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Kinetic Features of the Oxidation of Aliphatic Dialdehydes by Quinolinium Dichromate[1]

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Abstract—Kinetic data on the rates of quinolinium dichromate oxidation of glyoxal and glutaraldehyde are determined and discussed with reference to aldehyde hydration equilibria. The effect of variations in solvent composition and temperature are studied. The solvent effect is analyzed. Kinetic results support a pathway via a rate-determining oxidative decomposition of a chromate ester of an aldehyde hydrate. A cyclic transition state is suggested; being a Hückel-type system (4*n* + 2), this is an allowed process.

INTRODUCTION

Aliphatic aldehydes are oxidized to carboxylic acids in a neutral permanganate solution, but in alkali or concentrated acid, competition between the oxidation reaction and carbon–carbon bond fission occurs. The carbon–carbon bond fission proceeds via the cleavage of the enol [1]. Earlier reports had indicated the participation of an intermediate Cr(V) species in the chromic acid oxidation of aldehydes [2]. It has been suggested that the chromium(VI) oxidation of aldehydes could be understood better if it was regarded as the oxidation of an aldehyde hydrate rather than of the free carbonyl compound [3, 4]. As a part of our continuing investigation of the oxidation of organic substrates by quinolinium dichromate (QDC) [5], we report the kinetic features of the oxidation of aliphatic dialdehydes (glyoxal and glutaraldehyde) by QDC in an acidic medium in a nitrogen atmosphere.

EXPERIMENTAL

(a) Materials, methods, and stoichiometry. Glyoxal (S.D's) and glutaraldehyde (S.d. fine-chem. Ltd.) were used after checking their physical constants. Quinolinium dichromate [QDC, $(C_9H_7NH^+)_2Cr_2O_7^{2-}$] was prepared by the reported method [6], and its purity was checked by spectroscopy. Infrared spectrum (KBr) had bands at 930, 875, 765, and 730 cm^{-1} characteristic of the dichromate ion. Acetic acid (A.R. grade, S.d. fine-chem. Ltd.) was purified by distillation. Sulfuric acid (Merck) was used after checking its physical constants. Doubly distilled water was used to prepare all solutions. IR spectra were recorded on an FT-IR (DA-8, Bomen) spectrophotometer.

Pseudo-first-order conditions were used (large excess of substrate over QDC). The reactions were carried out at a constant temperature (±0.1 K) with the monitoring of an absorption band at 440 nm by spectrophotometry (Beckman 650, USA), as described earlier [5]. The rate constants were evaluated from the linear ($r > 0.996$) plots of log[QDC] on time. The values reported were the mean of two or more runs (accuracy, ±3%). The reactions were carried out in an aqueous medium, and water–acetic acid mixtures were used for studying the effect of the dielectric constant on the rates of reactions. All reactions were performed in a nitrogen atmosphere.

The stoichiometry of the reaction was determined [5] to be

$$\begin{aligned}&3RCHO + 2Cr^{6+} + 3H_2O\\&\longrightarrow 3RCO_2H + 2Cr^{3+} + 6H^+.\end{aligned}\qquad (I)$$

(b) Product analysis. Quinolinium dichromate (0.5 mol/l) was taken in distilled water (15 ml) and H_2SO_4 (4.2 ml). A solution of substrate (0.015 mol/l) was added to the reaction mixture and stirred for 24 h in a nitrogen atmosphere at 30–35°C. Ether was added to the reaction mixture. The organic layer was extracted, washed with water, and dried over anhydrous Na_2SO_4. Ether was removed by warming, and the products were obtained (oxalic acid from glyoxal; and glutaric acid from glutaraldehyde), whose melting points were in agreement with literature values (yields ≈85–90%). Each reaction product was subjected to IR (KBr) analysis and characterized as follows:

(i) Oxalic acid: ν = 3425 (br, s, –OH), 1718 (s, C=O), 1685, 1406, 1262, and 725 cm^{-1}.

(ii) Glutaric acid: ν = 2707 (br, s, –OH), 1696 (s, C=O), 1467, 1305, 1265, 920, and 761 cm^{-1}.

RESULTS AND DISCUSSION

Kinetic Results

Under pseudo-first-order conditions, individual kinetic runs were first-order in QDC. The pseudo-first-

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[1] This article was submitted by the authors in English.

Table 1. Rate data for the oxidation of dialdehydes in aqueous solution at 313 K

[Substrate] × 10^2, mol/l	[QDC] × 10^3, mol/l	[H_2SO_4], mol/l	$k \times 10^4$, s^{-1}	
			glyoxal	glutaraldehyde
1.0	1.0	0.5	31.0	1.15
2.5	1.0	0.5	76.5	2.90
5.0	1.0	0.5	158	5.92
7.5	1.0	0.5	258	8.50
10.0	1.0	0.5	311	11.6
1.0	0.75	0.5	31.5	1.17
1.0	0.50	0.5	30.8	1.13
1.0	0.25	0.5	31.2	1.14
1.0	0.10	0.5	31.1	1.16
1.0	1.0	0.75	41.2	1.60
1.0	1.0	1.0	51.5	2.10
1.0	1.0	1.25	62.0	2.60
1.0	1.0	1.50	71.2	3.10

Table 2. Dependence of rate constants on temperature[a] and activation parameters

	T, K	glyoxal	glutaraldehyde
$k \times 10^4$, s^{-1}	303	15.6	0.60
	308	23.3	0.88
	313	31.0	1.15
	318	46.0	1.80
	323	63.0	2.43
$\Delta H^{\neq}$, kJ mol^{-1}	–	53 ± 3	56 ± 3
$\Delta S^{\neq}$, J K^{-1} mol^{-1}	–	–121 ± 3	–147 ± 3
$\Delta G^{\neq}$, kJ mol^{-1}	–	91 ± 1	92 ± 1
E_a, kJ mol^{-1}	–	58 ± 1	59 ± 1

Note: [a] [Substrate] = 1.0×10^{-2} mol/l, [QDC] = 1.0×10^{-3} mol/l, [H_2SO_4] = 0.5 mol/l.

order rate constants (k) did not alter appreciably with changing QDC concentrations (tenfold range) given a constant substrate concentration (large excess); this indicated a first-order dependence on QDC (Table 1). The reactions were first-order in both substrate and acid (Table 1). A linear increase in the rate of oxidation with acidity indicated the involvement of a protonated Cr(VI) species. Earlier reports had established the involvement of protonated Cr(VI) species in chromic acid oxidation reactions [7, 8]. These data suggest the following rate law:

$$w = k'[\text{substrate}][\text{QDC}][\text{H}^+]. \qquad (1)$$

The oxidation reactions were studied in solutions containing variable proportions of water and acetic acid. There was an increase in the rate of oxidation with an increase in the percentage composition of acetic acid (or decreasing water content) in the medium. The rate of the reaction increased with an increase in the temperature; the calculated activation parameters are shown in Table 2.

There was no induced polymerization of acrylonitrile or the reduction of mercury(II) chloride [9], indicating that one-electron oxidation was unlikely. Control experiments in the absence of substrates showed no change in [QDC].

Mechanism

The rate of oxidation of the aldehydes was dependent on the first powers of the concentrations of each—substrate, oxidant, and acid. The order in [H^+] was unity, indicating the involvement of one proton in the rate-determining step of the reaction. The acid catalysis must be related to the structure of the oxidant (QDC), which was converted into a protonated species at the concentrations of mineral acid used. Quinolinium dichromate (QDC) is a bimetallic species, an anionic condensed form of chromic acid. Aqueous solutions of chromic acid contain such ions as CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$, besides other protonated species, such as $H_2Cr_2O_7$, $HCr_2O_7^-$, and H_2CrO_4 [10]. The ionization constant for the $HCrO_4^-$ ion, $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$, is 3.0×10^{-7} mol/l; hence, in dilute aqueous acid, the concentration of CrO_4^{2-} ions is negligible. This has been amply substantiated by Michel *et al.* [11], who examined the Raman spectra of chromate, dichromate, and chlorochromate species and found that the protonated form of chromate $HCrO_4^-$ does not exist in aqueous solutions of Cr(VI) compounds. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of dilute mineral acid are $HCrO_4^-$ and $Cr_2O_7^{2-}$. These ions are in equilibrium with each other, according to the equation $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, with the value of $K_d = 35.5$. According to this equilibrium, an increase in the hydrochromate concentration should be significant with dilution. When the Raman lines were examined under dilution, it was established that at pH = 11 the Cr(VI) ion was 100% present in the form of the CrO_4^{2-}

Table 3. Solvent effect for oxidation of dialdehydes by QDC at 313 K

Compound	H_2O : AcOH (%, vol/vol)	D	$k \times 10^4$, s^{-1}	$\log k_0$	Y
Glyoxal	100 : 0	73.3	31.0	–2.51	0
	95 : 5	69.9	38.2		0.09
	90 : 10	66.6	45.1		0.16
	85 : 15	63.2	52.1		0.23
	80 : 20	59.9	59.1		0.28
Glutaraldehyde	100 : 0	73.3	1.15	–3.94	0
	95 : 5	69.9	1.36		0.07
	90 : 10	66.6	1.56		0.13
	85 : 15	63.2	1.76		0.19
	80 : 20	59.9	1.95		0.23

Note: [Substrate] = 1.0×10^{-2} mol/l, [QDC] = 1.0×10^{-3} mol/l, $[H_2SO_4]$ = 0.5 mol/l.
D is the dielectric constant.

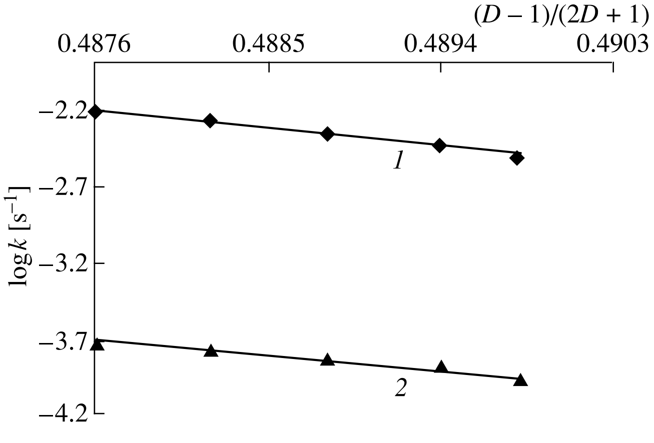
ion, whereas at pH = 1.2 it was 100% as the $Cr_2O_7^{2-}$ ion [11]. At acid concentrations higher than 0.05 mol/l, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $K_2Cr_2O_7$, spectral studies have shown that $Cr_2O_7^{2-}$ was the predominant species [12]. In the present investigation, since the concentrations of acid used were in the range from 0.5 to 1.5 mol/l, the dichromate ion (or its protonated form) would be the predominant species. Moreover, the protonated Cr(VI) species would be a more reactive electrophile capable of increasing its rate of coordination to the substrate.

At constant $[H_2SO_4]$ and temperature, an increase in water content of the medium showed a decrease in the rate of oxidation (Table 3). The absence of any salt effects on the rate of oxidation indicated that the reaction was not of the ion–ion type. The effect of solvent was analyzed in terms of its ionizing power. The parameter Y represents a measure of the ionizing power of the solvent [13] and can be defined by the equation

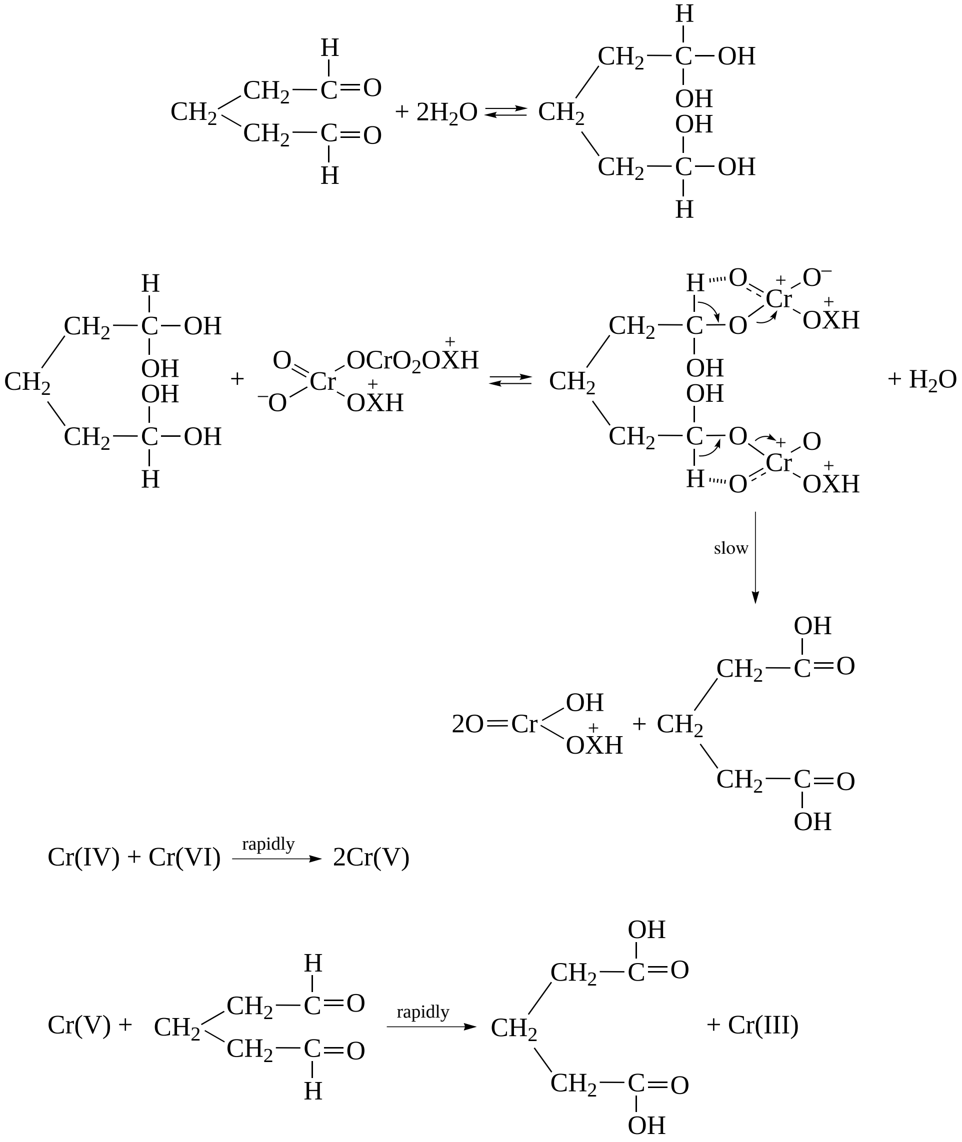
$$Y = \log k(H_2O) - \log k_0(H_2O), \qquad (2)$$

where $k_0(H_2O)$ and $k(H_2O)$ are the rate constants of these substrates at 40°C in 100% water and in successive solvent mixtures (water–acetic acid), respectively. Using this definition, Y is zero in 100% water, and Y varies for the solvent range used (Table 3). The variation of the solvolysis rate constant k with solvent gives a linear free energy relation [13], where m represents the parameter measuring the sensitivity of the solvolysis rate to Y. Using the Kirkwood relationship [14], plots of $\log k$ versus $(D - 1)/(2D + 1)$ were made (figure). Although the range of dielectric constants used in this investigation was not large, linearity was observed in these plots. The values of $\log k_0$ have been shown (Table 3); $m = 1$ (for glyoxal and glutaraldehyde) suggested that passage to the transition state involved a decrease in charge. Hence, a change to a more strongly ionizing medium (80% H_2O to 100% H_2O) resulted in a decrease in the rate of the reaction (Table 3).

Aliphatic aldehydes are extensively hydrated in aqueous solutions, and many oxidation reactions proceed via the hydrate form [15–17]. Since aldehyde hydrates very closely resemble alcohols both in structure and in many aspects of oxidation, there should be a similarity in the nature of the two oxidation reactions. The mechanism of oxidation of alcohols by chromic



Plot of $\log k$ against $(D - 1)/(2D + 1)$. (*1*) Glyoxal, (*2*) glutaral. [Substrate] = 1.0×10^{-2} mol/l, [QDC] = 1.0×10^{-3} mol/l, $[H_2SO_4]$ = 0.5 mol/l, T = 313 K.



X—quinolinium

Scheme 1.

acid has shown that the rate-determining step involved the decomposition of the protonated acid chromate ester [18]. By analogy, the oxidation of aldehydes should proceed via the reversible formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-determining step. The ester of the aldehyde hydrate would be in equilibrium with the free aldehyde and the aldehyde hydrate [19]. It could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate. It may be added that the esterification reaction has more utility since it helps one understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols [20].

The order of reactivity observed was: glyoxal > glutaraldehyde (Table 1). This showed that the rate of oxidation was dependent on the length of the chain of the aldehydes. The presence of methylene groups between two aldehydic moieties would decrease the electron availability at the oxygen of the aldehydic carbonyl group. This would prevent the attack of the electrophile (protonated QDC) as more methylene groups were inserted between the two aldehydic groups. Hence, this would result in the retardation of the rate of oxidation of the aldehydes. The slow step of the reaction involved the participation of the aldehyde hydrate, QDC, and two electrons in a cyclic system. The removal of hydrogen (on the carbon) was part of this step. The mechanistic pathway involved the rapid formation of the ester (step 1) followed by the slow oxidative decomposition of the ester of aldehyde hydrate (step 2). The overall rate of the reaction would depend on the position of equilibrium (step 1) and the rate of the reaction (step 2). A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The large negative entropies of activation ($\Delta S^{\neq}$) would be consistent with the formation of a cyclic intermediate in a bimolecular reaction. If the chromium were coordinated through the O–H group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and conversion to the corresponding carboxylic acid could be realized. The similarity in the values for the free energies of activation ($\Delta G^{\neq}$) for both substrates indicated that these reactions involved similar rate-determining steps.

The manner of electron transfer has to be established. The first step involved the transfer of the hydrogen atom from the –OH group (of the aldehyde hydrate) to the oxidant enabling the formation of the ester. A unimolecular decomposition of the ester can be written in which the hydrogen is bonded in the transition state to both the aldehydic carbon atom and the oxygen attached to chromium. The electron flow in a cyclic transition state has been considered [21, 22] and could be realized by assuming that if the chromium was coordinated through the –OH group (of the aldehyde hydrate), then the process of electron transfer could take place through the carbon–oxygen–chromium bond. This would not only facilitate the formation of the chromate ester but would enhance the ease of conversion to the product. The proton is removed in the cyclic transition state (coplanarity of all the atoms involved), the center of which resides on an electron-dense oxygen atom in the chromate ester [23]. Such a transition state envisages the transfer of electrons toward chromium, which occurs through the formation of the carbon–hydrogen–oxygen bonds, as well as the carbon–oxygen–chromium bonds.

The second step of the reaction was the transfer of two electrons in a cyclic system. This electrocyclic mechanism for the oxidation of aldehyde hydrates by QDC involved six electrons, and being a Hückel-type system ($4n + 2$), this was an allowed process [24]. This mechanism was supported by the observation that the oxidation reactions were acid catalyzed. Oxidant protonation would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant.

The mechanism for the oxidation of aliphatic dialdehydes (glyoxal and glutaraldehyde) by QDC was shown (Scheme 1). The conversion of Cr(IV) to Cr(III) proceeds by a disproportionation reaction. It was shown that for the reaction $\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)}$, the standard potential for the Cr(VI)–Cr(V) couple is extremely favorable ($E^0 = 0.62$ V) [25], and this reaction would proceed rapidly. The Cr(V)–Cr(III) couple has a potential of 1.75 V, which would enable the rapid conversion of Cr(V) to Cr(III) after the reaction with the substrate [25, 26].

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