complex (ca. 2×10^{-4} mol dm^{-3}) is added to these reaction mixtures, a heavy precipitate appears almost immediately for the EDTA containing mixture and after about 5—10 minutes for NTA and IDA containing solutions. No polymerization of the monomer is observed when acrylonitrile is added separately to solutions of the complex and amine-*N*-carboxylates. This suggests that the reaction proceeds via the generation of free radicals in solution.

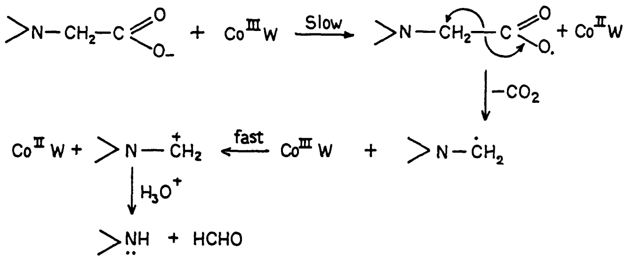
Stoichiometry and Reaction Products. To determine the stoichiometry of the reactions, the amine-*N*-carboxylates have been mixed with a large excess of $Co^{III}W$, and then kept under the reaction conditions, ($(1—5)\times10^{-4}$ mol dm^{-3} $HClO_4$, $[Na^+]=1.0$ mol dm^{-3}) for several days. In the oxidation of iminodiacetic acid, one mole of IDA was consumed per two moles of the $Co^{III}W$ complex after ca. two weeks of the reaction. The organic products which have been identified by paper electrophoresis are glycine and formaldehyde. For NTA oxidation, the same stoichiometry 2 : 1 is obtained, and the organic products are iminodiacetic acid and formaldehyde. In the case of EDTA oxidation, time dependent stoichiometry is obtained which becomes constant at a complex : reductant ratio of 16 : 1. Analysis of the products of a 1 : 1 mixture of complex: EDTA shows the presence of a mixture of ethylenediaminediacetic acid (EDDA), formaldehyde and unreacted EDTA. Carbon dioxide has been detected as one of the oxidation products for all the acids. For EDTA oxidation, following the first decarboxylation, several paths for further oxidation are available. These consecutive and concurrent reactions are expected to yield the observed time dependent stoichiometry. The stoichiometric reactions may therefore be depicted as follows

$$2\,Co^{III}W + HN(CH_2COOH)_2 \longrightarrow 2\,Co^{II}W + \text{other products} \quad (1)$$

$$2\,Co^{III}W + N(CH_2COOH)_3 \longrightarrow 2\,Co^{II}W + \text{other products} \quad (2)$$

$$16\,Co^{III}W + (HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2 \longrightarrow 16\,Co^{II}W + \text{other products.} \quad (3)$$

A similar time dependent stoichiometry for EDTA oxidation by Ce(IV) has been observed by Hanna et al.[14] However, the elementary process requires two moles of $Co^{III}W$ per mole of amine-*N*-carboxylate represented by a generalized Scheme 1.



Scheme 1.

Results and Discussions

General Kinetic Features of the Reactions. The kinetics of the oxidation of amine-*N*-polycarboxylates by $Co^{III}W$ has been studied in the pH range 0.05—5.45 at varying alkali metal ion concentrations which have been used as supporting electrolyte. The spectral changes observed during the reactions of $Co^{III}W$ with different carboxylates give a clear isosbestic point near 510 nm in each case. This indicates the absence of appreciable amounts of reaction intermediates. Under pseudo-first-order conditions with excess reductant, the plots of $-\log(A_t-A_\infty)$ vs. time (t), where A_t and A_∞ are the absorbances at times t and infinity respectively, show excellent linearity upto ca. 80—90% of the reactions. Linearity of a plot of k_s vs. $[\text{reductant}]_T$ (where k_s includes the stoiochiometric factor 2 and is defined by $k_s=k_{obs}/2$) holds good at any point in the pH range experimented for the individual amine-*N*-polycarboxylates suggesting a first-order dependence of rate on $[\text{reductant}]_T$. The k_s values for the reduction of $Co^{III}W$ by IDA, NTA, and EDTA are shown in Table 1.

Effect of Specific Ions on Reaction Rates. Reactions between two similarly charged ions are usually found to be catalyzed by a third substance bearing an opposite charge.[17—19] In the reactions of $Co^{III}W$ with the deprotonated forms of the amine-*N*-polycarboxylates, rate acceleration by alkali metal ions have been noticed. Both the change in nature and concentration of supporting electrolytes have considerable effect on the rates. The individual effects of K^+, Na^+, and Li^+ ($=M^+$) on the reaction rate were investigated. In each case, a positive intercept is obtained on the rate axis, and the rate of oxidation is given by the following expression

$$k_{ox} = k^\circ + k[M^+]^n \quad (4)$$

where $k_{ox}=k_s/[L]_T$($[L]_T$=total concentration of a particular amine-*N*-polycarboxylate) and n may have values 1 or 2 depending on the nature of M^+. The terms k° and k account for the rate constants of the spontaneous and catalyzed paths respectively. In the cases of IDA, NTA, and EDTA oxidations, a second-order dependence on $[Li^+]$ is obtained. When $[H_3edta]^-$ is the reacting species, the order with respect to $[Na^+]$ is also 2. Dependence on $[K^+]$ is always first-order, and the cation catalytic order[20] is $K^+>Na^+>Li^+$. The kinetic data are presented in Table 2. Equations 5—7 quantitatively describe all of these salt effect results, considering that constant ionic strength was not maintained. The intrinsic effect of ionic strength alone on the reaction was, however, verified by using a mixture of $MClO_4$ (or MNO_3) and M_2SO_4 whereby the total $[M^+]$ was kept constant but ionic strength varied. The results show that the effect of ionic strength on rates for the present system is negligibly small.

To ensure further that the rate enhancement is caused by catalysis and not an ionic strength effect, the rate parameters obtained for $[M^+]$ variation has been subjected to the Bronsted–Bjerrum–Christiansen relationship (Eq. 5) from which $\log k_0'$ defined by Eq. 6[21] has been calculated by using a value of +5 for Z_AZ_B

Table 1. Values of k_s[a] for the Reduction of $\mathrm{Co^{III}W}$ by Iminodiacetate, Nitrilotriacetate, and Ethylenediaminetetraacetate

$[\mathrm{IDA}]_\mathrm{T}$	$10^5 \times k_s$[b]	$10^2 \times [\mathrm{NTA}]_\mathrm{T}$	$10^4 \times k_s$[c]	$10^2 \times [\mathrm{EDTA}]_\mathrm{T}$	$10^4 \times k_s$[d]
$\mathrm{mol\,dm^{-3}}$	$\mathrm{s^{-1}}$	$\mathrm{mol\,dm^{-3}}$	$\mathrm{s^{-1}}$	$\mathrm{mol\,dm^{-3}}$	$\mathrm{s^{-1}}$
0.02	1.25	0.40	2.00	0.20	0.48
0.04	1.75	0.70	3.42	0.40	1.06
0.06	2.90	1.00	4.51	0.60	1.71
0.08	3.60	1.20	5.23	0.80	2.25
0.10	4.30	1.60	7.41	1.00	2.58
0.20	8.45				
0.30	12.10				

a) In all cases, the k_s values are reproducible by ±3%, $[\mathrm{Co^{III}W}]=0.0002\ \mathrm{mol\,dm^{-3}}$. b) pH=4.45, temp=50 °C, $[\mathrm{Na^+}]=1.00\ \mathrm{mol\,dm^{-3}}$. c) pH=3.90, temp=30 °C, $[\mathrm{Na^+}]=0.90\ \mathrm{mol\,dm^{-3}}$. d) pH=1.10, temp=15 °C, $[\mathrm{Na^+}]=0.40\ \mathrm{mol\,dm^{-3}}$.

Table 2. Variation of Alkali Metal Ions for the Reaction of Iminodiacetate, Nitrilotriacetate, and Ethylenediaminetetraacetate with $\mathrm{Co^{III}W}$. $[\mathrm{Co^{III}W}]=0.0002\ \mathrm{mol\,dm^{-3}}$

Medium	$[\mathrm{M^+}]$	$10^4 \times k_s$[a]	$10^4 \times k_s$[b]	$10^3 \times k_s$[c]
	$\mathrm{mol\,dm^{-3}}$	$\mathrm{s^{-1}}$	$\mathrm{s^{-1}}$	$\mathrm{s^{-1}}$
$\mathrm{LiClO_4}$	0.20	0.23		
	0.30		1.07	1.30
	0.50	0.62		
	0.60		2.01	2.41
	0.80	1.20	3.33	3.37
	1.00	1.70	4.65	5.14
	1.20	2.46	6.42	7.22
	1.60	4.20		
$\mathrm{NaClO_4}$	0.20	0.21		2.22
	0.30		1.85	
	0.40			3.15
	0.50	0.42		
	0.60		3.12	4.69
	0.80	0.65		6.27
	0.90		4.51	
	1.00	0.84		7.41
	1.20	1.00	5.62	
	1.50		6.45	
	1.60	1.20		
	2.00	1.42		
$\mathrm{Na_2SO_4}$	0.60		3.14	4.80
	1.00	0.86		7.55
	1.20	1.00	5.65	
$\mathrm{KNO_3}$	0.20	0.33	2.06	2.62
	0.40		3.53	4.38
	0.50	0.77		
	0.60		5.30	6.01
	0.80	1.04	6.47	7.67
	1.00	1.26	7.54	8.43
	1.20	1.46		
	1.60	1.81		
	2.00	2.40		

a) pH=4.45, temp=50 °C, $[\mathrm{IDA}]_\mathrm{T}=0.20\ \mathrm{mol\,dm^{-3}}$.
b) pH=3.90, temp=30 °C, $[\mathrm{NTA}]_\mathrm{T}=0.01\ \mathrm{mol\,dm^{-3}}$.
c) pH=4.50, temp=15 °C, $[\mathrm{EDTA}]_\mathrm{T}=0.003\ \mathrm{mol\,dm^{-3}}$.

and a theoretical value[22] of −0.504 for the constant A.

$$\log k_\mathrm{ox} = \log k_0 + 2AZ_\mathrm{A}Z_\mathrm{B}\frac{\sqrt{I}}{1+\sqrt{I}} + BI \tag{5}$$

$$\log k_0' = \log k_\mathrm{ox} - 2AZ_\mathrm{A}Z_\mathrm{B}\frac{\sqrt{I}}{1+\sqrt{I}} \tag{6}$$

Combining these two equations, we get

$$\log k_0' = \log k_0 + BI. \tag{7}$$

Judging from a simple electrostatic approach, based on the Bronsted-Christiansen-Scatchard equation (Eq. 7),[23] all points should fall on straight line very close together, because the coefficient B should depend mainly on the nature of the ions of opposite signs to that of the reactants.[24] Although this relation has been verified for several reactions, for the present system the plot of $\log k_0'$ vs. I deviates from linearity for each of the cations experimented (Fig. 1). Inter-

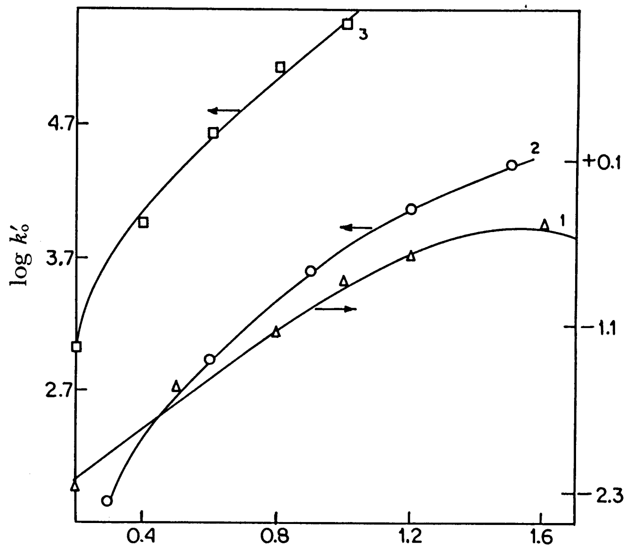


Fig. 1. A plot of $\log k_0'$ vs. I (calculated from $[\mathrm{Na^+}]$ variation data for the reactions of $\mathrm{Co^{III}W}$ with 1) iminodiacetate at pH 4.45, $[\mathrm{IDA}]_\mathrm{T}=0.20\ \mathrm{mol\,dm^{-3}}$ and temperature 50 °C, 2) nitrilotriacetate at pH 3.90, $[\mathrm{NTA}]_\mathrm{T}=0.01\ \mathrm{mol\,dm^{-3}}$ and temperature 30 °C, and 3) ethylenediaminetetraacetate at pH 4.50, $[\mathrm{EDTA}]_\mathrm{T}=0.003\ \mathrm{mol\,dm^{-3}}$ and temperature 15 °C.

pretation of such deviation obviously requires some specific catalytic intervention by M^+, possibly through a combination of reduction of anion-anion repulsion and facilitation of actual electron transfer through a superexchange type process.[25,26)]

The foregoing discussions lead us to believe that the reactions of $Co^{III}W$ with the amine-*N*-polycarboxylates take place in two pathways—a spontaneous and an alkali metal ion catalyzed path. Considering the fact that the heteropolyanion under study is a substitution inert species, the sequence of reactions may be described by assuming an outer-sphere association between the reactants. In general, the mechanism may be depicted as follows

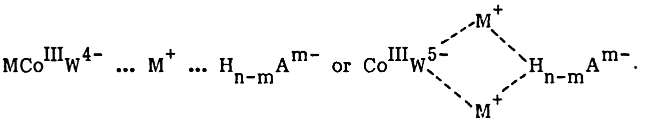
$$Co^{III}W^{5-}+H_n A \rightleftarrows Co^{III}W^{5-},H_nA \xrightarrow{k^\circ} Co^{II}W^{6-}+\text{free readical}_1. \tag{8}$$

The above equation describes the reactions of molecular species of the acids (H_nA). For the anionic forms, the spontaneous path would be the same as in above, and the catalyzed path would incorporate M^+ in the rate-determining step as follows[27)]

$$Co^{III}W^{5-}+H_{n-m} A^{m-} \rightleftarrows Co^{III}W^{5-},\ H_{n-m} A^{m-} \xrightarrow{k} Co^{II}W^{6-}+\text{free radical}_2 \tag{9}$$

$$Co^{III}W^{5-}+M^+ +H_{n-m} A^{m-} \rightleftarrows Co^{III}W^{5-}\cdots M^+\cdots H_{n-m}A^{m-} \xrightarrow{k} Co^{II}W^{6-}+\text{free radical}_2. \tag{10}$$

The second order dependence on $[M^+]$ may be explained by incorporating another M^+ in the transition state, i.e., the transition state may be a doubly bridged species of the types



$$MCo^{III}W^{4-} \cdots M^+ \cdots H_{n-m}A^{m-} \quad \text{or} \quad Co^{III}W^{5-} \begin{smallmatrix} M^+ \\ \\ M^+ \end{smallmatrix} H_{n-m}A^{m-}.$$

(A) (B)

A recent vibration spectral study[28)] of ionic association has suggested the formation of (B) type of species of mixed aggregates between lithium thiocyanate and lithium halides in nonaqueous solvents.

Reactivities of Different Amine-*N*-polycarboxylate Species. Determination of reactivities of different reacting species present in a reaction mixture is one of the major criteria for the elucidation and interpretation of kinetic data. So an attempt has been made to identify the possible reactants under given conditions and to determine their reactivities. For all the acids and their anions, plots of k_s vs. $[\text{reductant}]_T$ where the subscript T denotes the total concentration of any particular amine-*N*-polycarboxylate give straight lines passing through the origin ensuing a first-order dependence of the rate on the reductant concentrations. The rate parameters corresponding to the oxidation of molecular forms of the acids have thus been determined directly from the slope of the plot of k_s vs. $[\text{reductant}]_T$ at pH 0.05 for NTA and at pH 0.50 for EDTA. Since the reactions with the anionic amine-*N*-polycarboxylates are catalyzed by alkali metal ions, the rate parameters corresponding to the spontaneous and catalyzed paths have been evaluated by considering the dissociation constants of the acids and identifying the reaction species in solution. For the oxidation of iminodiacetate, though the spontaneous (k°) and catalyzed (k) paths have been evaluated from a plot of $k_{ox}(=k_s/[\text{reductant}])$ vs. $[Na^+]$, the reactivity of the molecular form could not be determined, owing to its extremely slow reaction and poor solubility in water. However, for nitrilotriacetate oxidation, H_3nta is reasonably soluble in aqueous medium and its reactivity (k°_{10}) has been determined by plotting k_s vs. $[H_3nta]$ at pH 0.05. Since the pK_1, pK_2, and pK_3 values of H_3nta are 1.70, 2.40, and 9.67 respectively,[29)] rate parameters (k°_{12} and k_{12}) corresponding to the oxidation of $[Hnta]^{2-}$ have been obtained by plotting the values of $k_s/[Hnta^{2-}]$ vs. $[Na^+]$ at pH 3.90±0.02. To determine the reactivity of the monoanionic species (H_2nta^-), a set of experiments have been carried out at pH 1.05±0.02 (where the reacting species are H_3nta and H_2nta^-) varying $[Na^+]$. Utilizing these k_{obs} values, k°_{10} and K_1 (the first acid dissociation constant of H_3nta), the reactivities of the catalyzed (k_{11}) and spontaneous (k°_{11}) paths of $[H_2nta]^-$ have been evaluated from the slope and intercept of the plot of left hand side (LHS) vs. $[Na^+]$ (Fig. 2) in Eq. 11,

$$\frac{k_s(K_1+[H^+])-L_T[H^+]k^\circ_{10}}{K_1 L_T} = k^\circ_{11}+k_{11}[Na^+] \tag{11}$$

where L_T denotes the total amount of nitrilotriacetate added. The values of the rate parameters are shown in Table 3.

A similar approach has been followed to evaluate the reactivities of the EDTA. A series of kinetic experiments were carried out at constant $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}, $[EDTA]_T=(2—3)\times10^{-3}$ mol dm^{-3} but at varying pH and $[Na^+]$. (i) At pH 0.50, kinetic studies have been carried out by varying $[EDTA]_T$ with $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}. From the slope of k_s vs. $[EDTA]_T$ plot, we can get k°_{20}, the reactivity of H_4edta. (ii) At pH 1.10±0.02 kinetic studies have been carried out by varying $[Na^+]$ at constant $[EDTA]_T=2\times10^{-3}$ mol dm^{-3} and $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}. It is to be noted here that the acid dissociation constants of H_4edta are given by pK_1'=1.99, pK_2'=2.67, pK_3'=6.16, and pK_4'=10.26 respectively,[30)] and at pH 1.10, the species taking part in the reaction are H_4edta (k°_{20}) and $[H_3edta]^-$ (k°_{21} and k_{21}). Utilizing the k_s values at pH 1.10, K_1' and k°_{20}, we can evaluate the values of k°_{21} and k_{21} from the slope and intercept of the plot of LHS vs. $[Na^+]^2$ of Eq. 12

$$\frac{k_s(K_1'+[H^+])-L_T[H^+]k^\circ_{20}}{K_1' L_T} = k^\circ_{21}+k_{21}[Na^+]^2 \tag{12}$$

The evaluated parameters are shown in Table 3. (iii) At pH 4.50 ± 0.02, a set of kinetic experiments has

Table 3. Kinetic Data for the Reaction of $Co^{III}W$ with Iminodiacetate, Nitrilotriacetate, and Ethylenediaminetetraacetate at Varying $[Na^+]$ under Different pH

	IDA	NTA			EDTA			
pH	4.45	0.05	1.05	3.90	0.50	1.10	4.50	5.45
$[Na^+]$/ mol dm^3	10^4k_s/ [IDA]/ dm^3 mol^{-1} s^{-1}	10^3k_s/ [NTA]/ dm^3 mol^{-1} s^{-1}	10^2k_s/ [NTA]/ dm^3 mol^{-1} s^{-1}	10^2k_s/ [NTA]/ dm^3 mol^{-1} s^{-1}	10^2k_s/ [EDTA]/ dm^3 mol^{-1} s^{-1}	10^2k_s/ [EDTA]/ dm^3 mol^{-1} s^{-1}	k_s/ [EDTA]/ dm^3 mol^{-1} s^{-1}	$10k_s$/ [EDTA]/ dm^3 mol^{-1} s^{-1}
0.10								1.16
0.20	1.03	1.09				1.20	0.74	1.69
0.30			0.43	1.83	0.71			2.22
0.40						2.42	1.05	2.96
0.50	2.11	1.11			0.69			3.69
0.60			0.56	3.12		3.90	1.56	
0.80	3.25	1.13			0.67	5.36	2.09	
0.90			0.84	4.51		6.34		
1.00	4.22						2.47	
1.20	4.98	1.09	1.01	5.62	0.65			
1.50		1.13	1.06	6.45				
1.60	6.00							
2.00	7.10							

$k^\circ=4.70\times10^{-5}$ dm^{3}mol^{-1}s^{-1}
$k_1=3.44\times10^{-4}$ dm^{6}mol^{-2}s^{-1}

$k^\circ_{10}=1.11\times10^{-3}$dm^{3}mol^{-1}s^{-1}
$k^\circ_{11}=7.00\times10^{-3}$dm^{3}mol^{-1}s^{-1}
$k_{11}=3.50\times10^{-2}$dm^{6}mol^{-2}s^{-1}
$k^\circ_{12}=7.20\times10^{-3}$dm^{3}mol^{-1}s^{-1}
$k_{12}=4.01\times10^{-2}$dm^{6}mol^{-2}s^{-1}

$k^\circ_{20}=6.80\times10^{-3}$ dm^{3}mol^{-1}s^{-1};
$k_{21}=0.48$ dm^{9}mol^{-3}s^{-1} ;
$k_{22}=1.70$ dm^{6}mol^{-2}s^{-1} ;
$k_{23}=30.00$ dm^{6}mol^{-2}s^{-1}

$k^\circ_{21}=4.80\times10^{-2}$ dm^{3}mol^{-1}s^{-1}
$k^\circ_{22}=0.21$ dm^{3}mol^{-1}s^{-1}
$k^\circ_{23}=1.71$ dm^{3}mol^{-1}s^{-1}

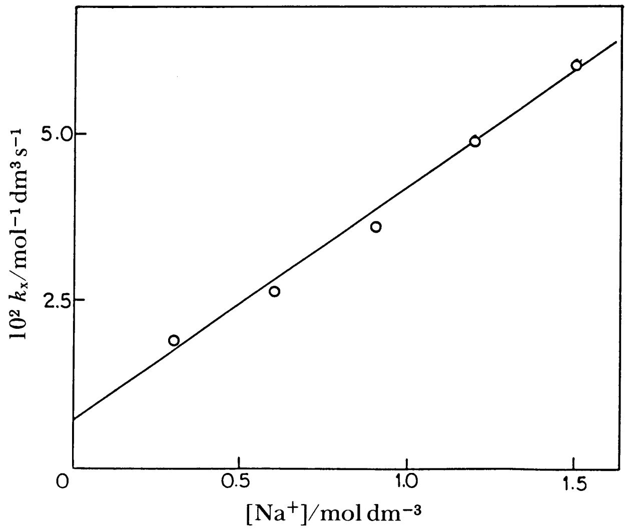


Fig. 2. Representative plot for the evaluation of k°_{11} and k_{11} for H_2nta^- oxidation at pH 1.05±0.02. The ordinate k_x represents the LHS of Eq. 11.

been carried out by varying $[Na^+]$ at a constant $[EDTA]_T=3\times10^{-3}$ mol dm^{-3} and $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}. Considering the second and third acid dissociation constants of H_4edta, the reaction mixture consists of largely $[H_2edta]^{2-}$ species. A plot of k_{ox} vs. $[Na^+]$ gives a straight line from which we can extract a pair of kinetic parameters k°_{22} and k_{22}. We consider these as apparent values since a little amount of $[Hedta]^{3-}$ is also present at this pH. (iv) By varying $[Na^+]=0.10$—0.50 mol dm^{-3}, the rates of the reduction have been followed at $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3} having $[EDTA]_T=2\times10^{-3}$ mol dm^{-3} at pH 5.45±0.02. The apparent values of k°_{22} and k_{22} were substituted to the rate equation (Eq. 13) to get again a set of apparent k°_{23} and k_{23} values, the uncatalyzed and catalyzed rates for the species $[Hedta]^{3-}$, from a plot of LHS of Eq. 13 vs. $[Na^+]$,

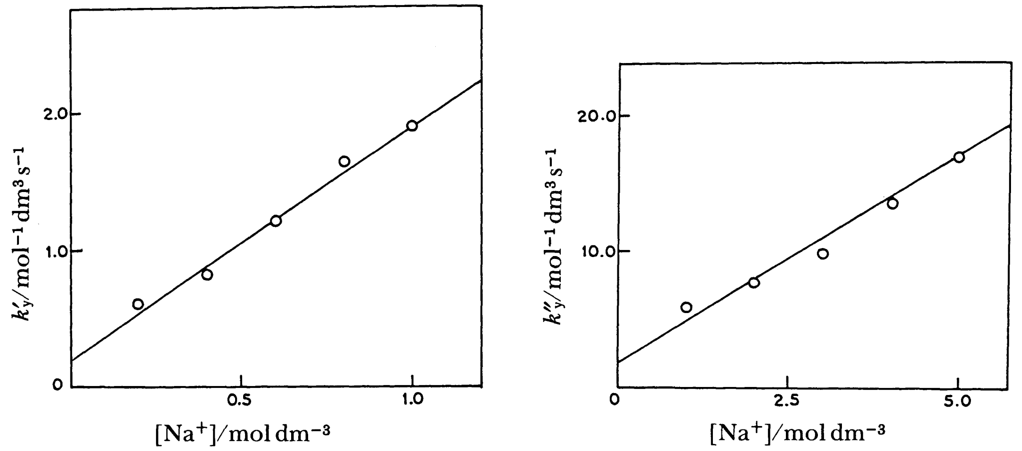
$$\frac{k_s(K_3' + [H^+]) - L_T[H^+](k_{22}+k_{22}[Na^+])}{K_3' L_T} = k^\circ_{23} + k_{23}[Na^+] \tag{13}$$

where L_T denotes the total concentration of EDTA. For the refinement of k°_{22} and k_{22}, the apparent k°_{23} and k_{23} values from Eq. 13 were substituted to the rearranged form Eq. 14 of Eq. 13 but now with the k_s values at pH 4.50.

$$\frac{k_s(K_3' + [H^+]) - K_3'L_T(k^\circ_{23} + k_{23}[Na^+])}{L_T[H^+]} = k^\circ_{22} + k_{22}[Na^+] \tag{14}$$

A new set of k°_{23} and k_{23} can now be generated from Eq. 13 utilizing refined k°_{22} and k_{22} values. The refined parameters obtained by this procedure are listed in Table 3 and the representative plots are shown in Figs. 3(a) and 3(b).

pH-Rate Profiles and the Generalized Rate Equations for NTA and EDTA Oxidations. A general pH variation study has been carried out for both the NTA and EDTA oxidations, and an attempt has been made to match the experimental data with the calculated rate parameters. For this purpose generalized rate expressions have been derived (given by Eqs. 15 and 16) based on the respective reaction schemes (Schemes 2 and 3).



(a) (b)

Fig. 3. Representative plots for the evaluation of (a) k°_{22} and k_{22} (refined parameters as presented in Table 3) for H_2edta^{2-} oxidation at pH 4.50±0.02. k'_y represents the LHS of Eq. 14. (b) k°_{23} and k_{23} (refined parameters as presented in Table 3) for $Hedta^{3-}$ oxidation. k''_y denotes the LHS of Eq. 13.

$$k_s = L_T \frac{k^{\circ}_{10}[H^+]^2 + K_1[H^+](k^{\circ}_{11} + k_{11}[Na^+]) + K_1K_2(k^{\circ}_{12} + k_{12}[Na^+])}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{15}$$

$$Co^{III}W^{5-} + H_3nta \xrightarrow{k^{\circ}_{10}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + H_2nta^- \xrightarrow{k^{\circ}_{11}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + Na^+ + H_2nta^- \xrightarrow{k_{11}} Co^{II}W^{6-} + Na^+$$

$$Co^{III}W^{5-} + Hnta^{2-} \xrightarrow{k^{\circ}_{12}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + Na^+ + Hnta^{2-} \xrightarrow{k_{12}} Co^{II}W^{6-} + Na^+$$

Scheme 2.

and

$$k_s = L_T \frac{k^{\circ}_{20}[H^+]^3 + K'_1[H^+]^2(k^{\circ}_{21} + k_{21}[Na^+]^2) + K'_1K'_2[H^+](k^{\circ}_{22} + k_{22}[Na^+]) + K'_1K'_2K'_3(k^{\circ}_{23} + k_{23}[Na^+])}{[H^+]^3 + K'_1[H^+]^2 + K'_1K'_2[H^+] + K'_1K'_2K'_3} \tag{16}$$

$$Co^{III}W^{5-} + H_4edta \xrightarrow{k_{20}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + H_3edta^- \xrightarrow{k^{\circ}_{21}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + Na^+ + H_3edta^- \xrightarrow{k_{21}} Co^{II}W^{6-} + Na^+$$

$$Co^{III}W^{5-} + H_2edta^{2-} \xrightarrow{k^{\circ}_{22}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + Na^+ + H_2edta^{2-} \xrightarrow{k_{22}} Co^{II}W^{6-} + Na^+$$

$$Co^{III}W^{5-} + Hedta^{3-} \xrightarrow{k^{\circ}_{23}} Co^{II}W^{6-}$$

$$Co^{III}W^{5-} + Na^+ + Hedta^{3-} \xrightarrow{k_{23}} Co^{II}W^{6-} + Na^+$$

Scheme 3.

All the reaction sequences generate respective amine-*N*-polycarboxylate free radicals as stated earlier.

With the help of the various rate parameters included in Table 3, the k_s values at different pH have been calculated. An excellent agreement between the theoretical and experimental values has been obtained (Figs. 4 and 5) and thus the mechanistic formulations are supported strongly.

The pH-rate profile in Fig. 4 for NTA oxidation shows that the rate of reaction increases with increase in pH of the solution at the first phase. It is due to the increase in [H_2nta^-], which has a higher reactivity than H_3nta. Rate saturation starts at pH≈2.80 where [$Hnta$]$^{2-}$ starts to prevail and no inflexion in the profile is noted below this pH indicating very close reactivities of [H_2nta]$^-$ and [$Hnta$]$^{2-}$. This is also reflected in the evaluated rate parameters (Table 3). In the case of EDTA, an examination of the pH-rate profile in Fig. 5 reveals that the increase in rate at the first phase is attributable to the increase in [H_3edta]$^-$ reactivity and to a lesser extent by [H_2edta]$^{2-}$ species,

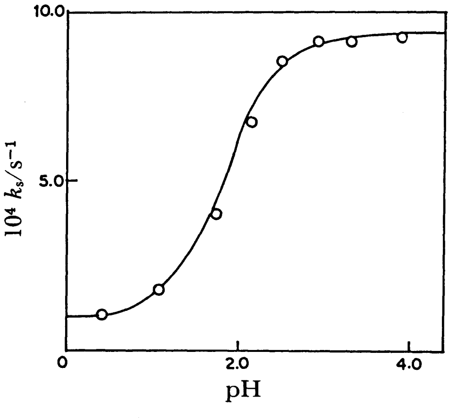


Fig. 4. pH variation results for the reaction of $Co^{III}W$ with nta at $[NTA]_T$=0.02 mol dm^{-3}, [Na$^+$]=1.00 mol dm^{-3} and temperature=30 °C. Bold line represents the theoretical graph and the experimental values are shown by points O.

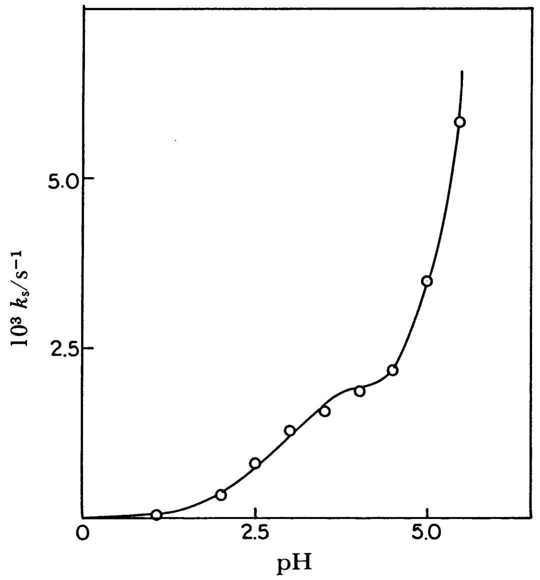


Fig. 5. pH variation results for the reaction of $Co^{III}W$ with edta at $[EDTA]_T=0.002$ mol dm^{-3}, $[Na^+]=0.40$ mol dm^{-3} and temperature=15 °C. The solid line represents the theoretical graph and the experimental values are given by points.

since the pK_1' and pK_2' values are close enough. This trend is followed upto pH≈4.0 where the rate saturation due to both $[H_3edta]^-$ and $[H_2edta]^{2-}$ occurs. This is manifested by a little inflexion in the profile at pH ca. 4.0—4.5. The rate increases sharply beyond pH 4.50, and obviously due to the increased reactivity of $[Hedta]^{3-}$ (Table 3). Since the complex is stable in the pH range 0.0—5.5, kinetic experiments had to be carried out in this range only.

Conclusion

The present study thus provides a systematic approach to the oxidation of amine-*N*-polycarboxylates by $Co^{III}W$. Previous studies on these acids[31-33] have been made in strong acid solutions mainly characterizing a particular species as the reductant. However, in spite of the complications arising out from the overlapping p*K* values, we could experimentally design and evaluate the different reactivities of various reacting species present in the reaction mixture within our experimental pH range. A comparison of the reactivities of these amine-*N*-polycarboxylates shows a general trend EDTA>NTA>IDA. It has been experimentally recognized that glycine is inert towards $Co^{III}W$. Thus it may be concluded that the increase in number of carboxylate functions for the amino acids increases the reactivities of the molecules i.e., the reducing power. The reactivities of different species for the individual acids have also shown some interesting feature. For EDTA, the trend is $H_4edta<H_3edta^-<H_2edta^{2-}<Hedta^{3-}$. However, for NTA oxidation it is $H_3nta<H_2nta^-\approx Hnta^{2-}$. The above sequences are also true for the catalyzed paths.

The cation catalytic order $K^+>Na^+>Li^+$ obtained in this study is similar to our previous studies[10,11,13] and may be explained by considering the aquated cationic sizes which falls in the order $K^+<Na^+<Li^+$. Thus K^+ will be more effective than Na^+ or Li^+ in bringing the two negatively charged reacting ions together. The absence of catalysis in the oxidation of molecular species is reasonable since the reductant does not carry any charge. But the observation that less effective Li^+ shows a second-order dependence is rather difficult to explain. The greater tendency of the smaller cations to associate with a negatively-charged species[34] is the likely cause for this. Also the second-order dependence on $[Na^+]$ for H_3edta^- in contrast to those observed for H_2edta^{2-} and $Hedta^{3-}$ oxidations seems interesting. Such type of anomaly was encountered in our earlier study in the redox interactions of this heteropolyanion with oxalate.[11] A proper justification of this phenomenon seems difficult because of several factors like size and charge of the reactants, their polarizability as also the size and polarizability of the various cations are associated. An apparent explanation may be put forward by considering the charges of the reactants. As shown in Eqs. 9 and 10, the proposed mechanism involves a cation bridged activated complex where both the complex and the reductant share the alkali metal ion in the transition state. It may be assumed that H_2edta^{2-} and $Hedta^{3-}$ can compete for the Na^+ in the ion pair by virtue of their greater negative charge and utilize it to act as a bridging metal ion in the transition state. Hence the first-order dependence of rate on $[Na^+]$ prevails for these two species. For H_3edta^-, the mononegative charge may not be sufficient to compete for Na^+ in the ion pair. The bridge formation is facilitated by the incorporation of another Na^+ in the ion pair i.e., by reducing the effective charge on the complex, and it results in a second-order dependence on $[Na^+]$.[35]

References

1) P. G. Rasmussen and C. H. Brubaker, *Inorg. Chem.*, **3**, 977 (1964).

2) Z. Amjad, J. Brodovitch, and A. McAuley, *Can. J. Chem.*, **55**, 3581 (1977).

3) G. A. Ayoko and M. A. Olatunji, *Polyhedron*, **2**, 577 (1983).

4) G. A. Ayoko and M. A. Olatunji, *Inorg. Chim. Acta*, **80**, L15 (1983).

5) M. A. Olatunji and G. A. Ayoko, *Polyhedron*, **3**, 191 (1984).

6) G. A. Ayoko and M. A. Olatunji, *Indian J. Chem., Sect. A*, **23**, 769 (1984).

7) G. A. Ayoko and M. A. Olatunji, *Transition Met. Chem.*, **10**, 218 (1985).

8) M. A. Olatunji and G. A. Ayoko, *Bull.de-la Soc. Chim. De France*, **5**, 705 (1985).

9) L. Eberson, *J. Am. Chem. Soc.*, **105**, 3192 (1983).

10) S. K. Saha, M. C. Ghosh, and P. Banerjee, *Inorg. Chim. Acta,* **126**, 29 (1986).

11) S. K. Saha, M. C. Ghosh, and P. Banerjee, *J. Chem. Soc., Dalton Trans.,* **1986**, 1301.

12) S. K. Saha, M. C. Ghosh, and P. Banerjee, Proc. 4th Int. Conf. on the Mechanism of Reactions in Solution, University of Kent, Canterbury (1986), p. 18.

13) S. K. Saha, M. C. Ghosh, and P. Banerjee, *Int. J. Chem. Kinet.,* **20**, 699 (1988).

14) S. B. Hanna, W. R. Carroll, S. A. Attiga, and W. H. Webb, *Z. Naturforsch,* **30B**, 409 (1975).

15) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.,* **78**, 4503 (1956).

16) Although these formulations have been strictly followed when describing the actual species involved in preset pH conditions, designations such as IDA, NTA, and EDTA have also been used in a general way to describe a particular amine-*N*-polycarboxylate without any emphasis to the actual species.

17) Y. A. Majid and K. E. Howlett, *J. Chem. Soc. A,* **1968**, 679.

18) Y. Sulfab, M. S. Al-Obadie, and N. Al-Salem, *Z. Phys. Chem.,* **94**, 77 (1975).

19) R. J. Champion, C. F. Deck, P. King, and A. C. Wahl, *Inorg. Chem.,* **6**, 672 (1967).

20) Though the order $K^+ > Na^+ > Li^+$ does not hold good for ida oxidation at high $[Li^+]$, at very low $[Li^+]$ where a first-order plot prevails, the above order is valid.

21) E. A. Guggenheim and J. E. Prue, Physicochemical Calculations (Russian Translation), *Izd. Inostr. Lit., Moscow,* **1963**, 450.

22) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1970), p. 468.

23) E. S. Amis, "Kinetics of Chemical Change in Solution," Macmillan, New York (1949), p. 71.

24) E. A. Guggenheim and L. A. Wigeman, *Proc. R. Soc. London, Ser. A,* **203**, 17 (1950).

25) A. Indelli, G. Nollan, Jr., and E. S. Amis, *J. Am. Chem. Soc.,* **82**, 3233, 3237 (1960).

26) A. Indelli, *Israel J. Chem.,* **9**, 301 (1971).

27) Since the mechanism has been described in a generalized way, the different type of free radicals produced are indicated by their suffixes. It is assumed that free radicals are produced by -COO-H fission in case of molecular species and for the anionic species, it comes from the negative charge of $-COO^-$.

28) P. Goralski and M. Chabanel, *Inorg. Chem.,* **26**, 2169 (1987).

29) G. Anderegg, *Helv. Chim. Acta,* **50**, 2333 (1967).

30) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954).

31) G. N. Rao, *Indian J. Chem.,* **8**, 328 (1970).

32) E. Mentasti, E. Pelizzetti, and G. Saini, *J. Chem. Soc., Dalton Trans.,* **1974**, 1944.

33) R. Varadarajan and M. A. Hossain, *Indian J. Chem., Sect. A,* **18**, 46 (1979).

34) D. M. Druskovich and D. L. Kepert, *J. Chem. Soc., Dalton Trans.,* **1975**, 947.

35) A referee has commented that a higher order dependence on $[Na^+]$ is plausible for electrostatically more favorable species (e.g., H_2edta^{2-} and $Hedta^{3-}$). This is not unlikely, though we could not find such phenomenon even at $[Na^+] \leq 0.50$ mol dm^{-3} with $[EDTA] = 0.002$ mol dm^{-3}. Beyond this $[Na^+]$, experiments could not be carried out by conventional spectrophotometric method owing to rapidity of the reaction.