Quinolinium Dichromate Oxidation of Aliphatic Aldehydes: A Kinetic Study

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Kinetic data on the rates of quinolinium dichromate oxidation of a series of aliphatic aldehydes have been determined and discussed with reference to aldehyde hydration equilibria. Kinetic results support a pathway proceeding *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 ($4n + 2$), this would be an allowed process. The deuterium isotope effect for the oxidation of acetaldehyde ($k_H / k_D = 6.4$) indicated a carbon-hydrogen cleavage rather than a carbon-carbon cleavage.

INTRODUCTION

Aliphatic aldehydes were oxidized to carboxylic acids in 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 was suggested that the chromium(VI) oxidation of aldehydes could be better understood if it was regarded as an oxidation of an aldehyde hydrate rather than of the free carbonyl compound.[3,4] As part of our continuing investigations on the oxidation of organic substrates by quinolinium dichromate (QDC),[5] this paper reports the kinetic features of the oxidation of aliphatic aldehydes (acetaldehyde, propionaldehyde, butyraldehyde and valeraldehyde) by QDC in acidic medium, under a nitrogen atmosphere. The rates have been compared and rationalized on the basis of equilibria for both, the hydrated form and the free carbonyl compound.

EXPERIMENTAL

*Materials, Methods and Stoichiometry.*

Valeraldehyde, butyraldehyde and propionaldehyde (Fluka) were used after checking their physical constants. Acetaldehyde (S.d. fine-chem. Ltd.) was purified by distillation. Quinolinium dichromate [QDC, $(C_9H_7NH^+)_2Cr_2O_7^{2-}$] was prepared by the reported method,[6] and its purity was checked spectrally. Infrared spectrum (KBr) gave bands at 930, 875, 765 and 730 cm^{-1}, characteristic of dichromate ion. Acetic acid (A.R. grade, S.d. fine-chem. Ltd.) was purified by distillation. Sulfuric acid (E. Merck) was used after checking its physical constants. Double distilled water was used to prepare all solutions. IR spectra were recorded on FT-IR (DA-8, Bomem) spectrophotometer. Deuterated acetaldehyde (CH$_3$CDO) was obtained from Sigma (USA).

Pseudo-first-order conditions were used (large excess of substrate over QDC). The reactions were done at constant temperature ($\pm$ 0.1 K), and followed by monitoring the absorption band at 440 nm, spectrophotometrically (Systronics, Model-108), as described earlier.[5] Rate constants

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were evaluated from the linear ($r > 0.996$) plots of log [QDC] against time. The values reported were the mean of two or more runs (reproducibility $\pm 3\%$). The reactions were carried out in aqueous medium, and water – acetic acid mixtures were used for studying the effect of dielectric constant on the rates of the reactions. All reactions were performed under a nitrogen atmosphere.

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

$$3\ RCHO + 2\ Cr^{6+} + 3\ H_2O \rightarrow$$
$$3\ RCO_2H + 2\ Cr^{3+} + 6\ H^+ . \tag{1}$$
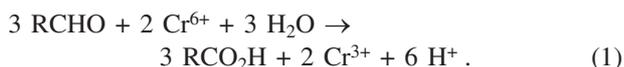
Product Analysis

Quinolinium dichromate (0.5 mol dm^{-3}) was taken in distilled water (15 ml) and H_2SO_4 (4.2 ml). A solution of substrate (0.015 mol dm^{-3}) was added to the reaction mixture and stirred for 24 h under nitrogen, at 30–35 °C. Ether was added to the reaction mixture. The organic layer was extracted, washed with water, and dried over anhydrous $MgSO_4$. Ether was removed by warming, and the products were obtained (acetic acid from acetaldehyde, propionic acid from propionaldehyde, butyric acid from butyraldehyde, and valeric acid from valeraldehyde), whose boiling points were in agreement with literature values (yields $\approx$ 85–90 %). Each reaction product was subjected to IR (CHCl$_3$) analysis, and characterized as follows:

(i) Acetic acid:
ν = 2945 (br, s, –OH), 2663, 1711 (s, C=O)
1405, 1350, 1291, 940 cm^{-1};

(ii) Propionic acid:
ν = 2980 (br, s, –OH), 2540, 1714 (s, C=O),
1467, 1234, 1079, 841 cm^{-1};

(iii) Butyric acid:
ν = 2972 (br, s, –OH), 1716 (s, C=O),
1420, 1236, 1105, 937, 762 cm^{-1};

(iv) Valeric acid:
ν = 2940 (br, s, –OH), 2630, 1720 (s, C=O),
1427, 1220, 940, 755 cm^{-1}.

RESULTS AND DISCUSSION

Kinetic Results

Under pseudo-first-order conditions, individual kinetic runs were first order in QDC. The pseudo-first-order rate constants (k_{ex}) did not alter appreciably with changing QDC concentrations (10-fold range), at constant substrate concentration (large excess); this indicated a first-order dependence on QDC (Table I). The reactions were first order in each substrate (Figure 1), and acid (Figure 2). At present, the results reported do not offer

TABLE I. Dependence of rate constant on oxidant concentration[a] at 313 K

[QDC]	$10^4\ k_{ex}\ /\ s^{-1}$			
$10^3 \times$ mol dm^{-3}	C$_4$H$_9$CHO	C$_3$H$_7$CHO	C$_2$H$_5$CHO	CH$_3$CHO
1.0	0.91	0.85	0.77	0.30
0.75	0.94	0.81	0.75	0.31
0.50	0.91	0.81	0.74	0.30
0.25	0.92	0.83	0.78	0.29
0.10	0.90	0.82	0.76	0.30

[a] [Substrate] = 0.01 mol dm^{-3}; [H$_2$SO$_4$] = 0.5 mol dm^{-3}.
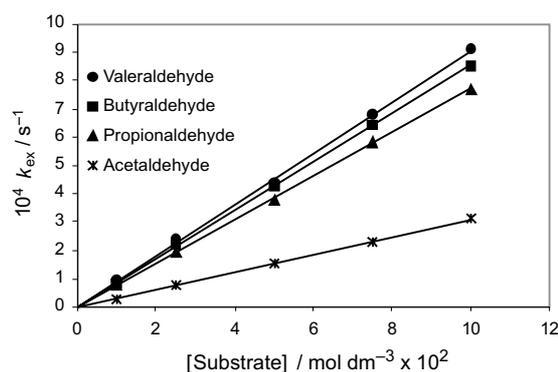
Figure 1. Plot of k_{ex} against substrate concentration.
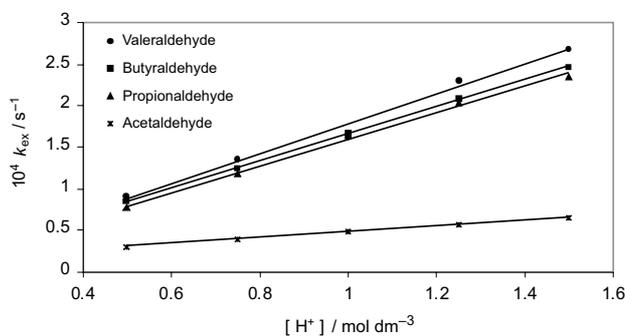
Figure 2. Plot of k_{ex} against [H$^+$].

the possibility to decide whether protonation of the aldehyde or the protonation of dichromate lead to the observed acid catalysis since the two processes cannot be distinguished on the basis of the kinetic results obtained. In addition, there is no obvious evidence against the involving of the protonated aldehyde in the reaction. Hence, it would be justified to propose that in the range of acid concentrations used, the oxidant QDC was converted to the 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:

$$\upsilon = k\ [\text{substrate}]\ [\text{QDC}]\ [\text{H}^+] . \tag{2}$$

The oxidation reactions were studied in solutions containing varying proportions of water and acetic acid. There was an increase in the rate of oxidation with a decrease in the polarity of the solvent.

The rate of oxidation of CH_3CDO was measured under experimental conditions identical with those used for the oxidation of CH_3CHO. The rates of oxidation of CH_3CHO and CH_3CDO at 313 K were $10^4 k_{ex} / s^{-1} = 0.30$ and 0.047, respectively. The kinetic isotope effect, k_H / k_D, was 6.4 at 313 K.

There was no induced polymerization of acrylonitrile or the reduction of mercury(II) chloride,[9] indicating that a one-electron oxidation was unlikely. Control experiments, done in the absence of the substrates, did not show any 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 acid catalysis must be related to the structure of the oxidant (QDC) which was converted to a protonated species, at the concentrations of mineral acid used. Quinolinium dichromate (QDC) is a dimetallic species, an anionic condensed form of chromic acid. Aqueous solutions of chromic acid contain ions such 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 dm^{-3}; 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. The ionization constant for the $HCr_2O_7^-$ ion given by $HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}$ is 0.85 mol dm^{-3}; hence, in solutions where pH $\geq$ 1, the ionization may be considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of dilute mineral acid will be $HCrO_4^-$ and $Cr_2O_7^{2-}$. These ions are in equilibrium with each other, according to the equation: $2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, with the value of $K_d = 35.5$. According to this equilibrium, an increase of 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-} ion, whereas at pH = 1.2, it was 100 % as the $Cr_2O_7^{2-}$ ion.[11] At concentrations of acid larger than 0.05 mol dm^{-3}, 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 0.5 to 1.5 mol dm^{-3}, 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.

Aliphatic aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed *via* the hydrate form.[13–15] Table II records the experimental rate constants (k_{ex}) for the oxidation of the aldehydes by QDC. The aldehyde hydrate dissociation constant (K_d) pertaining to the reaction

$$RCH(OH)_2 \underset{}{\overset{k_d}{\rightleftharpoons}} RCHO + H_2O$$
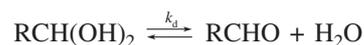
are also given.[13,15] From k_{ex} and K_d, two sets of rate constants referring to the oxidation of the aldehyde in only one of the forms present in solution were computed. The values of k_{Hy} were obtained by assuming that only the hydrate form appears in the rate law:

$$\upsilon = k_{Hy}\,[QDC]\,[RCH(OH)_2]\,[H^+]. \qquad (3)$$

Similarly, the values of k_A were calculated using the concentration of free aldehydes according to the rate law:

$$\upsilon = k_A\,[QDC]\,[RCHO]\,[H^+]. \qquad (4)$$

The rate constants for the oxidation of the aliphatic aldehydes, as determined in this study, could be in agreement qualitatively with the expectations based on the corresponding electronic and steric properties of the group attached to the hydrated carbonyl group (Table II). The observation possibly suggests the reaction pathway *via* the hydrated carbonyl substrate rather than the process that could involve carbonyl substrate alone.

Since aldehyde hydrates very closely resemble alcohols both in structure and in many aspects of oxidation, there would be a similarity in the nature of the two oxidation reactions. The mechanism of oxidation of alcohols by chromic acid had shown that the rate-determining step involved the decomposition of the protonated acid chromate ester.[16] By analogy, the oxidation of aldehydes would proceed *via* the reversible formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-deter-

TABLE II. QDC oxidation of aliphatic aldehydes[(a)] at 313 K

Aldehyde	K_d 10^4	k_{ex} / s^{-1}	$k_{Hy} / mol^{-2}dm^{-6}s^{-1}$	$k_A / mol^{-2}dm^{-6}s^{-1}$
CH_3CHO	0.67[(b)]	0.30	0.10	0.15
C_2H_5CHO	1.4[(c)]	0.77	0.37	0.26
C_3H_7CHO	2.1[(c)]	0.85	0.53	0.25
C_4H_9CHO	2.8[(c)]	0.91	0.69	0.25

[(a)] $[H_2SO_4] = 0.5$ mol dm^{-3}; [(b)] Ref. 15; [(c)] Ref. 13.

mining step. The hydration of the aldehydes was not rate-determining for the oxidation reaction.[17] The ester of the aldehyde hydrate would be in equilibrium with the free aldehyde and the aldehyde hydrate, and could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate.[18]

The order of reactivity observed was: acetaldehyde < propionaldehyde < butyraldehyde < valeraldehyde, showing that the rate of oxidation was dependent on the length of the alkyl chain of the aldehydes. Furthermore, electron-releasing groups ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9) accelerated the oxidation process by increasing the electron availability at the oxygen of the aldehydic carbonyl group. This facilitated the attack of the electrophile (protonated QDC). The slow step of the reaction involved the participation of the aldehyde hydrate, QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, which was confirmed by the kinetic isotope effect observed for the oxidation of acetaldehyde ($k_H / k_D = 6.4$). The mechanistic pathway involved the rapid formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the 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. If the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and the conversion to the corresponding carboxylic acid could be rationalized.

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. Electron flow in a cyclic transition state has been considered,[19,20] and could be rationalized 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 kinetic isotope effect ($k_H / k_D = 6.4$) indicated a cleavage of the carbon-hydrogen bond in the

Scheme 1.

rate-determining step of the reaction, similar to earlier observations.[21–23] The proton is removed in the cyclic transition state (co-planarity of all the atoms involved), the center of which resides on an electron-dense oxygen in the chromate ester.[24] Such a transition state envisages the transfer of electrons towards the chromium, occurring by 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.[25] This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant 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 aldehydes by QDC has been shown (Scheme 1). The conversion of Cr^{IV} to Cr^{III} proceeds by a disproportionation reaction. It has been shown that for the reaction $Cr^{IV} + Cr^{VI} \rightarrow 2\ Cr^{V}$, the standard potential for the Cr^{VI}-Cr^{V} couple is extremely favorable ($E^0 = 0.62$ volt),[26] and this reaction would proceed rapidly. The Cr^{V}-Cr^{III} couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr^{V} to Cr^{III}, after the reaction with the substrate.[26,27]

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SAŽETAK

Oksidacija alifatskih aldehida pomoću kinolinium bikromata: kinetička studija

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Provedena su kinetička mjerenja oksidacije niza alifatskih aldehida pomoću kinolinium bikromata i razmatrana su u odnosu na ravnotežu aldehidske hidratacije. Kinetički rezultati podupiru reakcijski mehanizam koji se odvija preko oksidativne dekompozicije bikromatskoga estera aldehidnoga hidrata. Predloženo je cikličko prijelazno stanje, jer se radi o Hückelovome (4n + 2) sustavu, a to je dozvoljeno stanje. Deuterijski izotopni efekt za oksidaciju acetaldehida ($k_H/k_D = 6.4$) ukazuje da dolazi do cijepanja veze ugljik-vodik, a ne ugljik-ugljik.