Kinetics of oxidation of α , β -unsaturated aldehydes by quinolinium dichromate

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Abstract: A series of α , β -unsaturated aldehydes (crotonaldehyde, cinnamaldehyde, acrylaldehyde, and methacrylaldehyde) were oxidized by quinolinium dichromate in sulfuric acid to the corresponding acids in 50% (v/v) acetic acid – water medium. The kinetic data have been discussed with reference to the aldehyde hydration equilibria. The kinetic results support a mechanistic pathway proceeding via a rate-determining oxidative decomposition of the chromate ester of the aldehyde hydrate.

Key words: kinetics, oxidation, unsaturated aldehydes, quinolinium dichromate.

Résumé : Le dichromate de quinolinium dans l'acide sulfurique utilisé en solution d'acide acétique aqueux à 50% (v/v) permet d'oxyder une série d'aldéhydes α,β -insaturés (crotonaldéhyde; cinnamaldéhyde; acrylaldéhyde; méthacrylaldéhyde) en acides correspondants. On discute des données cinétiques en fonction de l'équilibre d'hydratation de l'aldéhyde. Les données cinétiques sont en accord avec un mécanisme réactionnel impliquant une décomposition oxydante de l'ester chromique de l'hydrate d'aldéhyde qui serait cinétiquement limitante.

Mots clés : cinétique, oxydation, aldéhydes insaturés, dichromate de quinolinium.

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Introduction

In the oxidation of α , β -unsaturated aldehydes, it has been suggested that the reaction could proceed by way of (*a*) enolization being the rate-determining step (1, 2); (*b*) hydration of the double bond to form a β -hydroxyaldehyde (3); or (*c*) oxidation of the aldehyde hydrate (4).

With a view to establishing the mechanistic pathway for this oxidation process, we have carried out a kinetic study of the oxidation of α , β -unsaturated aldehydes (crotonaldehyde, cinnamaldehyde, acrylaldehyde, and methacrylaldehyde) by quinolinium dichromate (QDC, (C₉H₇N⁺H)₂Cr₂O₇^{2–}) in 50% acetic acid – water medium under a nitrogen atmosphere. This study forms part of our continuing efforts, concerning the quinolinium dichromate oxidation of organic substrates in general (5) and aldehydes in particular (6).

Experimental

Materials and methods

Acrylaldehyde and methacrylaldehyde (Aldrich) and crotonaldehyde and cinnamaldehyde (Merck-Schuchardt) were used without further purification. The oxidant, quinolinium dichromate (QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$) was prepared by the reported method (7), and its purity was checked by spectral analysis. The IR spectrum (KBr) exhibited bands at 930, 875, 765, and 730 cm⁻¹, characteristic of

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the dichromate ion. Acetic acid (SD, AR grade) was distilled before use. Sulfuric acid (E. Merck) was used after a check of its physical constants. The deuterated compounds were prepared by the reported method (8). The IR spectra were recorded on a Bomem DA-8 FT-IR spectrophotometer.

The method used for the kinetic determinations has been described previously (5). All the reactions were performed under nitrogen. The rate constants have been evaluated from the linear (r > 0.995) plots of log[QDC] against time, and the values reported are the mean of two or more runs (reproducibility ±3%). The solvent was 50% aqueous acetic acid, and the dielectric constant was varied using acetic acid – water mixtures. The reaction mixtures remained homogeneous in the solvent systems used.

Product analysis

Thirty mL of water was taken and cooled in ice. Concentrated H₂SO₄ (7.9 g, 0.08 M) was added slowly with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g, 0.02 M) was added and the mixture was warmed to 313 K for complete dissolution of the QDC. To this mixture, 0.01 M of substrate (0.71 g of methacrylaldehyde, 0.57 g of acrylaldehyde, 0.71 g of crotonaldehyde, and 1.33 g of cinnamaldehyde) taken up in 25 mL of a 50% acetic acid - water solution was added. The reaction mixture was stirred at 313 K for 48 h under nitrogen. The organic layer was extracted thrice with ether (25 mL each time) and the combined organic extracts were washed with water and dried over anhydrous Na₂SO₄. The oxidized products (methacrylic from methacrylaldehyde, acrylic acid acid from acrylaldehyde, crotonic acid from crotonaldehyde, and cinnamic acid from cinnamaldehyde) were obtained after the complete removal of ether (boiling and melting points were

10 ² [Substrate] (M)	10 ² [QDC] (M)	[H ₂ SO ₄] (M)	$10^3 k (s^{-1})$			
			Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde
3.1	0.31	0.51	1.3	1.2	0.51	0.080
10.0	0.30	0.52	4.6	4.0	1.5	0.26
17.0	0.31	0.51	7.6	7.1	2.9	0.41
25.0	0.30	0.51	11	9.9	4.1	0.62
30.0	0.32	0.53	14	12	4.9	0.78
3.0	0.12	0.50	1.3	1.2	0.52	0.081
3.2	0.06	0.52	1.3	1.3	0.51	0.080
3.1	0.04	0.50	1.3	1.2	0.54	0.082
3.0	0.03	0.51	1.3	1.2	0.53	0.083
3.1	0.31	0.75	2.0	1.8	0.81	0.12
3.1	0.32	1.02	2.7	2.4	1.1	0.16
3.0	0.30	1.25	3.4	3.1	1.4	0.21
3.2	0.31	1.50	4.0	3.7	1.6	0.25

Table 1. Rate data for the oxidation of α , β -unsaturated aldehydes in 50% acetic acid at 313 K.

in agreement with literature values; yields $\approx 85-90\%$). Each reaction product was characterized by IR analysis.

Results and discussion

The oxidation of α , β -unsaturated aldehydes (crotonaldehyde, cinnamaldehyde, acrylaldehyde, and methacrylaldehyde) by QDC results in the formation of the corresponding acids. Under the present experimental conditions, there is no further oxidation of the acids.

The stoichiometry of the reaction was determined (5). Stoichiometric ratios, Δ [QDC]/ Δ [substrate], in the range 0.66 to 0.69 conform to the following overall equation (representative):

[1]
$$3C_3H_4O + 2Cr(VI) + 3H_2O \rightarrow 3C_3H_4O_2$$

+ 2Cr(III) + 6H⁺ (acrylaldehyde)

Using pseudo-first-order conditions, individual kinetic runs are first order in QDC. The pseudo-first-order rate constants (k) are independent of the initial concentration of the oxidant (Table 1). The order of the reaction with respect to substrate concentration has been obtained by varying the aldehyde concentration and observing the effect on the rate at constant [QDC] and [H⁺]. The order with respect to the concentration of acid, at constant [aldehyde] and [QDC], is unity. The kinetic results are shown in Table 1. In the range of acid concentrations used, the protonation of the aldehydes would be less significant, though it cannot be ruled out. At present, it may not be possible to decide whether protonation of the aldehyde or protonation of the dichromate results in the observed acid catalysis, since these two processes cannot be distinguished on the basis of the data obtained. Since the acid concentrations used were in the range 0.5 to 1.5 M, it would be justified to suggest that the dichromate ion would be the predominant species in these oxidation reactions.

The oxidation of the substrates by QDC has been studied over the temperature range 303–323 K. The rate data and activation parameters are shown in Table 2. The negative values of ΔS^* provide support for a polar bimolecular reaction.

The effect of a change in the solvent composition (water – acetic acid, %, v/v) on the rate of oxidation has been deter-

mined. The dielectric constants (*D*) of water – acetic acid mixtures have been calculated (at 313 K: water = 73.28, acetic acid = 6.29) (9). The data in Table 3 shows that a decrease in *D* of the medium results in an increase in the rate of the reaction (Table 3). The magnitude of this effect could be analyzed by suggesting that, for the equilibrium $2\text{HCrO}_4 \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$, a decrease in *D* of the medium (increase in the acetic acid content) favors the dichromate form over the chromate form. If ion pairs are formed in this medium, they would have a higher ion-pair association constant for the dichromate ion, and this would again favor the dichromate ion. Although the range of *D* used for these reactions is not large, plots of log *k* versus 1/*D* are linear, with positive slopes, suggesting an ion-dipole type of interaction (10).

There is no induced polymerization of acrylonitrile (11), which indicates that a one-electron oxidation is quite unlikely. Control experiments, performed in the absence of the substrate, did not show any appreciable change in the concentration of QDC.

Variations in the ionic strength of the medium, using sodium perchlorate ($\mu = 0.01-0.25$ M), did not influence the rates of these reactions.

Aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions have been reported to proceed via the hydrated form (12–17). Table 4 records the experimental rate constants (k) for the oxidation of the aldehydes by QDC. The aldehyde hydrate dissociation constants (K_d) pertaining to the reaction:

$$[2] \qquad \text{RCH(OH)}_2 \stackrel{\text{Ad}}{\rightleftharpoons} \text{RCHO} + \text{H}_2\text{O}$$

are also given (12). From k and K_d , two sets of rate constants for the oxidation of the aldehyde in only one of the forms present in solution are computed. The values of k_{Hy} (**Hy** = hydrated form of the substrate) are obtained by assuming that only the hydrate form appears in the rate law:

[3] $v = k_{Hy}$ [QDC] [RCH(OH)₂].

Similarly, the values of k_A (**A** = substrate) are calculated using the concentration of free aldehyde according to the rate law:

	$10^{3}k$ (s ⁻¹)						
<i>T</i> (K)	Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde			
303.0	0.71	0.62	0.25	0.031			
308.1	1.0	0.91	0.39	0.062			
313.0	1.3	1.2	0.51	0.081			
318.0	2.0	1.9	0.77	0.130			
323.1	2.7	2.5	1.10	0.16			
ΔH^* (kJ mol ⁻¹)	52 ± 1.9	54 ± 2.6	57 ± 2.2	63 ± 2.4			
$\Delta S^* (J \text{ mol}^{-1} \text{ K}^{-1})$	-135 ± 6	-129 ± 7	-127 ± 6	-123 ± 8			

Table 2. Temperature and activation parameters for the oxidation of α , β -unsaturated aldehydes^{*a*} in 50% acetic acid by QDC.

^{*a*}[Substrate] = 0.03 M; [QDC] = 0.003 M; $[H_2SO_4] = 0.5 M$.

Table 3. Solvent effect for oxidation of α , β -unsaturated aldehydes^{*a*} by QDC at 313 K.

H ₂ O:AcOH (%, v/v)		$10^3 \ k \ (s^{-1})$					
	Dielectric constants D	Methacrylaldehyde	Acrylaldehyde	Crotonaldehyde	Cinnamaldehyde		
60:40	46.48	0.79	0.64	0.36	0.053		
55:45	43.14	1.1	0.93	0.43	0.065		
50:50	39.79	1.3	1.2	0.51	0.080		
45:55	36.44	1.7	1.5	0.59	0.10		
40:60	33.09	2.1	1.9	0.67	0.13		

^{*a*}[Substrate] = 0.03 M; [QDC] = 0.003 M; $[H_2SO_4] = 0.5$ M.

Table 4. QDC oxidation of α , β -unsaturated aldehydes at 313 K.

		$10^{3} k$	k _{Hv}	k _A
Aldehydes	K_{d}^{a}	(s^{-1})	$(M^{-1} s^{-1})$	$(M^{-1} s^{-1})$
Methacrylaldehyde	2.3	1.3	34 ± 0.23	15 ± 0.30
Acrylaldehyde	1.7	1.2	23 ± 0.24	13 ± 0.23
Crotonaldehyde	1.1	0.51	5.9 ± 0.25	5.4 ± 0.27
Cinnamaldehyde	0.6	0.080	0.51 ± 0.22	0.85 ± 0.24

^aReference 12.

[4] $v = k_A$ [QDC] [RCHO].

The values of k_{Hy} and k_{A} have been shown in Table 4. Using the σ values as reported by Taft and co-workers (18), a plot of log k_{Hy} against σ is found to be linear, with a slope of $\rho = -0.92$ (r = 0.993). On the other hand, the correlation of σ with k_{A} gave a value of $\rho = -0.56$ (r = 0.997). This might suggest the involvement of the aldehyde hydrate in the oxidation process. Hence, a mechanism involving a direct hydrogen transfer reaction between a free aldehyde and QDC is very unlikely. In the chromic acid oxidation of benzaldehyde, it has been shown that the reaction proceeds via the chromic acid ester of hydrated benzaldehyde as the intermediate (19). This similarity provides additional support for the mechanistic pathway suggested in the present investigation: that the rate-determining step involves the oxidative decomposition of the chromate ester of an aldehyde hydrate.

Since aldehyde hydrates very closely resemble alcohols both in structure and in many aspects of oxidation, a similarity in the nature of the two oxidation reactions is expected. In the oxidation of alcohols by chromic acid, the ratedetermining step has been shown to be the decomposition of the protonated acid chromate ester (20). By analogy, the oxidation of aldehydes would proceed via the formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-determining step (21). 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 the esterification of the hydrate (22). It may be added that the esterification reaction has more utility, since it helps one to understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols.

The rate data shows that both acrylaldehyde and methacrylaldehyde are oxidized at approximately equal rates, with methacrylaldehyde reacting marginally faster than acrylaldehyde (Table 1), which suggests that the α -CH₃ group has little influence on the rates. It is justified to assume that the oxidation process does not involve an enolization step. The enolization of acrylaldehyde would have yielded hydroxyallene, which would be improbable. Further, the oxidation of methacrylaldehyde is a rapid reaction even though there is no enolizable hydrogen atom. The argument that unsaturated aldehydes could undergo a reaction involving the hydration of the double bond to form a β hydroxyaldehyde can be ruled out, since no such intermediate could be isolated from the reaction. The order of reactivity is: methacrylaldehyde > acrylaldehyde > crotonaldehyde > cinnamaldehyde (Table 1). The presence of the methyl group (in methacrylaldehyde) accelerates the reaction by increasing the electron availability at the oxygen of the aldehydic carbonyl group. In crotonaldehyde, the methyl group at the β-position is far removed from the site of reaction, suggesting that β -substitution influences the rate of the reaction to a much lesser extent. Hence, the reactivity of crotonaldehyde is much less than that of methacrylaldehyde. The presence of the phenyl group in cinnamaldehyde exerts a deactivating influence on the rate of the reaction and hence its reactivity is the lowest in the series.

Scheme 1.



The mechanistic pathway involves the formation of the ester of the aldehyde hydrate (step 1), followed by the slow oxidative decomposition of this ester (step 2). A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The manner of electron transfer must be established. Electron flow in a cyclic transition state has been considered (23) and can be rationalized by assuming that if the chromium is coordinated through the -OH group (of the aldehyde hydrate), then the process of electron transfer could take place through the carbon oxygen—chromium bonds, enabling the formation of the chromate ester and enhancing the ease of conversion to the product.

The slow step of the reaction involves the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) is part of this step, as seen from the kinetic isotope effect for the oxidation of the respective aldehyde- d_1 compounds (Table 5), which indicates a cleavage of the carbon—hydrogen bond in the rate-determining step of the reaction.

This step allows one to envisage a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system (4n+2), this is an allowed process (24). The kinetic isotope effect could be interpreted to indicate that the reaction proceeds via the formation of the chromate ester of the aldehyde hydrate as an intermediate, and that this is converted to the product in the rate-determining step.

Table 5. Kinetic isotope effect at 313 K.^a

Substrate	$10^3 k_{\rm H} \ ({\rm s}^{-1})$	$10^3 k_{\rm D} \ ({\rm s}^{-1})$	$k_{\rm H}/k_{\rm D}$
Crotonaldehyde-d ₁	0.51	0.084	6.25
Cinnamaldehyde-d ₁	0.080	0.013	6.15

^{*a*}[Substrate] = 0.03 M; [QDC] = 0.003 M; $[H_2SO_4] = 0.5 M.$

The last step would be rate-determining, in accord with the observation of the deuterium kinetic isotope effect. Further, the oxidation rate for the aldehydes is not increased as rapidly by a decrease in the water concentration in acetic acid – water mixtures (Table 3), which suggests that a molecule of water is involved in a kinetically important stage in the oxidation of the aldehydes.

The sequence of reactions for the oxidation of α , β -unsaturated aldehydes by QDC is shown in Scheme 1. In acidic medium, the oxidant QDC is converted to the protonated dimetallic chromium(VI) species (**PQ**) (in the acid range used for the present investigation, the Cr(VI) in the protonated QDC would exist mainly as Cr₂O₇²⁻). The substrate (**A**) is converted to the hydrated form (**Hy**). The reaction of the hydrated form (**Hy**) with the protonated QDC (**PQ**) results in the formation of the monochromate ester (**E**) and a Cr(VI) monomer. The monochromate ester (**E**) undergoes decomposition in the rate-determining step to give the product (the corresponding acid), along with the Cr(IV) species. The conversion of Cr(IV) to Cr(III) is a dispropor-

tionation reaction. It has been shown that for the reaction $Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$, the standard potential for the Cr(VI)–Cr(V) couple is extremely favourable ($E^{\circ} = 0.62 \text{ V}$) (25), and this reaction proceeds rapidly. The Cr(V)–Cr(III) couple has a potential of 1.75 V, which enables the rapid conversion of Cr(V) to Cr(III) after the reaction of Cr(V) with the substrate (25, 26).

If the mechanism shown in Scheme 1 is correct, then the attack of the protonated QDC (PQ) on the aldehyde hydrate (Hy) is crucial and would be favored by the formation of the cyclic chromate ester (E). The rate law has been derived as follows:

[5] $-d[QDC]/dt = k_3[E] = k_3[Hy][PQ],$

where $[PQ] = K_1[QDC][H^+]$ and $[Hy] = K_2[A][H_2O]$.

Hence, $-d[QDC]/dt = K_1K_2 k_3[A][QDC][H^+]$, which shows a first-order dependence on each of the concentrations (substrate, oxidant, and acid). Hence, $-2.303d(log[QDC])/dt = k = K_1K_2 k_3[A][QDC][H^+]$. This rate law explains all the experimentally observed results.

The data collected demonstrates that the QDC oxidation of α,β -unsaturated aldehydes results in the formation of carboxylic acids, substantiating the mechanism wherein there is an attack of the oxidant on the aldehyde hydrate. There is no cleavage of the carbon—carbon bond, thus ruling out the possibility of any enolization. This study emphasizes the efficiency of QDC reacting with α,β -unsaturated aldehydes, suggesting a regioselective route for the synthesis of carboxylic acids.

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