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Oxidation of Substituted Glycollic Acids by Ce(IV) in Sulphuric Acid Solutions

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A comparison of the rate constants, dissociation constants, tendency of complex formation and catalytic activity of Mn(II) in the oxidation of substituted glycollic acids (benzilic, DL-atrolactic, 2-hydroxyisobutyric, *p*-chloromandelic, *p*-bromomandelic, mandelic and lactic acids) by Ce(IV) in sulphuric acid solutions has been made. Hydrolyzed species of Ce(IV) are reactive and the kinetics conform to the empirical rate law

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{kK[\mathrm{Ce(IV)}][\mathrm{Org.\ Acid}]}{[\mathrm{HSO_4^-}]^2([\mathrm{H^+}]+K[\mathrm{Org.\ Acid}])}$$

The reactivity and the chelating tendency of the acids seem to follow the substituent order, $C_6H_5>CH_3>H$. The catalytic activity of Mn(II) appears to follow the same order as in the oxidation of these acids by Mn(III).

Oxidation of glycollic acid by Ce(IV) has been studied by McAuley,[1] and Bakore *et al.* and rupture of C–H bond is said[2] to be rate determining. In the oxidation of substituted acids also, *i.e.*, mandelic and lactic acids, Krishna and Tewari,[3] and Bhargava *et al.*[4] assume the same mechanism, while Kemp and Waters[5] from their experiments with deuterated mandelic acid showed that the slow step preferably involves C–C bond breaking. A detailed systematic study was, therefore, considered desirable and the present paper reports and compares the rate and other data of the phenyl and methyl substituted acids.

Experimental

Reagents. Ceric sulphate (E. Merck G. R.) was used without further purification. Benzilic, mandelic, *p*-chloromandelic and *p*-bromomandelic acids were Riedel products. DL-Atrolactic and 2-hydroxyisobutyric acids were obtained from Koch-Light Co. All other chemicals were either B.D.H. Analar and E. Merck G. R. quality.

Preparation of Solutions. Ce(IV) solutions in sulphuric acid were prepared as described[6] earlier. Ceric perchlorate was prepared in the following way. Ceric ammonium hydroxide was precipitated from a solution of ceric ammonium nitrate by ammonium hydroxide. The precipitate was allowed to settle (48 hr), leached several times with water, dissolved in perchloric acid and filtered. Ce(IV) solutions were standardized against ferrous ammonium sulphate using *N*-phenyl anthralinic acid indicator. Solution of benzilic, mandelic, *p*-chloromandelic and *p*-bromomandelic acids were prepared by dissolving them in equivalent amounts of caustic soda and adjusting the pH between 6—8. 2-Hydroxyisobutyric acid was dissolved in hot water. All other acids were soluble in cold eater.

Kinetic Procedure. Reactions were carried out at 35±0.05°C in a thermostat. They were initiated by adding a temperature equilibrated solution of the organic acid to the reaction vessel containing the desired amount of ceric solution, sulphuric acid and water at 35°C. The kinetics were followed by removing a 10 m*l* aliquot portion after suitable intervals and quenching the reaction by adding it to a known excess of ferrous ammonium sulphate solution. The excess was determined against standard ceric solution using *N*-phenylanthranilic acid indicator. The maximum error in the analysis of the aliquots was ±0.02 m*l* of Ce(IV). This introduced an error of ±1 to 6% in the rate constants depending on the volume of the titrant. In most cases duplicate rate measurements were reproducible to ±5%.

Spectrophotometric Work. Optical density measurements were made on Beckmann spectrophotometer (DU-G 2400) using 1 cm cell. Measurements were carried out to obtain information about the complex formation between Ce(IV) and the organic acid. All the measurements were done in perchloric acid solutions because in sulphuric acid solutions strong sulphate complexes of Ce(IV) are formed, and any complex with the organic substrate, even if formed, would not be indicated spectrophotometrically.

Ionization Constants. Ionization constants of the organic acids were determined in water-dioxane (1:4 v/v) potentiometrically.

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1) A. McAuley, *J. Chem. Soc.*, **1965**, 4054.

2) G. V. Bakore, R. Dayal and P. Nath, *Z. Physik. Chem.*, **227**, 19 (1964).

3) B. Krishna and K. C. Tewari, *J. Chem. Soc.*, **1961**, 3097.

4) K. P. Bhargava, R. Shankar and S. N. Joshi, *J. Sci. Ind. Res., India*, **218**, 573 (1963).

5) T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, **1964**, 1192.

Stoichiometry. The stoichiometry was determined as described[6] earlier. In each case two moles of Ce(IV) were used up by one mole of the organic acid. The products of oxidation, benzophenone, *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde, methyl ethyl ketone and acetone were estimated either as such or as hydrazones. The yields were 70—80%. The volume of carbondioxide was measured in case of benzilic acid and was found to be about 90% of the expected amounts. Stoichiometry for lactic and glycollic acids was not determined, but it is reported[3] to be 5.75 and 4 mol of Ce(IV) for each mole of the acid respectively.

Products. The products of oxidation of the organic acids were as follows:

Benzilic acid - benzophenone; *p*-chloromandelic acid - *p*-chlorobenzaldehyde; *p*-bromomandelic acid - *p*-bromobenzaldehyde; DL-atrolactic acid - methyl phenyl ketone; 2-hydroxyisobutyric acid - acetone. Products of oxidation of lactic and glycollic acids have already been identified. Benzophenone and *p*-bromobenzaldehyde were obtained as white insoluble solid from concentrated solution. They were recrystallised from alcohol or benzene and were identified by melting points, IR spectra and other tests. In the case of *p*-chloromandelic acid, the white crude solid product responds to the tests of *p*-chlorobenzaldehyde, but it undergoes slow air oxidation yielding the acid. It is interesting to note, however, that experiments on stoichiometry indicate no oxidation of *p*-chlorobenzaldehyde by Ce(IV). Acetone was identified in the form of hydrazone. Methyl phenyl ketone was obtained as a solid at about 0°C and was identified by the melting point and its characteristic hydrazone.

Results and Discussion

The orders with respect to the various reactants conform to either of the following two empirical rate laws:

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{k_{11}[\mathrm{Ce(IV)}][\mathrm{Org.\ Acid}]}{[\mathrm{HSO_4^-}]^2[\mathrm{H^+}]} \qquad (1)$$

and

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{kK[\mathrm{Ce(IV)}][\mathrm{Org.\ Acid}]}{[\mathrm{HSO_4^-}]^2([\mathrm{H^+}]+K[\mathrm{Org.\ Acid}])} \qquad (2)$$

The results are shown in Table 1 and Figs. 1 and 2. Although kinetic evidence for complex formation has been obtained[6] only in the case of benzilic acid, spectrophotometric results provide evidence in all the cases and hence in general, rate law (2) appears to be applicable in all the cases. The various equilibria,[6–9] involving the cerium(IV) species and the mechanism are given below:

$$\mathrm{Ce^{4+} + H_2O \overset{K_{h1}}{\rightleftharpoons} CeOH^{3+} + H^+} \qquad (3)$$

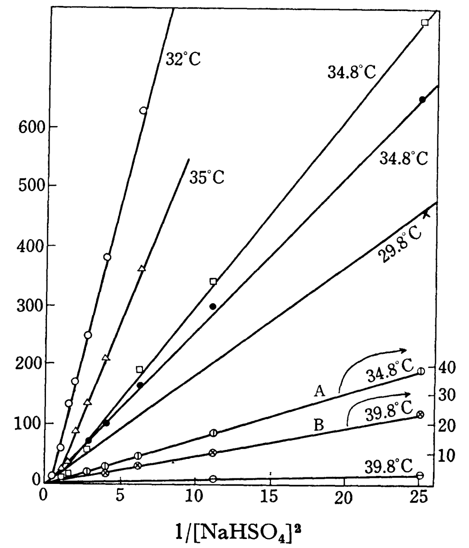


Fig. 1. Effect of bisulphate ion.
[HClO$_4$]=0.5M. ○, benzilic acid; △, atrolactic acid; ●, mandelic acid; □, *p*-chloromandelic acid; ×, *p*-bromomandelic acid; ⦶, 2-hydroxy isobutyric acid; ⊗, lactic acid; ⊖, glycollic acid. Straight lines A and B refer to the right scale.

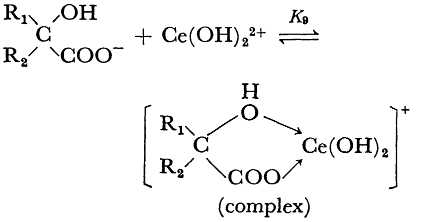
$$\mathrm{CeOH^{3+} + H_2O \overset{K_{h2}}{\rightleftharpoons} Ce(OH)_2^{2+} + H^+} \qquad (4)$$

$$\mathrm{Ce^{4+} + HSO_4^- \overset{K_5}{\rightleftharpoons} CeSO_4^{2+} + H^+} \qquad (5)$$

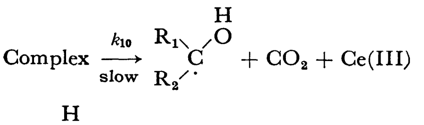
$$\mathrm{CeSO_4^{2+} + HSO_4^- \overset{K_6}{\rightleftharpoons} Ce(SO_4)_2 + H^+} \qquad (6)$$

$$\mathrm{Ce(SO_4)_2 + HSO_4^- \overset{K_7}{\rightleftharpoons} HCe(SO_4)_3^-} \qquad (7)$$

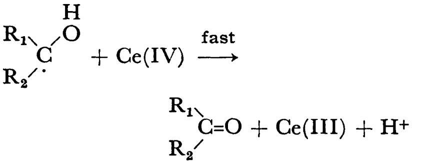
$$\mathrm{Org.\ Acid \overset{K_d}{\rightleftharpoons} Anion + H^+} \qquad (8)$$



(9)



$$\mathrm{Complex \xrightarrow[slow]{k_{10}} R_1R_2\dot{C}OH + CO_2 + Ce(III)} \qquad (10)$$



$$\mathrm{R_1R_2\dot{C}OH + Ce(IV) \xrightarrow{fast} R_1R_2C{=}O + Ce(III) + H^+} \qquad (11)$$

The predominant species[8,9] of Ce(IV) is Ce(SO$_4$)$_2$ in bisulphate solutions employed in this work, but the reactive species as indicated by bisulphate and hydrogen ion effects, is Ce(OH)$_2^{2+}$. The rate law can be deduced only on such basis.

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The above equations and equilibria lead to the rate law

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{2k_{10}K_9K_{h1}K_{h2}K_d[\mathrm{Ce(IV)}][\mathrm{Org.\ Acid}]}{K_5K_6[\mathrm{HSO_4^-}]^2([\mathrm{H^+}]+K_9K_d[\mathrm{Org.\ Acid}])} \tag{12}$$

which has the same form as (2). An alternative mechanism conforming to the rate law (1) is as follows.

$$\mathrm{Ce(OH)_2^{2+}} + \text{Anion} \xrightarrow{k_{13}} \text{Org. free radical} + \mathrm{CO_2} + \mathrm{Ce(III)} + \mathrm{H^+} \tag{13}$$

$$\text{Org. free radical} + \mathrm{Ce(IV)} \xrightarrow{\text{fast}} \text{product} + \mathrm{Ce(III)} \tag{14}$$

The complete rate law similar to (1) is:

$$-\frac{d[\mathrm{Ce(IV)}]}{dt}=\frac{2k_{13}K_{h1}K_{h2}K_d[\mathrm{Ce(IV)}][\mathrm{Org.\ Acid}]}{K_5K_6[\mathrm{HSO_4^-}]^2[\mathrm{H^+}]} \tag{15}$$

These rate laws explain the observed order of the bisulphate ion. The rate decreases by the increase of hydrogen ion too, but a plot of k_{11} (observed second order rate constant) against $1/\mathrm{H^+}$ does not yield a straight line as expected from (1) or (15). Thus these rate laws are not of the correct form so far as hydrogen ion dependence is concerned. On the other hand (2) or (12) conform to the observed hydrogen ion dependence (Fig. 2), but absence of kinetic evidence for complex formation does not justify their forms. Unfortunately the study with regard to hydrogen ion effect and complex formation could not be made under identical conditions. The effect of hydrogen ion was studied by varying perchloric acid concentration in a constant bisulphate medium. The reaction was fast in this medium. It could be made of measurable speed only by employing low concentrations of the reactants, particularly the organic acid, and consequently a study of complex formation could not be made.

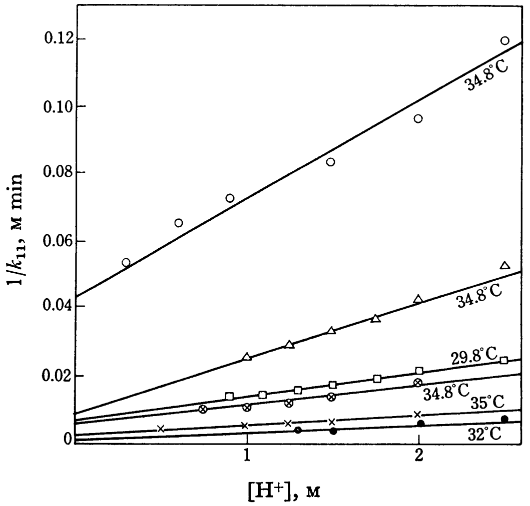

Fig. 2. Effect of hydrogen ions.
○, 2-hydroxy isobutyric acid, $[\mathrm{HSO_4^-}]=0.4$M
△, *p*-chloromandelic acid, $[\mathrm{HSO_4^-}]=1.0$M
□, *p*-bromomandelic acid, $[\mathrm{HSO_4^-}]=0.5$M
⊗, mandelic acid, $[\mathrm{HSO_4^-}]=0.5$M
×, atrolactic acid, $[\mathrm{HSO_4^-}]=0.5$M
●, benzilic acid, $[\mathrm{HSO_4^-}]=1.0$M

Under such a situation, in view of the general characteristics of Ce(IV) oxidation of hydroxy acids, tendency of complex formation from optical density measurements and kinetic evidence for the complex formation in the oxidation of benzilic acid,[6] we are inclined to regard (12) as the correct form of the rate expression. However, since no kinetic evidence for complex formation has been obtained in other cases, it is better to retain it in the same form but with 'A' as unspecified constant in the denominator in place of K_9K_d[Org. Acid]. The second order rate constant, k_{11} which has no reference to Eq. (11) can be defined by

$$k_{11}=\frac{2k_{10}K_9K_dK_{h1}K_{h2}}{K_5K_6[\mathrm{HSO_4^-}]^2([\mathrm{H^+}]+\mathrm{A})} \tag{16}$$

Table 1. PSEUDO-FIRST ORDER AND SECOND ORDER RATE CONSTANTS OF THE REACTION BETWEEN Ce(IV) AND THE ORGANIC ACIDS IN SULPHURIC ACID SOLUTIONS
$[\mathrm{Ce(IV)}] = 5\times10^{-4}$M

$[\mathrm{H_2SO_4}]$ M	[Org. Acid] M $\times10^3$	Pseudo-first order rate constant $k_1\times10$ min^{-1}	$k_{11}=k_1/$[Org. Acid] l/mol·min
	DL-Atrolactic acid, t=35°C		
1.5	6.44	1.70	26.4
1.5	5.52	1.44	26.8
1.5	5.06	1.33	26.3
2.0	6.44	0.81	12.6
2.0	4.60	0.60	13.0
2.5	5.52	0.35	6.5
2.5	4.60	0.28	6.0
	2-Hydroxyisobutyric acid, t=34.8°C		
0.5	14.0	1.10	7.8
0.5	10.0	0.80	8.0
0.5	7.0	0.56	8.0
0.75	16.0	0.58	3.62
0.75	7.0	0.25	3.57
	p-Chloromandelic acid, t=34.8°C		
1.0	5.0	0.97	19.4
1.0	10.0	1.96	19.6
1.5	6.0	0.42	7.0
1.5	15.0	1.07	7.1
	p-Bromomandelic acid, t=29.8°C		
1.0	6.0	0.62	10.3
1.0	12.0	0.12	10.0
1.5	4.5	0.19	4.2
1.5	10.0	0.42	4.2
	Benzilic acid, t=32°C		
1.5	2.0	2.26	113
1.5	3.5	3.68	103
2.0	1.5	0.78	52
2.0	4.5	2.13	47

TABLE 2. OXIDATIONS OF SUBSTITUTED GLYCOLLIC ACIDS BY Ce(IV)
10^3[Ce(IV)]=1.0 M; [H_2SO_4]=1.0 M, t=35°C

Acid	Concn. M × 10^4	k_{11} l/mol·sec × 10^2	Ionization constant × 10^5	Maxima of the complex in the UV spectrum mμ	k_{Mn} l/mol·sec × 10^{-4}	E_a kcal
Benzilic	5.0	560	17.80	255	33 (2M H_2SO_4, 32°C)	18.7 (1.0M H_2SO_4)
DL- Atrolactic	5.0	113	8.320	242	14 (1.5M H_2SO_4, 34.8°C)	21.3 (1.5M H_2SO_4)
p-Chloromandelic	5.0	66.6	14.45	256	2.4 (1M H_2SO_4, 34.8°C)	19.8 (0.5M H_2SO_4)
p-Bromomandelic	5.0	64.4	12.88	255	2.0 (0.5M H_2SO_4, 29.8°C)	19.7 (0.5M H_2SO_4)
Mandelic	5.0	58.8	10.96	251	—	19.9 (1.0M H_2SO_4)
2-Hydroxyisobutyric	160	3.90	3.80	flat band 245—255	1.0 (0.5M H_2SO_4 34.8°C)	23.2 (0.5M H_2SO_4)
Lactic	160	1.60	4.40	flat band 245—255	—	27.4 (0.5M H_2SO_4)
Glycollic	400	0.11	6.17	flat band 245—255	—	25.5 (0.15M H_2SO_4)

Ce(IV) oxidation in general is without any isotopic effect as shown by Waters and coworkers in the oxidation of deuterated alcohols[10] and mandelic acid.[5] We have also carried out rate experiments with deuterated acids and the ratio k_H/k_D was in no case more than 1.1. Hence C–C fission is considered to be rate determining in the oxidation. The products of oxidation of the organic acids also support the involvement of C–C cleavage in the slow step. On the other hand Cr(VI) and V(V) oxidation is characterized by large isotopic effect suggesting C–H fission. Reactions in the presence of acrylamide further show that C–C fission occurs with the evolution of carbon dioxide. Acrylamide does not react[11] with Ce(IV), but it captures the free radical produced in step (10). This strongly suggests that carbon dioxide is produced in the slow step rather than in the fast step suggested by other workers.[2,3,12]

Mn (II) greatly catalyzes all these oxidations as is obvious from Fig. 3. These results can be expressed in the form

$$k_T = k_{11} + k_{Mn}[\mathrm{Mn(II)}] \qquad (16a)$$

where k_T and k_{11} are the rate constants in the presence and absence of Mn(II) and k_{Mn} is the specific rate constant for the catalyzed path. The catalytic activity of Mn(II) is ascribed to the rapid equilibrium[13]

$$\mathrm{Ce(IV)} + \mathrm{Mn(II)} \rightleftharpoons \mathrm{Ce(III)} + \mathrm{Mn(III)} \qquad (17)$$

and the larger rate[5,14] for the oxidation of the organic acids by Mn(III). Table 1 shows the various data for all the acids. Mandelic acid is more readily oxidized than 2-hydroxyisobutyric acid[14] or lactic acid[15] by Mn(III) sulphate. Some visual observations have also indicated that the order of oxidation of different acids by Mn(III) is the same as given by the values of k_{Mn} of Table 2.

Spectrophotometric results indicate complex formation between Ce(IV) and the organic acid. Absorption curves typical of complex formation have

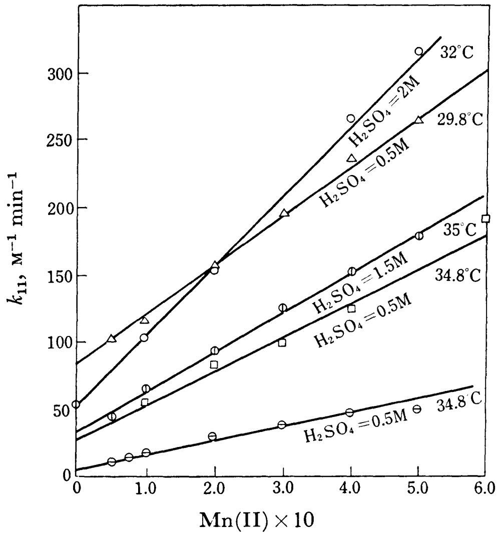

Fig. 3. Effect of Mn(II) on the oxidations of organic acids by Ce(IV).
○, benzilic acid; △, p-bromo mandelic acid; □, p-chloro mandelic acid; ⦶, atrolactic acid; ⊖, 2-hydroxy isobutyric acid

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been shown earlier[6] in the oxidation of benzilic acid. Similar curves were obtained for mandelic, *p*-chloromandelic, *p*-bromomandelic and DL-atrolactic acids. Flat bands with less absorption than that of Ce(IV) were obtained in case of 2-hydroxyisobutyric, lactic and glycollic acids. Complex formation seems to depend on two factors; the ionization constant of the organic acid and the substituted group C_6H_5 or CH_3 for H in CH_2. The ionization constants are in the sequence as expected from the $-I$ effect of C_6H_5 and $+I$ effect of CH_3 groups, it being largest for two C_6H_5 groups (benzilic acid) and lowest for two CH_3 groups (2-hydroxyisobutyric acid). The larger the ionization constant the greater is the tendency of complex formation as is obvious from Eq. (9). Another factor which seems to influence this tendency is the size of the group. A bulky group like C_6H_5 in benzilic acid facilitates complex formation. The larger value of the equilibrium constant[16] in case of *trans*-1,2-cyclohexanediol than that of *trans*-2-methoxycyclohexanol, has been explained on the basis of the steric hindrance. The same reason has been assigned to the failure for the complex formation by 2,3-butanediol as compared to ethylene glycol.[10] At first sight the formation of a complex in case of benzilic acid seems to violate the principle of steric hindrance, but closer examination would reveal that the steric hindrance of the phenyl groups brings the hydroxyl and the carboxyl groups closer facilitating the chelate formation with Ce(IV). On the other hand in case of *trans*-2-methoxy-cyclohexanol and 2,3-butanediol the substitution is in the hydroxyl group which may prevent the chelate formation. No maximum was obtained for lactic and 2-hydroxyisobutyric acids. On the other hand the corresponding absorption curves run below the curve of Ce(IV). A probable explanation for this may be the fact that the steric effect of the methyl group is less important than its inductive effect as suggested,[17] in the rare earth chelates of these organic acids. Kinetic evidence for the complex formation was obtained only in the case of benzilic acid obviously because both the factors, inductive and steric effects of the phenyl group act in the same direction.

The order of reactivity of different acids in general can be explained on the basis of free radical character developing in the activated complex at the carbon atom.[19] The formation of free radical is facilitated by the substituents of R in the order $C_6H_5 \gg CH_3 > H$.

k_{11} of Table 2 is a complex rate constant. It may be regarded as a product kK, where k and K are rate and equilibrium constants, respectively. It has not been possible to separate these two constants but it appears that the overall rate constant k_{11} follows the same order as that of the tendency of complex formation. Co(III) and V(V) oxidation of these acids also probably takes place *via* complex formation. The overall rate constants are in the same order, *i.e.*, atrolactic>mandelic>2-hydroxyisobutyric>lactic in 3.14M $[ClO_4^-]$ at 15°C in the case of Co(III)[20,21] and, mandelic>2-hydroxyisobutyric>lactic in 5M $[ClO_4^-]$ at 25°C in the case of V(V).[22]

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