BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3841—3845 (1970)

Kinetics of the Chromic Acid Oxidation of Glycollic and Benzilic Acids

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(Received December 15, 1969)

The kinetics of chromic acid oxidation of glycollic and benzilic acids have been studied. Catalysis by H^+ ions has been noticed in both cases of oxidation. The results show that the logarithm of the rate constants increases with increase in the proportion of acetic acid in the mixture. Ionic strength decreases the rate of oxidation. Pyridine catalyzes the oxidation of glycollic acid whereas the catalysis in the case of benzilic acid is negligible. The energy of activation and entropy of activation have been calculated. Both kinetics and spectrophotometric results indicate the formation of intermediate chromium(VI)-hydroxycarboxylate complex in each case. The complex finally decomposes to give reaction products. Glycollic acid initially produces glyoxylic acid which subsequently gives formic acid whereas benzilic acid is oxidized to benzophenone.

Oxidation of a variety of organic compounds by chromic acid has been extensively studied. Bakore *et al.* have studied the oxidation of a number of α-hydroxy acids[1] *viz.*, lactic, malic and mandelic acids (all of them having C–H bond in the α-carbon atom) and explained the mechanism on the basis of the Kwart-Francis scheme,[2] which is a minor variation of the well known Westheimer's[3] mechanism. In the previous case[2] proton is removed intramolecularly instead of by an external base. However, no kinetic data for the oxidation of glycollic acid with chromic acid are known which may also be explained in the light of the above mechanisms. On the other hand, for benzilic acid having no C–H linkage in the molecule, the Kwart-Francis mechanism as well as Westheimer[3] type of mechanism (applicable in the case of chromic acid oxidation of isopropyl alcohol) could not be operative. Westheimer[3] considered that the oxidation of alcohols by chromic acid involves reversible formation of a chromate ester which slowly decomposes by a process catalyzed by bases. Presumably, the oxidation of benzilic acid may be explained on the basis of rupture of C–C bond[4] which is the other possible alternative. With this idea, we report in this communication, the chromic acid oxidation of two α-hydroxy acids, *viz.*, glycollic and benzilic acids.

Experimental

Potassium dichromate (G. R., Merck), glycollic acid (Riedel, Germany) and benzilic acid (Pure, E. Merck) were used without further purification. Manganous sulphate used was of 'Anala R' grade. 60% perchloric acid (E. Merck) was used. Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. Neutralized benzilic acid solution was used. All other reagents were chemically pure. Details of kinetic measurements have been described elsewhere.[5] All experiments were carried out at 35°C unless otherwise mentioned. Spectral measurements were carried out with a Beckman DB. model spectrophotometer.

Results

The stoichiometry of the reactions were determined by allowing reaction mixtures, containing a large excess of dichromate ion, to stand for 48 hrs at 30°C. The unreacted oxidant was then estimated by the usual procedure.[5] The reactions may be represented by the following equations.

$$6CH_2(OH)COOH + 4Cr_2O_7^{2-} + 32H^+ \rightarrow 6HCOOH + 8Cr^{3+} + 22H_2O + 6CO_2$$

Found: 0.63 mol of the oxidant per mol of the substrate.

$$3(C_6H_5)_2C(OH)COOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3(C_6H_5)_2CO + 2Cr^{3+} + 7H_2O + 3CO_2$$

Found: 0.31 mol of the oxidant per mol of the substrate. The products of the reactions were formic acid and benzophenone respectively which were confirmed by the usual tests. Formic acid was tested by the chromotropic acid reaction and benzophenone was tested by the preparation of a 2,4-dinitrophenyl hydrazine derivative.

In both cases of oxidation a 8 min period of

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[1] G. V. Bakore and S. Narain, *J. Chem. Soc.*, **1963**, 3419.

[2] H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, **77**, 4097 (1955).

[3] F. H. Westheimer, *Chem. Rev.*, **80**, 3022 (1958).

[4] Y. W. Chang and F. H. Westheimer, *J. Amer. Chem. Soc.*, **82**, 1401 (1960).

[5] K. K. Sen Gupta, This Bulletin, **43**, 590 (1970).

Table 1. Effect of oxidant on the reaction rate
(a) [Glycollic Acid] $=3.00\times10^{-2}$ M, $\mu=0.22$, pH $=0.69$
(b) [Benzilic Acid] $=8.3\times10^{-3}$ M, $\mu=0.14$, pH $=0.90$

	a		b	
No.	[Cr(VI)] $\times 10^3$ M	$k_a\times10^3$(sec^{-1})	[Cr(VI)] $\times 10^3$ M	$k_b\times10^3$(sec^{-1})
1	5.0	3.53	1.38	1.34
2	6.6	3.22	2.07	1.21
3	8.3	2.88	2.77	0.89
4	10.0	2.57	3.47	0.63

disturbance was observed. This disturbance is possibly due to some side reactions which progressively slow down as the complex formation approaches completion. A good first order reaction kinetics was found to occur after this period. Table 1 summarizes the values of rate constants at various initial concentrations of chromic acid. It is seen that the rates decreased with the increase of initial concentration of chromic acid.

To study the effect of [α-hydroxy group]$_0$ on k, a series of runs were made holding all the initial parameters constant. Increase in the concentration of α-hydroxy acids increased the rate of oxidation. The data on the effect of α-hydroxy acids on the rate of oxidation is shown in Fig. 1. The plots of $1/k$ against 1/[substrate] cut y-axis indicating the formation of an intermediate compound in both cases of oxidation. The spectrophotometric results also support the contention.

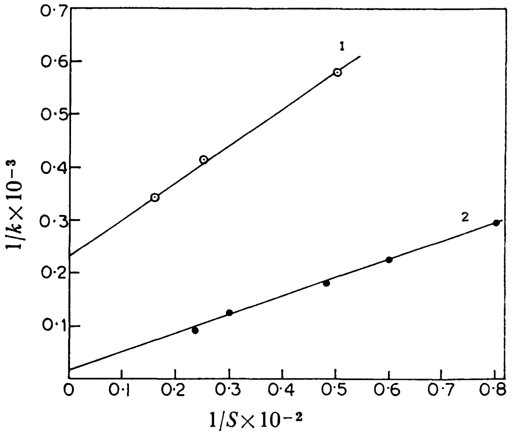

Fig. 1. Influence of substrate on the rate constant.

1. [Cr(VI)] $=3.30\times10^{-3}$ M
2. [Cr(VI)] $=1.38\times10^{-3}$ M

The experimental curves of Fig. 2 are physical evidences for complexation between chromium(VI) and hydroxy acids used. The spectra reported here were all taken after immediate mixing of the components. The strength of the dichromate solution was of the same order as used in the kinetic study. The change in the nature of the optical density/wavelength trend in the region 410—450 mμ of chromium(VI) (Curve 1), when ligands were added (Curves 2 and 3), seems to be due to new compound (complex) formation. A shift in the position of the shoulder towards longer wavelength from glycollate to benzilate was also noticed. The new nature of chromium(VI)-hydroxylate spectra cannot be due to change of pH. The effect of pH on the absorption spectra of dichromate solution is presented in curves 4, 5 and 6. Addition of glycollate and benzilate both changed (increased) the pH of the dechromate solution. The nature of both the curves (2 and 3), though similar to each other, differs from that of dichromate solutions having different acidities (curves 4, 5 and 6). All these observations support the

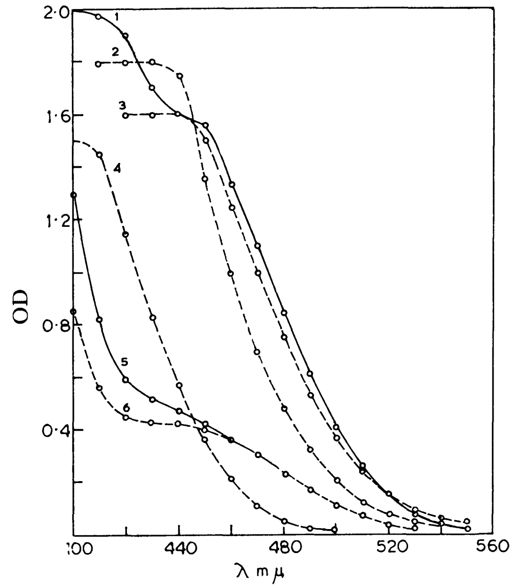

Fig. 2. Absorption spectra of chromium(VI) and its complexes.

1. [Cr(VI)] in water $=3.3\times10^{-3}$ M
2. [Cr(VI)] $=3.3\times10^{-3}$ M, [Na-glycollate] $=0.48$ M
3. [Cr(VI)] $=3.3\times10^{-3}$ M, [Na-benzilate] $=0.48$ M
4. [Cr(VI)] in water $=1\times10^{-3}$ M at pH 12.3
5. [Cr(VI)] in water $=1\times10^{-3}$ M at pH 4.53
6. [Cr(VI)] in water $=1\times10^{-3}$ M at pH 1.70

formation of chromium (VI)-hydroxycarboxylate complex upon immediate mixing.

The rate studies were made at various hydrogen ion concentrations. The acid dependence was studied, in a series of runs at fixed $[\text{substrate}]_0$ and $[\text{Cr(VI)}]_0$, by varying perchloric acid concentration but keeping the ionic strength constant by the addition of sodium perchlorate. The rates increased with the increase in hydrogen ion concentration. The plots between log *k* against pH is linear in each case (Fig. 3).

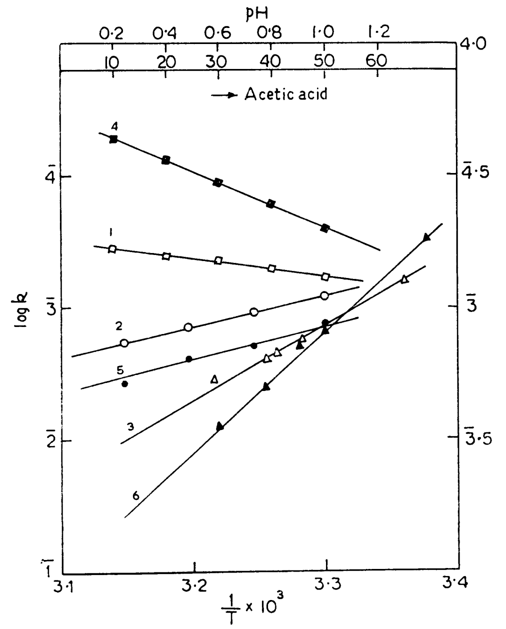

Fig. 3. Effect of solvent, temperature and pH on the rate constants.

1. $[\text{Cr(VI)}] = 3.33 \times 10^{-3}$ M, [Glycollic acid] $= 2.50 \times 10^{-2}$ M, pH $= 1.30$, $\mu = 0.06$, Temp. 35°C
2. $[\text{Cr(VI)}] = 4.15 \times 10^{-3}$ M, [Glycollic acid] $= 2.50 \times 10^{-2}$ M, pH $= 0.22$, $\mu = 0.61$
3. $[\text{Cr(VI)}] = 4.15 \times 10^{-3}$ M, [Glycollic acid] $= 2.50 \times 10^{-2}$ M
4. $[\text{Cr(VI)}] = 1.66 \times 10^{-3}$ M, [Benzilic acid] $= 1.00 \times 10^{-2}$ M, pH $= 1.0$, $\mu = 0.115$, Temp. 35°C
5. $[\text{Cr(VI)}] = 1.38 \times 10^{-3}$ M, [Benzilic acid] $= 8.3 \times 10^{-2}$ M, pH $= 0.90$, $\mu = 0.14$
6. $[\text{Cr(VI)}] = 1.38 \times 10^{-3}$ M, [Benzilic acid] $= 8.3 \times 10^{-2}$ M

The rates were also studied at different solvent composition of the reaction mixture. The solvent composition was varied by the addition of acetic acid. Figure 3 shows that the rate constant increases with increase in the proportion of acetic acid in the mixture. This is in agreement with previous observation.[5]

The results of the effect of pyridine on the rates of oxidations have been presented in Table 2. The base catalysis has been studied at constant $[\text{H}^+]$ with varying [free base]. Since pyridine removes hydrogen ions, the effective hydrogen ion concentration in the presence of pyridine would correspond to $\{[\text{H}^+]-[\text{Py}]\}$. If pyridine catalyzes oxidation,[1] the value of $k/\{[\text{H}^+]-[\text{Py}]\}$ increases with increase in the concentration of pyridine. The value would decrease if pyridine inhibits the reaction and would be constant if pyridine has no effect on the rate of oxidation. Westheimer[3] has shown that the addition of a base like pyridine catalyzes the oxidation of isopropyl alcohol by chromic acid, but this was later shown to be incorrect.[6] At present there is no evidence[6] for the involvement of an external base in the rate controlling steps nor is there good evidence against such a process. We have also observed catalyzing behaviour of pyridine in the case of glycollic acid oxidation and slight retarding effect in the case of benzilic acid.

The influence of temperature was studied under identical conditions of $[\alpha\text{-hydroxy acid}]_0$ and $[\text{Cr(VI)}]_0$. The Arrhenius plots of log *k* against $1/T$ gave straight lines (Fig. 3). The energies of activation were calculated to be 11.9 and 11.6 kcal/mol for glycollic and benzilic acids, respectively. The values of $-\Delta S^{\ne}$ were found to be 34.9 (e.u.) in each case. It is interesting that the values of energy and entropy of activation were found to be 12.86 kcal/mol and 34.6 (e.u.), respectively, in

TABLE 2. EFFECT OF PYRIDINE ON THE RATE OF OXIDATION

(a) [Glycollic Acid] $= 2.5 \times 10^{-2}$ M, $[\text{Cr(VI)}] = 2.77 \times 10^{-3}$ M, $[\text{H}^+] = 0.085$ M, $\mu = 0.1$
(b) [Benzilic Acid] $= 8.3 \times 10^{-3}$ M, $[\text{Cr(VI)}] = 1.38 \times 10^{-3}$ M, $[\text{H}^+] = 0.166$ M, $\mu = 0.18$

No.	$[\text{Pyridine}] \times 10^2$ M	$k_a \times 10^4(\text{sec}^{-1})$	$k_b \times 10^3(\text{sec}^{-1})$	$100k/\{[\text{H}^+]-[\text{Py}]\}$ (a)	(b)
1	0.00	2.34	1.88	2.75	1.13
2	1.66	1.92	1.34	2.81	0.90
3	3.32	1.53	1.16	2.97	0.87
4	4.98	—	1.00	—	0.86

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6) K. B. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York (1965), Part A, p. 162.

TABLE 3. INFLUENCE OF IONIC STRENGTH ON THE RATE OF OXIDATION
[α-Hydroxy compound]=8.33×10^{-3} M, [Cr(VI)]=1.38×10^{-3} M, pH=0.77

No.	μ	$k_{\text{glycollic}}\times10^4$(sec^{-1})	μ	$k_{\text{benzilic}}\times10^3$(sec^{-1})
1	0.254	7.88	0.254	1.15
2	0.337	7.80	0.337	0.90
3	0.420	6.95	0.420	0.85

the chromic acid oxidation of isopropyl alcohol.[7] Such close values suggest that the same mechanism may be operative for the rate controlling step of the reactions of α-hydroxy acids with chromic acid.

The effect of changing ionic strength was also examined (Table 3). The ionic strength was varied by the addition of sodium perchlorate. The changes in ionic strength of the medium had a definite retarding influence. This is in agreement with the observations made by Wiberg and Mill.[8] The results in Table 1 show that the rate of reaction is not directly proportional to chromium(VI) concentration because of the following monomer-dimer equilibrium which is a function of ionic strength,

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Wiberg and Mill[8] have shown that increase in ionic strength will favour the formation of a divalent ion, which have a higher ion pair association constants than a univalent ion. This will shift the equilibrium towards dichromate ion as the ionic strength is increased, and the rate of reaction would correspondingly decrease.

The rate constants of the reactions of some α-hydroxy acids by chromium(VI) were also studied under comparable conditions of [α-hydroxy acids]$_0$, [chromium(VI)]$_0$, pH and ionic strength. The concentrations of α-hydroxy acids and chromium (VI) used were 2.5×10^{-2} M and 2.70×10^{-3} M, respectively. Ionic strength and pH of each solution were maintained constant at 0.17 and 0.78, respectively. The rates increased with the increase in the substitution of hydrogen atom of the glycollic acid successively by phenyl nucleus. The values of 'k' in the cases of glycollic, mandelic and benzilic acids were found to be 0.767×10^{-3}, 0.921×10^{-3} and 4.07×10^{-3} (sec^{-1}), respectively. A comparison of the dissociation constants of glycollic, mandelic and benzilic acids show that the rates increased with the increase of dissociation constants which are 1.5×10^{-4}, 4.3×10^{-4} and 9.2×10^{-4}, respectively at 25°C. It will be difficult to interpret these data with rate constants, since the course of the reaction is mainly governed by two factors: (1) tendency of complex formation, (2) disproportionation of the complex to give products of the reaction. In the case of benzilic acid, the molecule appears to be sterically hindered due to the presence of two phenyl nucleus and the rate of the reaction with benzilic acid is expected to be the slowest. However, it seems very likely that benzilic acid molecule possibly violates the principle of steric hindrance, since due to the presence of two phenyl groups both hydroxyl and carboxyl groups are brought nearer, thereby facilitating the formation of the complex with chromic acid. Since hydroxyl and carboxyl groups are under strain, the benzilate chromate complex is expected to be most unstable in the series and hence its decomposition is fastest. In a similar way, glycollate chromate complex is more stable than benzilate chromate complex. This is possibly the reason why the rates follow the order $k_{\text{benzilate}}>k_{\text{mandelate}}>k_{\text{glycollate}}$.

Discussion

Kinetics and spectrophotometric results indicate that both glycollic and benzilic acids react with chromic acid to form an intermediate compound. They finally decompose slowly to give reaction products. Glycollic acid initially produces glyoxylic acid which subsequently is oxidized to formic acid. The other alternative would have been the oxidation of glyoxylic acid to oxalic acid, which on the way, might get oxidized to carbon dioxide. Since formic acid is one of the products of oxidation, it seems very unlikely that the reaction involves oxidation of glyoxylic acid to oxalic acid. Determination of stoichiometry also supports the above argument. Therefore, decarboxylation probably occurs as a part of the oxidation step. However, it has been shown recently during the oxidation of glyoxylic acid[9] by chromic acid, that decarboxylation of the molecule takes place followed by the oxidation of the hydrated formaldehyde molecule to afford formic acid. A few experiments were carried out using both glyoxylic acid with chromic acid and glycollic acid with chromic acid under comparable conditions. The rate constants were found to be 1.345×10^{-2} (sec^{-1}) and 1.072×10^{-3} (sec^{-1}), indicating the reaction is faster for glyoxylic acid. Again the activation energy in the case of the oxidation of glyoxylic acid by chromic acid

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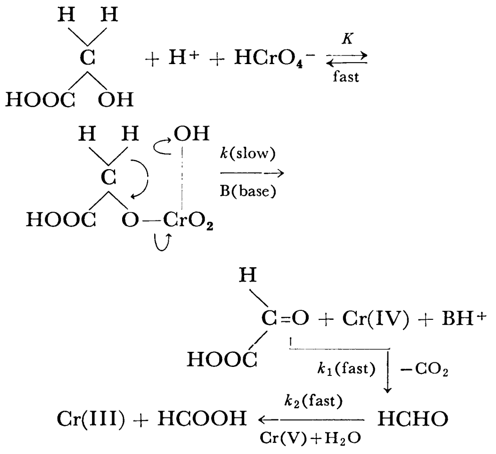
[7] N. Venkatsubramanian, *Proc. Indian Acad. Sci.*, **50**, 156 (1960).

[8] K. B. Wiberg and T. Mill, *J. Amer. Chem. Soc.*, **80**, 3022 (1958).

[9] K. K. Sen Gupta and S. D. Bhattacharya, *Z. Phys. Chem.* (Leipzig), **240**, 279 (1969).

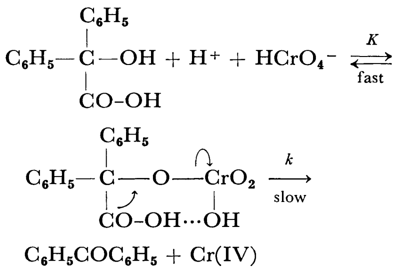
was found to be 5.5 kcal/mol as against 12.8 kcal/mol in the case of glycollic acid. This also supports that $k_{\text{glyoxylic}} > k_{\text{glycollic}}$.

On the basis of the above evidences, the reaction between glycollic acid and chromic acid may be explained in the following manner:



Scheme 1

The absence of C–H bond in benzilic acid suggests that the Westheimer type of mechanism is applicable in the other case. Moreover, the Kwart-Francis scheme in which proton is removed intramolecularly may also not be operative. In the case of benzilic acid, catalysis by pyridine has not been observed. Therefore, it may be proposed that the oxidation leads directly to the formation of a ketone and carbon dioxide by way of a chromate ester:



Scheme 2

In connection with the oxidation of pinacol by chromic acid, Chang and Westheimer have shown that an energy of 18.0 kcal/mol is needed during the rupture of a C–C bond. But in our case the value has been calculated to be 12.8 kcal/mol. This suggests that chromic acid possibly forms a more stable complex with symmetrical pinacol molecule than with benzilic acid.

It is clear that the first stage of the reaction involves a two electron transfer leading to chromium(IV), which is converted to chromium(V), either by reacting rapidly with chromium(VI) or chromium(IV) rapidly undergoing disproportionation to give chromium(V). The decreased rate of reaction on addition of Mn^{2+} ions suggests that intermediate valence states of chromium were formed.

Thanks are due to the Head of the Physical Chemistry Section for laboratory facilities.