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REDUCTION OF Ce(IV) BY CARBOXYLIC ACID IN SULPHATE MEDIUM PART 1. MONOCARBOXYLIC ACIDS

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ABSTRACT

The kinetics of reduction of Ce(IV) by a series of monocarboxylic acids in aqueous sulphuric acid solutions was followed spectrophotometrically. The reaction was found to be first order in both reactants with a rate constant independent of Ce(III) concentration and of ionic strength. The reactivity of the acids studied towards Ce(IV) increased in the following order, acetic <glycine <glycollic attributed to their chelating power. Activation parameters were evaluated and a mechanism was suggested which involves intermediate complex formation between Ce(IV) and the monocarboxylic acid prior to its decomposition as rate determining.

INTRODUCTION

Considerable work has been done on the kinetics of oxidation of organic compounds by Ce(IV) in perchlorate and sulphate media[1-5]. A systematic kinetic study of the oxidation of organic compounds in a series has only been recently made for cyclic alcohols[4], toluenes[5], and α-carboxylic acids[1-3], yet no attempt was made to correlate the rate data with the structural differences in these acids.

The present study is undertaken to investigate the effect of substitution in a monocarboxylic acid on its reaction with Ce(IV) sulphate. The acids studied are, acetic, monohydroxy-acetic (glycollic) and monoamino acetic (glycine) acids.

EXPERIMENTAL

Materials: Cerium sulphate (prolabo) pure grade was used without further purification. Acetic, glycollic and glycine acids were B.D.H., Analar or E. Merck G.R. quality.

A stock solution of Ce(IV) in 1M sulphuric acid was prepared by direct weighing and standardized. The reaction was initiated by adding a temperature equilibrated solution of the acid under investigation to the desired amount of Ce(IV) solution, sulphuric acid and water and was then followed spectrophotometrically using a Unicam Sp1800 spectrophotometer.

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RESULTS AND DISCUSSION

(1) Stoichiometry: The stoichiometry of each reaction was measured by allowing mixtures containing large excess of Ce(IV) to stand for several days and the excess Ce(IV) was estimated iodometrically. It was found that the molar ratios of Ce(IV) reacted per mole of the substrate studied are 1, 3, and 1 for acetic, glycollic and glycine acids, respectively.

(2) Kinetics of the Reaction: The reaction is first order in cerium (IV) total and some of the first order plots in excess of the substrate studied are shown in Fig. 1 and the values of the observed first order rate constants, k_o, were evaluated from the slopes of such lines. The order with respect to acetic acid is also one and the deviation from unity in case of glycollic and glycine is attributed to complexation, Table 1. Table 1, also shows that the reactivity of these acids towards Ce(IV) is in the following order: glycollic > glycine > acetic which is in good agreement with their formation constant towards Cu^{2+} or Zn^{2+} [6] except for glycine attributed to the protonation of its amino group in acidic solutions.

Variation in Ce(III) concentration in the range $0-8x10^{-2}M$ and in the ionic strength in the range 0.006 - 0.8M were found to have no influence on the reaction rate.

The effect of hydrogen ion concentration on the rate of reaction varied for each substrate studied, and accordingly a mechanism was suggested to account for the results obtained. The mechanism involves complex formation between two reactive Ce(IV) species in the medium under investigation, namely, the aquo and the hydroxo disulphate cerium (IV) [1, 7] and the predominant species of the substrate, namely, its unionized form, HA, prior to their decomposition with two rate determining steps.

$$Ce^{IV}(SO_4)_2 \overset{K_h}{\rightleftarrows} Ce^{IV}(SO_4)_2OH^- + H^+ \qquad (1)$$

$$Ce^{IV}(SO_4)_2 + HA \overset{K_1}{\rightleftarrows} Ce^{IV}(SO_4)_2.HA \qquad (2)$$

$$Ce^{IV}(SO_4)_2OH^- + HA \overset{K_2}{\rightleftarrows} Ce^{IV}(SO_4)_2.\bar{A} + H_2O \qquad (3)$$

$$Ce^{IV}(SO_4)_2.HA \xrightarrow{k_1} Ce(III) + \text{oxidation products} \qquad (4)$$

$$Ce(SO_4)_2.\bar{A} \xrightarrow{k_2} Ce(III) + \text{oxidation products} \qquad (5)$$

The mechanism suggested yields a first order rate constant of

$$k_o = (k_1K_1 + k_2K_2h^{-1})[HA]/1 + K_hh^{-1} + (K_1 + K_2K_hh^{-1})[HA] \qquad (6)$$

where $h^{-1} = 1/[H^+]$.

From equation (6), the reaction kinetics for each substrate studied is explained as follows:

(a) Acetic Acid: The linear dependence of $1/k_o$ versus $1/[HA]$, with no intercept, Fig. 2, together with an order of unity in the substrate, Table 1, justifies neglecting the value of $(K_1 + K_2K_h h^{-1})[HA]$ in the denominator of equation (6) together with unity compared to $K_h h^{-1} \approx 20$[8] and thus,

$$k_o = \{ \frac{k_1K_1}{K_h} [H^+] + k_2K_2\}[HA] \qquad (7)$$

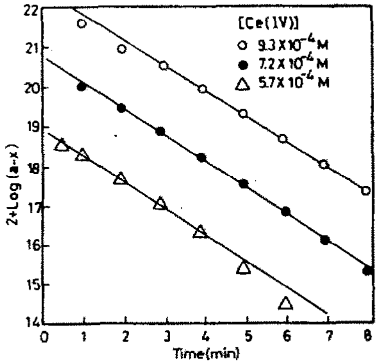


Fig.1 First order plots for glycollic acid at 36°C

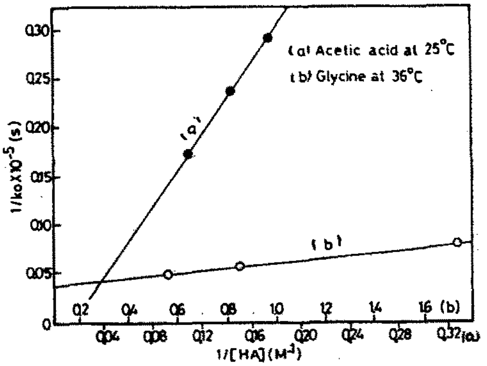


Fig.2 Variation of $1/k_o$ vs/1[HA]

(b) Glycine: When $1/k_o$ was plotted against $1/[HA]$, a straight line was obtained, Fig. 2, with an intercept attributed to complex formation and hence equation (6) reduces to equation (8) upon neglecting unity in the denominator.

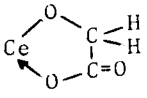
$$k_o = (k_1K_1 + k_2K_2K_h h^{-1})[HA] / K_h h^{-1} + (K_1 + K_2K_h h^{-1})[HA] \qquad (8)$$

(c) Glycollic Acid: The reaction is accelerated by hydrogen ions at low acidities reaching a maximum rate at $[H^+] \approx 0.03M$, thereafter the reaction became retarded by hydrogen ions. Similar observations were reported earlier by Jones et al[9] and Mehrotora[10] and was attributed to the variation in the reactive species involved in both media.

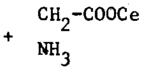
TABLE 1. Observed first and second order rate constants at varying substrate, HA, concentration.

Acetic acid at 25°C			Glycine at 36°C			Glycollic acid at 36°C		
$[H^+] = 0.79M$, $\mu = 8M$			$[H^+] = 3.6x10^{-3}M$, $\mu = 1.7M$			$[H^+] = 0.14M$, $\mu = 1.65M$		
$[Ce(VI)] = 4.5 \times 10^{-4}M$			$[Ce(IV)] = 5.1x10^{-4}M$			$[Ce(IV)] = 5.1x10^{-4}M$		
[HA] (M)	$k_o x10^4$ (s^{-1})	$k_b x10^5$ (mol $\ell^{-1}s^{-1}$)	[HA] (M)	$k_o x10^4$ (s^{-1})	$k_b x10^5$ (mol $\ell^{-1}s^{-1}$)	[HA] (M)	$k_o x10^4$ (s^{-1})	$k_b x10^5$ (mol $\ell^{-1}s^{-1}$)
5.71	0.34	0.60	0.57	1.25	21.9	0.28	7.03	25.10
6.86	0.42	0.61	1.14	1.82	15.9	0.55	16.30	29.60
9.4	0.58	0.64	1.71	2.07	12.1	1.10	25.00	22.70

The suggested mechanism equations (1-5) involves formation of complexes between Ce(IV) and the acid as intermediates during the reaction. This is essential for the transfer of an electron from the reductant to cerium (IV) with the simultaneous breaking of the C-C bond of the acid. This constitutes the first step in the reaction chain and is followed by a number of rapid steps to form the final products[1]. The suggested intermediates are given by the following formulae:



Ce(IV)glycollic,I



$$\overset{+}{NH_3}-CH_2-COOCe$$

Ce(IV)-glycine,II

CH_3COOCe

Ce(IV)-acetic,III

Intermediate I is believed to be a cyclic one[1], whereas intermediate II predicts the chelation to take place at the carboxylic group only, as the amino group is protonated in acidic solutions and thus explains the lower reactivity of glycine to that of glycollic acid, Table 1. Similar observations were reported earlier where the amino compounds were found to be far less reactive towards Ce(IV) $\approx 10^{-3}$ times, than the hydroxo ones[11]. The inductive effect of NH_3^+ in intermediate II, enhances the interaction of glycine with Ce(IV) as compared to the unsubstituted acid, acetic acid.

Values of 143.4, 89.4 and 47.4 kJ mol^{-1} were obtained for the energy of activation for acetic, glycine and glycollic acids, respectively. The corresponding values of the entropy of activation are 153.3, -19.8 and -136.4 $JK^{-1}mol^{-1}$. The high negative value for ΔS^* for glycollic acid supports the formation of a cyclic transition state and is due to the loss of translational and vibrational degrees of freedom.

The plot of ΔH^* and ΔS^* for catalyzed reactions is linear with a slope equal to 335°K which is the isokinetic temperarure. The isokinetic temperature is greater than the temperature range used in the present study (295-320°K) indicating that the reactions are enthalpy controlled.

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