OXIDATION OF α-HYDROXY ACIDS WITH QUINOLINIUM DICHROMATE – A KINETIC STUDY

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Received April 22, 1992
Accepted March 16, 1993

Oxidations of lactic acid, α-hydroxyphenyllactic acid and its 4-chloro derivative with quinolinium dichromate (QDC) in 30% (v/v) aqueous acetic acid at 303 K are first-order in QDC and first-order in hydroxy acids. The reactions are acid-catalyzed and a medium of low dielectric constant favours the oxidation. The products are the corresponding aldehydes. Thermodynamic parameters are evaluated and a mechanism involving a C–C bond cleavage is proposed.

A variety of chromium trioxide complexes have been recently prepared[1 – 5], and tested to be effective oxidants. Quinolinium dichromate (QDC) is one of them. As a part of our broad scheme on the reaction kinetics of organic substrates, we have studied the kinetics of oxidation of α-hydroxy acids with QDC. The results indicate that the oxidation of these bifunctional compounds with QDC and $K_2Cr_2O_7$ follow different mechanistic pathways[6]. The present paper deals with the results of the oxidation of lactic acid (*I*), α-hydroxyphenyllactic acid (*II*) and its 4-chloro derivative (*III*) with quinolinium dichromate.

EXPERIMENTAL

All the chemicals used were of analytical grade. Quinolinium dichromate (QDC) was prepared by dissolving chromium trioxide in water, adding quinoline and collecting the product[4]. Standard solutions of QDC were prepared in aqueous acetic acid by dissolving a weighed quantity of the oxidant in a known volume of the solvent. The acids *I*, *II*, *III* and benzilic acid (*IV*) were used without further purification. Their solutions were prepared in distilled water by dissolving known amounts of the acids and their concentrations were checked by titration with standard alkali.

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All the kinetic experiments were conducted in 30% (v/v) aqueous acetic acid at 303 K. The temperature was maintained constant within ±0.2 °C. The reaction mixture consisted of QDC (0.002 mol l^{-1}), hydroxy acid (0.04 mol l^{-1}) and sulfuric acid (0.5 mol l^{-1}). The progress of the reaction was followed by determining the unreacted QDC iodometrically at regular time intervals. Then log $[QDC]_t$ was plotted against time and the plots were found to be linear. From the slopes of these plots, the pseudo-first-order rate constants (k_{obs}) were obtained. The values of k_{obs} were found to be reproducible within 5%.

Aqueous acetic acid did not undergo oxidation with QDC under the experimental conditions. The added acrylonitrile did not polymerize thus indicating the absence of one-electron oxidation steps in the reaction system.

In a typical run with *I*, the reaction mixture, after completion of the reaction, was extracted with ether. TLC analysis of the extract using benzene as eluent indicated benzaldehyde after comparing with an authentic sample. This was further confirmed by preparation of some derivatives. The melting points of the 2,4-dinitrophenylhydrazone and semicarbazone were 235 °C and 224° C, respectively. (The literature[7] gives 237 °C and 224 °C, respectively).

RESULTS AND DISCUSSION

Under the conditions of much greater concentrations of the hydroxy acids than those of QDC the pseudo-first-order plots of log [QDC] vs time at different initial concentrations of QDC (0.001 to 0.005 mol l^{-1}) are all linear with nearly the same slope indicating the first-order dependence of the rate on QDC (Table I). In order to know the effect of the concentration of hydroxy acid on the rate of oxidation, the k_{obs} values are determined at different concentrations of hydroxy acids in the range 0.02 to 0.1 mol l^{-1} (Table II). The double logarithmic plots of log k_{obs} vs log [hydroxy acid] are linear with unit slopes, suggesting that the oxidation process is strictly first-order with respect to hydroxy acid. The double reciprocal plots of k_{obs}^{-1} vs $[\text{hydroxy acid}]^{-1}$ are also linear.

The oxidation was found to be acid-catalyzed. The k_{obs} values, determined at increasing concentrations of H_2SO_4 in the range 0.1 – 1.5 mol l^{-1}, increase (Table III). The slopes of the linear double logarithmic plots of log k_{obs} vs log $[H^+]$ suggested that the order of the reaction with respect to $[H^+]$ is not an integer. For the purpose of calculation of $[H^+]$, it was assumed that H_2SO_4 releases only one proton in the concentration range used in 30% (v/v) aqueous acetic acid medium. To study the influence of the

TABLE I

Oxidation of hydroxy acids with quinolinium dichromate in 30% (v/v) aqueous acetic acid at 303 K. Effect of initial concentration of quinolinium dichromate on k_{obs} (. 10^4, s^{-1}). $[HA]_0$ = 0.04 mol l^{-1}, $[H_2SO_4]$ = 0.5 mol l^{-1}

Hydroxy acid	$[QDC]_0$, mol l^{-1}			
	0.001	0.002	0.004	0.005
I	4.44	4.61	4.76	4.64
II	12.22	12.41	12.41	12.38

medium composition on the rate of oxidation, the reaction was investigated in 30 – 70% (v/v) aqueous acetic acid. An increase in the acetic acid content of the medium enhanced the rate of oxidation (Table IV). Further, the plots of log k_{obs} against the reciprocal of the dielectric constant of the medium are linear with the slopes +37.0 and +35.0 in the case of acids *I* and *II*, respectively. This observation suggests an ion–dipo-

TABLE II

Oxidation of hydroxy acids with quinolinium dichromate in 30% (v/v) aqueous acetic acid at 303 K. Effect of initial concentration of hydroxy acid on k_{obs} (. 10^4, s^{-1}). $[QDC]_0 = 0.002$ mol l^{-1}, $[H_2SO_4] = 0.5$ mol l^{-1}

Hydroxy acid	$[HA]_0$, mol l^{-1}			
	0.02	0.04	0.08	0.10
I	–	4.61	9.55	11.65
II	6.41	12.41	21.99	–

TABLE III

Oxidation of hydroxy acids with quinolinium dichromate in 30% (v/v) aqueous acetic acid at 303 K. Effect of initial concentration of H_2SO_4 on k_{obs} (. 10^4, s^{-1}). $[QDC]_0 = 0.002$ mol l^{-1}, $[HA]_0 = 0.04$ mol l^{-1}

Hydroxy acid	$[H_2SO_4]$, mol l^{-1}					
	0.1	0.2	0.5	0.8	1.0	1.5
I	2.06	3.07	4.61	5.42	5.87	–
II	5.27	8.10	12.41	–	16.53	19.50

TABLE IV

Oxidation of hydroxy acids with quinolinium dichromate in aqueous acetic acid medium at 303 K. Effect of concentration of acetic acid on k_{obs} (. 10^4, s^{-1}). $[QDC]_0 = 0.002$ mol l^{-1}, $[HA]_0 = 0.04$ mol l^{-1}, $[H_2SO_4] =$ 0.5 mol l^{-1}

Hydroxy acid	[AcOH], % (v/v)			
	30	40	60	70
I	4.61	5.63	11.37	24.60
II	12.41	15.35	30.10	53.41
III	12.05	–	–	–

le type interaction between the reactants[8]. An increase in ionic strength of the medium by adding Na_2SO_4 to the reaction mixture, decreased the rate of the reaction supporting the above statement. From these observations a possible rate law for the oxidation process can be given as

$$-\frac{d[QDC]}{dt} = k\,[\text{hydroxy acid}]\,[QDC]\,[H^+]^x \qquad (x < 1)\,. \tag{1}$$

The stoichiometric study indicates that two moles of *I* or *II* are oxidized by one mole of the oxidant. k_{D_2O}/k_{H_2O} was found to be 1.5 as expected for any acid-catalyzed process.

Oxidation of α-hydroxy acids with different oxidants[6,9 – 13] is known to proceed either with a C–H cleavage to give keto acid or with a C–C cleavage by a concerted mechanism leading to a carbonyl compound. Under similar experimental conditions, benzilic acid, which has no α-hydrogen atom, is also oxidized with QDC, with a k_{obs} value of $1.0 \,.\, 10^{-3}\ s^{-1}$. This relative ease of oxidation of benzilic acid with QDC suggests that the oxidation of α-hydroxy acids with QDC does not proceed with C–H bond cleavage.

Keeping these observations in mind a probable mechanism shown in Scheme 1 is suggested. It involves the slow formation of a chromate ester with HA. The subsequent fast step involves a C–C cleavage leading to a concerted oxidative decarboxylation yielding aldehyde as the product of the oxidation. The other product obtained from the oxidant can further oxidize another molecule of substrate leading to a stoichiometry of 1 : 2 which has been experimentally observed.

This leads to the rate expression

$$-\frac{d[QDC]}{dt} = \frac{K_1\,k_2\,[HA]\,[QDC]\,[H^+]}{1 + K_1\,[H^+]}\,, \tag{2}$$

which is consistent with the observed rate law in Eq. (*1*).

From Eq. (*2*) it can be shown that:

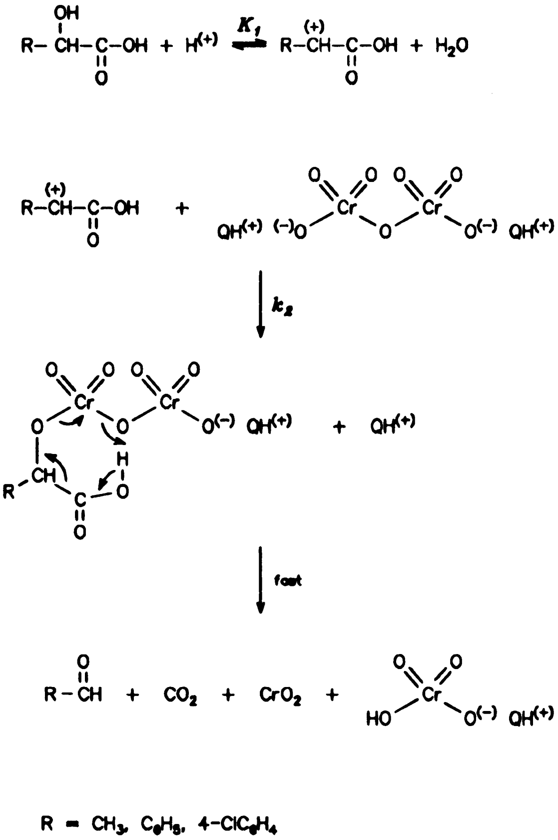
$$k_{obs} = \frac{K_1\,k_2\,[HA]\,[H^+]}{1 + K_1\,[H^+]}\,, \tag{3}$$

$$k_{obs}^{-1} = \frac{1}{k_2\,[HA]} + \frac{1}{K_1\,k_2\,[HA]}\,\frac{1}{[H^+]}\,. \tag{4}$$

Equation (*4*) shows that the plot k_{obs}^{-1} against $[H^+]^{-1}$ should be linear with a positive intercept and positive slope. This is confirmed in Fig. 1. From the value of the intercept, k_2, the rate constant of the formation of chromate ester can be determined. These values for *I* and *II* are $1.786 \cdot 10^{-2}$ and $5.21 \cdot 10^{-2}$ l mol^{-1} s^{-1}, respectively.

Among the three hydroxy acids studied the order of reactivity is *I* < *II* ≈ *III*. The low reactivity of *I* can be attributed to the electron-donor nature of the methyl group which does not facilitate the C–C cleavage shown in Scheme 1. The introduction of chlorine in the para position of the benzene ring has no effect on rate. Perhaps in *III*, the electronic effect on rate is not felt because of the great distance between Cl and the reaction centre.

The possibility of further oxidation of aldehyde with QDC under the experimental conditions has also been checked. Under similar experimental conditions, the k_{obs} values for the oxidation of *II* and benzaldehyde by QDC are $12.41 \cdot 10^{-4}$ and $0.21 \cdot 10^{-4}$ s^{-1}, respectively, indicating that further oxidation of benzaldehyde is negligible.



Scheme 1

The reactions were studied at different temperatures in the range 293 – 318 K and activation parameters E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were evaluated (Table V). The activation energies E_a vary between 45 – 33 kJ mol^{-1}. These low E_a values support the proposed concerted mechanism. The high negative values of activation entropies support the assumption of highly solvated transition state due to its increased polarity. They are also indicative of bimolecular rate-determining step[14] as shown in Scheme 1. $\Delta G^{\neq}$ values are nearly constant suggesting that the three hydroxy acids studied are oxidized by a similar mechanism.

Kemp and Waters[6] studied the kinetics of oxidation of α-hydroxy acids with chromic acid in perchloric acid. Basing on the difference in the ease of oxidizability of α-hydroxyisobutyric acid (havind no α-hydrogen atom) and α-hydroxyphenylacetic acid (oxidation leading to keto acid), they suggested C–H bond cleavage to be the rate-

TABLE V

Oxidation of hydroxy acids with quinolinium dichromate in 30% (v/v) aqueous acetic acid at 293 – 318 K. Activation parameters[a]

Hydroxy acid	E_a, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
I	33.28	30.76	−180	85.51
II	44.36	41.85	−135	83.01
III	38.29	35.78	−156	83.09

[a] For initial concentrations see Table IV.

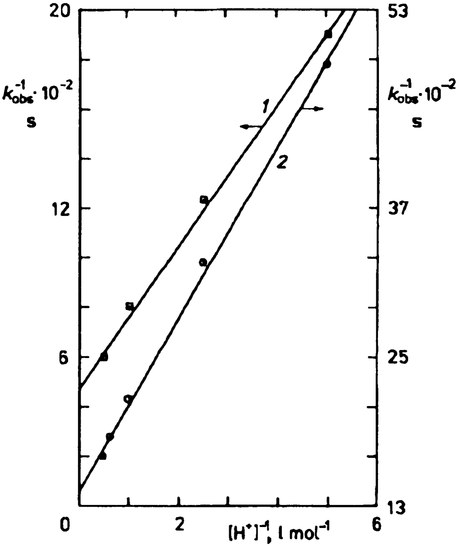


FIG. 1

Plot of k_{obs}^{-1} vs $[H^+]^{-1}$ for the oxidation of *1* α-hydroxyphenyllactic acid and *2* lactic acid with quinolinium dichromate determining step. In contrast, using complexed dichromate ion, we observed that benzilic acid, which has no α-hydrogen atom, is oxidized easily and the oxidation involves C–C cleavage leading to the corresponding aldehyde.

One of the authors (K. A.) gratefully acknowledges the UGC, New Delhi, India, for the award of a junior research fellowship.

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