Kinetics and Mechanism of Ce(IV) Oxidation of Free and Coordinated Glyoxylic Acid

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The kinetics and mechanism of Ce(IV) oxidation of glyoxylic acid and pentaammineglyoxylatocobalt(III) perchlorate have been investigated in acidic sulfate media in the temperature range 35 to 50 °C and at ionic strength 0.95 M. The rate of decrease of [Ce(IV)] was found to be first order in [substrate] and [Ce(IV)]. The observed second order rate constant, k_{obsd}, for the disappearance of [Ce(IV)] is satisfactorily given by,

$$k_{\text{obsd}} = \frac{k_1 + k_2K_3[\text{HSO}_4^-]/[\text{H}^+]}{1 + K_3[\text{HSO}_4^-]/[\text{H}^+]} \quad \text{(for glyoxylato complex)}$$

and

$$k_{\text{obsd}} = \frac{k_1}{1 + K_3[\text{HSO}_4^-]/[\text{H}^+]} \quad \text{(for glyoxylic acid)}$$

Both $Ce(SO_4)_2$ and $[Ce(SO_4)_3]^{2-}$ appear to be the oxidant species for coordinated glyoxylate while for free glyoxylic acid $Ce(SO_4)_2$ seems to be the only oxidant species. The values of k_1 and k_2 and the associated activation parameters have been computed. A suitable mechanism has been suggested for the reaction.

The mechanism of Ce(IV) oxidation of carboxylic acids has been extensively investigated.[1,2] Literature survey indicates that Ce(IV) oxidation of carboxylates coordinated to inert metal ion centres has been very sparsely investigated.[3–10] Ce(IV) in $HClO_4$ and H_2SO_4 media exists as different species.[11,12] So far attempt has not been made to establish the mechanism and the nature of reactive cerium species for the oxidation of carboxylates coordinated to metal centers. In the present investigation Ce(IV) oxidation of pentaammineglyoxylatocobalt(III) ion and glyoxylic acid in H_2SO_4–$HClO_4$ media has been undertaken to explore the mechanism, to determine the nature of active cerium species and to establish the complex formation, if any, between the substrate and the oxidant. The products of oxidation have been characterised. For comparison, Ce(IV) oxidation of free glyoxylic acid has also been studied.

Experimental

Pentaammineglyoxylatocobalt(III) perchlorate was prepared by the method of Price and Taube[13] and the purity of the complex was checked by estimating cobalt as described in literature.[14] Cerium(IV) sulfate solution was prepared by dissolving cerium(IV) sulfate (A.R., B.D.H.) in calculated amount of standard sulfuric acid and was standardized against standard ammoniumiron(II) sulfate using *N*-phenylanthranilic acid as indicator.[15] Sodium hydrogensulfate solution of known concentration was prepared by partial neutralisation of standard sulfuric acid with calculated amount of standard sodium hydroxide solution. Glyoxylic acid (A.R., E. Merck) was used as such for oxidation studies. All other chemicals were of reagent grade. All the solutions were prepared from double distilled water, the second distillation being from alkaline $KMnO_4$ in an all-glass distillation set.

Kinetics

To follow the kinetics of the reaction, known amounts of sulfuric acid, perchloric acid, sodium hydrogensulfate and cerium(IV) solutions were transferred into a 50 ml reaction flask and allowed to equilibrate at the reaction temperature. In another flask solution of the substrate (to be oxidized) of known concentration was equilibrated at the same temperature. After thermal equilibrium was attained a known volume of the substrate was transferred to the reaction flask and the volume was made up to the mark with distilled water previously equilibrated at the same temperature. Aliquots of the reaction mixture were drawn out at known time intervals and the reaction was quenched in ice–cold water. The optical density of the quenched solutions was measured at preset wavelengths (410 and 430 nm for glyoxylato complex and 340 and 390 nm for glyoxylic acid). One cm matched quartz cells were used for all measurements, distilled water being taken as 100 precent transmission standard. The oxidations were carried out under second-order conditions.

Stoichiometry

Stoichiometry of the Ce(IV) oxidation of pentaammineglyoxylatocobalt(III) ion was determined as follows: Oxidation of this compound produced Co^{2+} as one of the products which was detected by the formation of the usual blue $[Co(SCN)_4]^{2-}$ species with NH_4SCN solution. To determine the stoichiometry of the reaction, to a known amount of complex solution was added cerium(IV) sulfate in 4 to 5 fold excess in presence of excess sulfuric acid and allowed to react at 35 °C. Two aliquots of the reaction mixture were withdrawn. One aliquot was added to a calculated volume of ice–cold sulfuric acid to quench the reaction.[9,10] The solution was diluted to a known volume and the optical density of this solution was measured at the wavelength mentioned earlier at which the molar extinction coefficient of Ce(IV) had been determined previously in a separate experiment. From the knowledge of the extinction coefficient and the optical density of the reaction mixture at any time *t*, unreacted

[Ce(IV)] at that time was calculated. In the second aliquot (after quenching the reaction under ice-cold conditions) [Co(II)] was determined spectrophotometrically using the method of Kitson.[16] In this context it may be noted that the parent cobalt(III) complex was found not to absorb at these wavelengths under the experimental conditions. The stoichiometry for glyoxylato complex was found to be one. To determine the stoichiometry of oxidation of glyoxylic acid, 4—5 fold excess of a known amount of cerium(IV) sulfate was added to a known amount of glyoxylic acid at room temperature. Aliquots of the reaction mixture were withdrawn from time to time and cooled to ice-temperature and the optical density of the mixture was measured at the wavelength mentioned earlier. After about 24 h the absorbance of the reaction mixture was found to be unchanged indicating complete oxidation of glyoxylic acid. The stoichiometry calculated as the ratio of [Ce(IV)] consumed to the total [glyoxylic acid] was found to be 2.

Second Order Rate Expression

In the concentration range studied, preliminary experiments showed that Co(II) and Ce(III) did not absorb in the wavelength range 340—430 nm (at which all optical density measurements were made), the only absorbing species being the cobalt(III) substrate and Ce(IV). Let (i) D_0 and D_t be the optical densities of the reaction mixture at "zero" time and at time "t" respectively, (ii) "x" moles of substrate (henceforward will be known as "sub") react with "y" moles of Ce (IV) at time "t" (iii) E_1 and E_2 be the extinction coefficients of the substrate and Ce(IV) respectively, it is possible to derive the relationship

$$x = (D_0 - D_t)/(E_1 + SE_2) \tag{1}$$

Where "S" is the stoichiometry of the reaction given by

$$y = Sx \tag{2}$$

Thus from the knowledge of S, D_0, D_t, E_1, and E_2 it was possible to calculate x and y from Eqs. 1 and 2 respectively and the observed second order rate constant, "k_{obsd}" from the second order rate expression (3)

$$\ln\frac{([\text{Sub}]_0 - x)}{([\text{Ce(IV)}]_0 - y)} = \ln\frac{[\text{Sub}]_0}{[\text{Ce(IV)}]_0} + (b[\text{Sub}]_0 - a[\text{Ce(IV)}]_0)k_{\text{obsd}}\cdot t \tag{3}$$

for the stoichiometric reaction: $a\,\text{Sub} + b\,\text{Ce(IV)} \rightarrow$ products ($a=b=1$ for glyoxylato complex; $a=1$ and $b=2$ for glyoxylic acid) The experimental results were found to fit best to the above second order rate expression (Eq. 3). The k_{obsd} values were calculated from this expression using the method of least squares with the IBM 1130 computer of Utkal University. The k_{obsd} values and the least squares deviation are collected in Tables 1 and 2. The rate was found not to vary with ionic strength in the range 1 to 2 M†.

Product Analysis

Both glyoxylic acid and glyoxylato complex were found to produce formic acid on oxidation. Following the method of Sengupta and Aditya,[17] formic acid was separated by distillation from the reaction mixture. It was detected by the usual tests and estimated by titrating it with standard potassium permanganate

TABLE 1. EFFECTS ON $[\text{HSO}_4^-]/[\text{H}^+]$ ON THE OBSERVED SECOND ORDER RATE CONSTANT (k_{obsd}) FOR THE Ce(IV)-OXIDATION OF GLYOXYLATO COMPLEX

$[\text{Complex}] = 2.0\times10^{-3}$ M and $[\text{Ce(IV)}] = 1.0\times10^{-3}$ M

$[\text{HSO}_4^-]$/M	$[\text{H}^+]$/M	$[\text{HSO}_4^-]/[\text{H}^+]$	k_{obsd}/$\text{M}^{-1}\,\text{s}^{-1}$	k_{calcd}/$\text{M}^{-1}\,\text{s}^{-1}$	k_{obsd}/$\text{M}^{-1}\,\text{s}^{-1}$	k_{calcd}/$\text{M}^{-1}\,\text{s}^{-1}$	k_{obsd}/$\text{M}^{-1}\,\text{s}^{-1}$	k_{calcd}/$\text{M}^{-1}\,\text{s}^{-1}$
			35+0.1 °C		40+0.1 °C		45+0.1 °C	
0.95	0.95	1.0	0.44±0.05	0.47	0.88±0.04	0.83	1.38±0.02	1.35
0.95	0.80	1.19	0.45±0.03	0.43	0.87±0.06	0.74	1.28±0.08	1.19
0.95	0.65	1.46	0.39±0.02	0.38	0.69±0.04	0.65	1.02±0.06	1.09
0.95	0.55	1.72	0.38±0.03	0.35	0.59±0.03	0.59	0.91±0.04	0.93
0.95	0.50	1.90	0.37±0.03	0.34	0.54±0.03	0.56	0.84±0.03	0.88
0.85	0.95	0.90	0.62±0.03	0.50	0.96±0.05	0.89	1.75±0.08	1.46
0.75	0.95	0.79	0.64±0.05	0.54	1.03±0.07	0.97	1.65±0.10	1.60
0.60	0.95	0.63	0.69±0.05	0.62	1.13±0.06	1.14	1.81±0.10	1.90
0.50	0.95	0.53	0.70±0.04	0.70	1.26±0.06	1.30	1.84±0.15	2.19
0.45	0.95	0.47	0.64±0.01	0.75	—	—	2.17±0.12	2.37
0.32	0.95	0.34	0.81±0.02	0.94	1.65±0.09	1.82	2.55±0.22	3.10
0.24	0.95	0.25	1.10±0.04	1.15	2.04±0.09	2.27	3.54±0.21	3.89
0.20	0.95	0.21	1.22±0.05	1.31	2.29±0.11	2.59	—	—
0.15	0.95	0.16	1.57±0.05	1.60	2.86±0.15	3.19	—	—
0.135	0.95	0.14	1.65±0.05	1.71	3.49±0.01	3.44	—	—
0.125	0.95	0.13	1.93±0.05	1.80	3.37±0.19	3.62	—	—
0.095	0.95	0.10	2.11±0.12	2.13	4.53±0.24	4.32	—	—

k_{calcd} stands for the rate constant calculated from Eq. 11 using the best values of k_1 and k_2.

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† 1 M=1 mol dm^{-3}.

TABLE 2. EFFECT OF $[HSO_4^-]/[H^+]$ ON THE OBSERVED SECOND ORDER RATE CONSTANT (k_{obsd}) FOR THE Ce(IV)-OXIDATION OF GLYOXYLIC ACID

[Glyoxylic Acid] = 2.5×10^{-5} M and [Ce(IV)] = 1.0×10^{-4} M

$[HSO_4^-]$/M	$[H^+]$/M	$[HSO_4^-]/[H^+]$	k_{obsd}/$M^{-1}\,s^{-1}$	k_{calcd}/$M^{-1}\,s^{-1}$	k_{obsd}/$M^{-1}\,s^{-1}$	k_{calcd}/$M^{-1}\,s^{-1}$	k_{obsd}/$M^{-1}\,s^{-1}$	k_{calcd}/$M^{-1}\,s^{-1}$
			40±0.1 °C		45+0.1 °C		50+0.1 °C	
0.95	0.95	1.0	18.54±0.35	21.63	31.55±0.32	32.06	49.29±0.71	48.74
0.95	0.80	1.19	18.11±0.18	18.44	28.44±0.38	27.14	39.84±1.05	41.27
0.95	0.55	1.72	14.82±0.23	12.92	18.62±0.30	19.01	33.72±0.63	28.91
0.95	0.50	1.90	14.50±0.78	11.72	17.96±1.35	17.25	26.30±0.50	26.23
0.85	0.95	0.90	24.38±0.47	24.06	34.13±0.15	35.40	53.70±1.2	53.87
0.75	0.95	0.79	29.85±1.49	27.21	39.69±0.89	40.07	—	—
0.60	0.95	0.63	33.00±0.54	33.51	48.56±1.32	49.35	—	—

k_{calcd} stands for the rate calculated from Eq. 12 using the best value of k_1.

solution.[18] It was found that 1 mole of formic acid was produced per mole of the substrate, *i.e.*, glyoxylic acid and glyoxylato complex. The stoichiometry of the reactions can be represented as

$$\mathrm{CHOCOOH + 2\,Ce(IV) + H_2O}$$
$$\mathrm{= 2Ce(III) + HCOOH + 2H^+ + CO_2}$$
$$\mathrm{[(NH_3)_5CoOCOCHO]^{2+} + Ce(IV) + H_2O + 4H^+}$$
$$\mathrm{= Ce(III) + HCOOH + Co^{2+} + CO_2 + 5NH_4^+}$$

Results and Discussion

In acidic sulfate media Ce(IV) exists mainly in form of three ionic species, namely, $[CeSO_4]^{2+}$, $Ce(SO_4)_2$, and $[Ce(SO_4)_3]^{2-}$ according to the following equilibria[12]:

$$\mathrm{Ce^{4+} + HSO_4^-} \overset{K_2}{\rightleftharpoons} \mathrm{[CeSO_4]^{2+} + H^+} \tag{4}$$

$$\mathrm{[CeSO_4]^{2+} + HSO_4^-} \overset{K_2}{\rightleftharpoons} \mathrm{Ce(SO_4)_2 + H^+} \tag{5}$$

$$\mathrm{Ce(SO_4)_2 + HSO_4^-} \overset{K_3}{\rightleftharpoons} \mathrm{[Ce(SO_4)_3]^{2-} + H^+} \tag{6}$$

It is obvious from the above three equilibria that the proportions of Ce^{4+} and the three sulfatocerate species in solution are determined by the amounts of free HSO_4^- and H^+ ions. It is possible to express the concentrations of the various Ce(IV) species in terms of the total cerium(IV) ion concentration and the stability constants K_1, K_2, and K_3 as under:

$$[\mathrm{Ce^{4+}}] = [\mathrm{Co(IV)}]_T/K_1K_2R^2(1+RK_3) \tag{7}$$

$$[\mathrm{CeSO_4^{2+}}] = [\mathrm{Ce(IV)}]_T/K_2R(1+RK_3) \tag{8}$$

$$[\mathrm{Ce(SO_4)_2}] = [\mathrm{Ce(IV)}]_T/(1+RK_3) \tag{9}$$

$$[\mathrm{Ce(SO_4)_3^{2-}}] = RK_3[\mathrm{Ce(IV)}]_T/(1+RK_3) \tag{10}$$

$$\text{where } R = [\mathrm{HSO_4^-}]/[\mathrm{H^+}]$$

The values of K_1, K_2, and K_3 at 25 °C and ionic strength 2.0 M have been reported to be 3500, 200, and 20 respectively.[12] The ratio $[HSO_4^-]/[H^+](=R)$ maintained throughout the present investigation is in the range 0.1 to 2.0. Eq. 7 indicates that $[Ce^{4+}]$ is negligibly small compared to $[Ce(IV)]_T$ (for example, when $R=1$, $[Ce^{4+}]$ is one in 14×10^6 and was not considered to be one of the reactive species). To determine the active cerium species the concentrations of the various sulfatocerate species were varied by varying $[HSO^-]_4/[H^+]$ ratio. Such a variation resulted in a change in the rate of oxidation indicating that one or more of the sulfatocerate species acted as the oxidizing species. $[HSO_4^-]/[H^+]$ could be varied by adding different amounts of $NaHSO_4$, H_2SO_4, and $HClO_4$ to the reaction medium such that

$$[\mathrm{HSO_4^-}] = [\mathrm{H_2SO_4}] + [\mathrm{NaHSO_4}]$$

and

$$[\mathrm{H^+}] = [\mathrm{H_2SO_4}] + [\mathrm{HClO_4}],$$

the dissociation of HSO_4^- was assumed to be negligible under the present experimental conditions.

In Ce(IV)–oxidation of substrates, in aqueous H_2SO_4 media, usually the formation of precursor complex[17,20,21] between the substrate and sulfatocerate species has been visualized. The formation of such complexes has been established spectrophotometrically:[9,10] Two solutions, one containing Ce(IV) and the other containing the substrate, both having the same amount of HSO_4^- and H^+, on mixing had optical density less than the sum of the optical densities of the two individual solutions. This method could be applied to systems where the rate of oxidation was slow enough such that there was no change in optical density due to oixdation during the spectral measurements. Unfortunately, the oxidation of glyoxylic acid and glyoxylato complex were too fast to establish the precursor complex formation by the above method though we have been successful in establishing this fact in the case of pentaamminebis(oxalato)cobalt(III) ions.[22] Therefore, we presume the complex formation between Ce(IV) and the substrates (glyoxylic acid and glyoxylato complex).

To establish the nature of the active cerium species, one and more than one species at a time were considered and the corresponding rate expression was deduced. The experimental data fitted best to the rate expression 11 in case of glyoxylato complex and 12 in case of glyoxylic acid.

$$k_{obsd} = (k_1+k_2K_3R)/(1+K_3R) \tag{11}$$

and

$$k_{obsd} = k_1/(1+K_3R) \tag{12}$$

Table 3. Rate and activation parameters of the Ce(IV)-oxidation of pentaammineglyoxylatocobalt(III) ion and glyoxylic acid

Substrate	Pentaammineglyoxylatocobalt(III)			Glyoxylic acid		
Temp/°C	35±0.1	40±0.1	45±0.1	40±0.1	45±0.1	50±0.1
k_1/M^{-1} s^{-1}	6.01±0.07	12.45±0.05	21.75±0.7	457.5±3.0	673.5±3.0	1023±7.5
k_2/M^{-1} s^{-1}	0.19±0.01	0.24±0.01	0.33±0.03	—	—	—
ΔH^*(kcal/mol), k_1-path		25.4±0.6			15.5±0.2	
ΔH^*(kcal/mol), k_2-path		9.5±2.0			—	—
ΔS^*(e.u.), k_1-path		27.5±0.2			3.0±0.1	
ΔS^*(e.u.), k_2-path		−31.0±0.6			—	

The known values of k_{obsd}, K_3, and R were used as the inputs and the parameters k_1 and k_2 were calculated by the method already indicated.[14] Value of K_3 has been reported by Hardwick and Robertson[12] to be 20 at $\mu=2.0$ M and temperature 25 °C while in the present investigation the reactions have been studied at $\mu=0.95$ M and at temperature range 35—50 °C. To examine the change, if any, of K_3 with the change of ionic strength and temperature we have measured K_3 values, following the method of Hardwick and Robertson, in the temperature range 30—40 °C and ionic strength 1.0 to 2.0 M and found K_3 to be temperature and ionic strength independent in this range. Therefore, the value of K_3 reported by these authors[12] has been used for the iteration process. The best values of k_1 and k_2 have been presented in Table 3. The activation parameters for the k_1 and k_2 paths, calculated from transition state equation, have been collected in Table 3.

The form of the rate laws 11 and 12 indicates that for glyoxylato complex the oxidation proceeds *via* two kinetic paths (k_1 and k_2) while for glyoxylic acid *via* k_1 path only. Assuming that oxidation proceeds *via* precursor complex formation between the substrate and the oxidant, $\mathrm{Ce(SO_4)_2}$ and $[\mathrm{Ce(SO_4)_3}]^{2-}$ are the oxidant species for glyoxylato complex, and only $\mathrm{Ce(SO_4)_2}$ is the oxidant for glyoxylic acid the following general reaction scheme may be written down:

$$\text{Substrate} + \mathrm{Ce(SO_4)_2} \overset{K_1'}{\rightleftharpoons} (\text{Complex})_1 \xrightarrow{k_1'} \text{Products}$$

$$\text{Substrate} + [\mathrm{Ce(SO_4)_3}]^{2-} \overset{K_2'}{\rightleftharpoons} (\text{Complex})_2 \xrightarrow{k_2'} \text{Products}$$

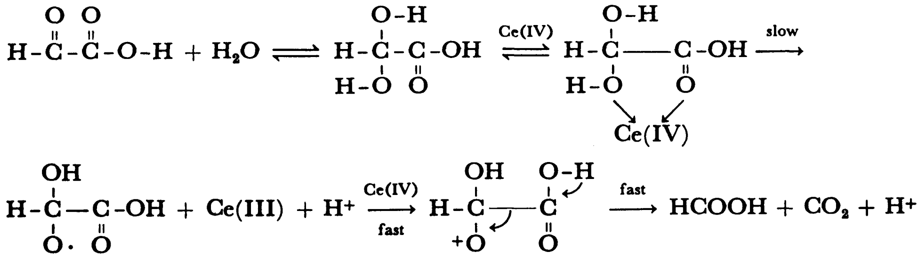
The rate of Ce(IV) loss, $-\mathrm{d[Ce(IV)]_T}/\mathrm{d}t$, is given by

$$-\frac{1}{b}\left(\frac{\mathrm{d[Ce(IV)]_{Total}}}{\mathrm{d}t}\right) = [\text{Substrate}]_{\text{Total}}\{k_1[\mathrm{Ce(SO_4)_2}] + k_2[\mathrm{Ce(SO_4)_3}^{2-}]\}$$

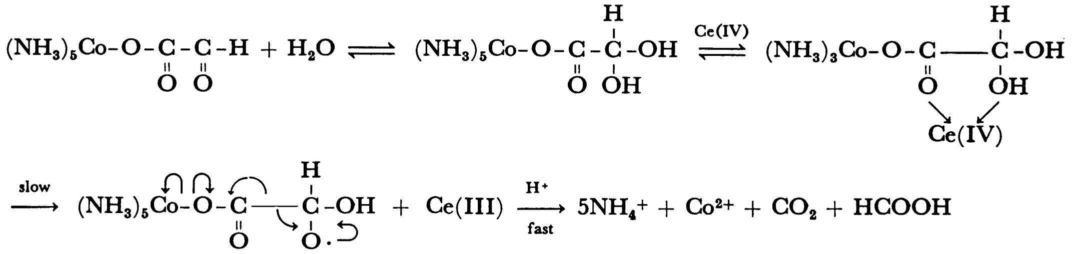
(where $k_1=k_1'K_1'$ and $k_2=k_2'K_2'$)

Substituting for $[\mathrm{Ce(SO_4)_2}]$ and $[\mathrm{Ce(SO_4)_3}^{2-}]$ from Eqs. 9 and 10 respectively, it is possible to show that the observed second order rate constant k_{obsd} is given by the expression 11. In the absence of k_2 path Eq. 11 reduces to Eq. 12. Thus kinetic results support that when glyoxylic acid is coordinated to positively charged $\mathrm{(NH_3)_5Co(III)}$ moiety, $[\mathrm{Ce(SO_4)_3}]^{2-}$, in addition to $\mathrm{Ce(SO_4)_2}$, acts as the oxidant species. This may be attributed to the fact that the substrate and the oxidant being oppositely charged, complex formation and subsequent electron transfer between them becomes favorable. The specific rate constants for the $\mathrm{Ce(SO_4)_2}$-path are greater than those for the $[\mathrm{Ce(SO_4)_3}]^{2-}$-path in case of the glyoxylato complex. This is again probably due to the greater complex forming ability of $\mathrm{Ce(SO_4)_2}$ with the substrate compared to $[\mathrm{Ce(SO_4)_3}]^{2-}$, *i.e.*, the precursor complex of $\mathrm{Ce(SO_4)_2}$ is considered to be innersphere type. Higher reactivity of glyoxylic acid compared to glyoxylato complex in $\mathrm{Ce(SO_4)_2}$-path is worth noting. This implies that when glyoxylate is coordinated to a positively charged center, electron transfer becomes difficult from electrostatic considerations. The lower reactivity of $[\mathrm{(NH_3)_5CoC_2O_4H}]^{2+}$ towards Ce(IV), compared to oxalic acid, has been similarly accounted for by Saffir and Taube.[3] The present kinetic results further indicate that $[\mathrm{CeSO_4}]^{2+}$ is not a reactive species for both the substrates which may be due to very low concentration of $[\mathrm{CeSO_4}]^{2+}$ under the present experimental conditions ($R=0.1$ to 2.0). For example, when $R=2$, Eqs. 8, 9, and 10 indicate that percentages of $[\mathrm{CeSO_4}]^{2+}$, $\mathrm{Ce(SO_4)_2}$, and $\mathrm{Ce(SO_4)_3}]^{2-}$ respectively are 0.002, 4.76, and 95.2. A possible mechanism consistent with our observations is delineated below:

1. Glyoxylic Acid



2. Glyoxylatopentaamminecobalt(III) Ion



The mechanism presented above invokes that the formation of a radical is rate limiting. Formation of such radicals in the oxidation of carboxylic acids by Ce(IV) has long since been suggested.[3,19,23] The reaction can also proceed *via* the formation of the radical at other donor atoms. Further, the reaction products can also be explained by a concerted mechanism suggested by Gould and Srinivasan.[24] However, with the kinetic results at hand it is not possible to answer all these questions.

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