Kinetics and Mechanism of the Oxidative Cleavage of Unsaturated Acids by Quinolinium Dichromate

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Synopsis. Quinolinium dichromate (QDC) oxidizes cinnamic and crotonic acids smoothly in *N*,*N*-dimethylformamide in the presence of an acid. The reaction has a unit dependence on each of the substrate, oxidant, and acid concentrations. The mechanistic pathway involves an electrophilic attack of the oxidant on the double bond of the substrate, giving a carbonium-ion intermediate. This is supported by a small inverse kinetic isotope effect ($k_H/k_D=0.78$) at the α-carbon and the value of $\rho=-4.0$.

The oxidation of cinnamic acid by permanganate in aqueous neutral,[1)] alkaline,[2)] and acidic media[3)] had resulted in a cleavage of the carbon–carbon double bond to yield benzaldehyde. The permanganate oxidation of unsaturated carboxylic acids showed that in basic solutions (above pH 12), permanganate was reduced to manganate and diols were obtained as the major product; at lower pH, Mn(IV) was obtained with the formation of hydroxy ketones.[3)]

In our earlier communications, we had used quinolinium dichromate (QDC) to oxidize benzyl alcohols,[4)] diphenylamines,[5)] arylalkanes,[6a)] polynuclear aromatic hydrocarbons,[6d)] fluorenes,[6c)] toluene and substituted toluenes,[6d,7)] and amino acids.[8)] We have now directed our attention to the oxidation of some unsaturated carboxylic acids (cinnamic and crotonic acids) by QDC, and have cleaved the carbon–carbon double bond to give identifiable products.

Experimental

Materials. Cinnamic acid, crotonic acid, and substituted cinnamic acids were purified by recrystallization. Quinolinium dichromate (QDC) was prepared by the reported method.[9)] *N*,*N*-Dimethylformamide was distilled under reduced pressure before use. Sulfuric acid (E. Merck) was used as such after checking its physical constants. The purity of the deuterated compounds (cinnamic-α-*d* acid and cinnamic-β-*d* acid) was checked by NMR analyses.

Kinetics. The reactions were performed at constant temperature (±0.1 K) under pseudo-first-order conditions by keeping a large excess of the substrates with respect to QDC, and were followed spectrophotometrically (Systronics, digital model). The rate constants were evaluated from linear ($r>0.992$) plots of log [QDC] against time. The reported values were the mean of two or more runs and were reproducible to within ±3%. All of the kinetic runs were performed under nitrogen. The solvents were DMF and DMF–water mixtures. The reaction mixture remained homogeneous in the solvent systems used.

Product Analysis. Using the same experimental conditions that were used for the kinetic determinations, a solution of the reaction mixture was kept under nitrogen for 24 h, for the completion of the reaction. The products were extracted with chloroform, and the organic layer was washed with water, dried under anhydrous $MgSO_4$, and then concentrated. The products were separated by column chromatography using silica gel and eluting with varying proportions (100 : 0 to 70 : 30, v/v) of hexane and chloroform and were identified after concentrating the different fractions.

(i) Products from oxidation of cinnamic acid: The IR spectrum exhibited a carbonyl band at 1700 cm^{-1} and other bands below 900 cm^{-1} characteristic of benzaldehyde. The yields were benzaldehyde (ca. 80%) and glyoxylic acid (ca. 10%). A small amount of cinnamic acid (ca. 5%) was recovered.

(ii) Products from oxidation of crotonic acid: The IR spectrum exhibited a carbonyl band at 1730 cm^{-1} and other bands in the region 2880—2670 cm^{-1}, characteristic of acetaldehyde, and further confirmed by UV analysis.[10)] The yields were: acetaldehyde (ca. 80%) and glyoxylic acid (ca. 10%). A small amount of crotonic acid (5—8%) was recovered.

Results and Discussion

The stoichiometry of the reaction was determined under the conditions $[QDC]_0>[substrate]_0$ under nitrogen at 313 K at varying acidities. The ratio $\Delta[QDC]/\Delta[substrate]$ was 1.33, which conformed to the following overall equation:

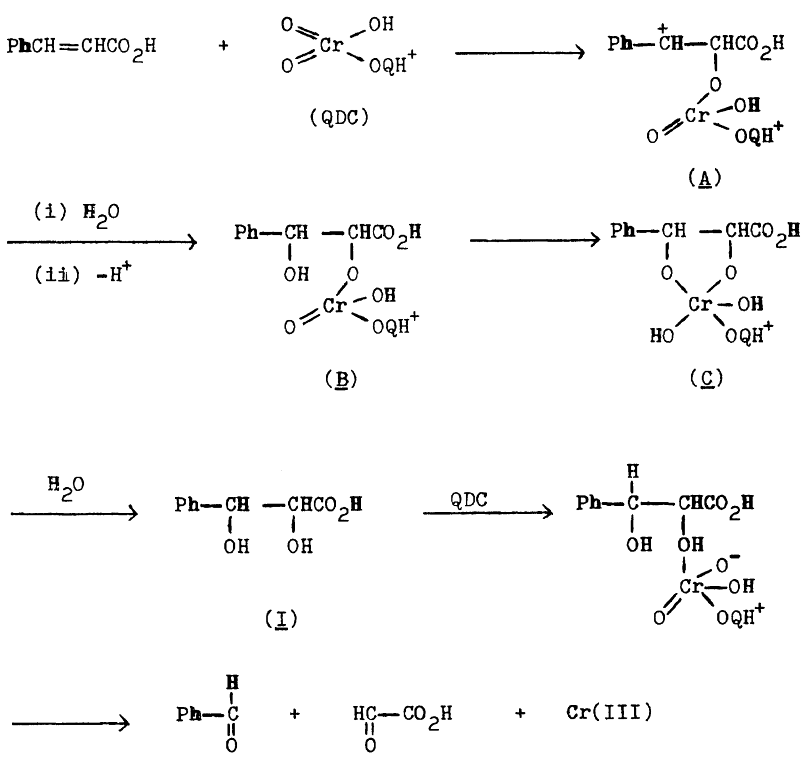
$$3RCH{=}CHCOOH + 4Cr(VI) + 6H_2O \rightarrow 3RCHO + 3C_2H_2O_3 + 4Cr(III) + 12H^+. \quad (1)$$

Under the present experimental conditions, wherein pseudo-first-order conditions were employed for all the kinetic runs, the reactions showed a first-order dependence on the concentrations of each reactant—substrate, oxidant, and acid (Table 1). The rate law could be represented as;

$$\text{Rate} = -d[Cr(VI)]/dt = k[\text{Substrate}][QDC][H^+]. \quad (2)$$

A liner increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in chromium trioxide oxidations.[11,12)] Moreover, the protonated Cr(VI) species would be a reactive electrophilic species to attack the double bond of unsaturated acids and to bring about an oxidative cleavage of the carbon–carbon double bond.

An increase in the dielectric constant of the medium (using varying proportions of DMF and water) reduced the rate of the reaction. Plots of log k_1 against the inverse of the dielectric constants were linear ($r=0.992$)



Scheme 1.

Table 1. Rate Data for the Oxidation of Unsaturated Acids at 40 °C[a)]

Substrate	QDC	H_2SO_4	Cinnamic acid	Crotonic acid
$10^2\times$M	$10^3\times$M	M	$10^4k_1/\mathrm{s}^{-1}$	
1.0	1.0	1.5	1.49	1.30
5.0	1.0	1.5	7.50	6.62
7.5	1.0	1.5	11.15	9.80
10.0	1.0	1.5	15.33	13.15
20.0	1.0	1.5	31.12	26.57
1.0	0.75	1.5	1.44	1.38
1.0	0.50	1.5	1.45	1.33
1.0	0.10	1.5	1.47	1.30
1.0	1.0	1.0	1.04	0.87
1.0	1.0	1.25	1.26	1.08
1.0	1.0	1.75	1.78	1.53
1.0	1.0	2.0	2.10	1.70

a) 1 M=1 mol dm^{-3}.

with positive slopes. This suggested an interaction between a positive ion and a dipole,[13)] and was in consonance with the observation that, in the presence of acid, the rate-determining step involved a protonated Cr(VI) species.[11)]

Table 2. Kinetic Isotope Effect at 40 °C

Substrate	$10^4k_1/\mathrm{s}^{-1}$	$k_\mathrm{H}/k_\mathrm{D}$
Cinnamic acid	1.49	
Cinnamic-*α*-*d* acid (**1**)	1.91	0.78
Cinnamic-*β*-*d* acid (**2**)	1.51	0.99

[Substrate] 0.01 M; [QDC] 0.001 M; [H_2SO_4] 1.5 M.

(1) **(2)**

Chart 1.

The isotope-effect data given in Table 2 show a clear distinction between the *α* and *β* carbon atoms of cinnamic acid in the transition state (Chart 1). The oxidation of cinnamic-*α*-*d* acid (**1**) gave an inverse secondary deuterium kinetic isotope effect ($k_\mathrm{H}/k_\mathrm{D}=0.78$), while the oxidation of cinnamic-*β*-*d* acid (**2**) gave a negligible secondary deuterium kinetic isotope effect ($k_\mathrm{H}/k_\mathrm{D}=0.99$). For the oxidation of **1**, $k_\mathrm{H}/k_\mathrm{D}=0.78$ indicated a change in the state of hybridization from sp^2 to sp^3 for the *α*-carbon atom. For the oxidation of **2**, $k_\mathrm{H}/k_\mathrm{D}=0.99$ is reasonable, since the *β* carbon, in going from an olefinic center to a carbonium ion-like character during the process of electron abstraction, would remain sp^2 in character. Since the oxidation of cinnamic acid exhibited an inverse secondary deuterium isotope effect only at the *α*-carbon, this would suggest that the rate-determining step of the reaction produced a carbonium ion in which the *α*-carbon remained sp^2 in character. This implied that in the transition state, there was substantial C_α–O bond formation (after QDC attack), but negligible C_β–O bond formation.

The rates of oxidation of ring-substituted cinnamic acids were determined (Table 3). The correlation of the rate constants[14)] gave the value of the reaction constant ρ as −4.0 (corr. coeff.=0.994). A hydrogen-abstraction

Table 3. Effects of substituents for Oxidation of Cinnamic Acids (40 °C)[a] and Activation Parameters

Substrate[a]	$10^5\times k_1$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
0.01 M	s^{-1}	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$	$kJ\,mol^{-1}$
p-Methyl-	35.7	75	−78	99.4
m-Methyl-	22.5	79	−67	100.0
H	14.9	82	−57	100.1
p-Chloro-	5.6	85	−50	100.7
m-Chloro-	3.2	87	−42	101.1
p-Nitro-	0.5	91	−32	101.0
Crotonic acid	13.0	93	−23	100.0

Error limits: $\Delta H^{\neq}\pm2$ kJ mol^{-1}; $\Delta S^{\neq}\pm2$J K^{-1} mol^{-1}; $\Delta G^{\neq}\pm2$kJ mol^{-1}

mechanism is unlikely, in view of the failure to induce the polymerization of acrylonitrile and the reduction of mercury(II) chloride.[15] The present kinetic data suggest the compatibility of an electrophilic attack of protonated QDC on the double bond of cinnamic acid to form a carbonium ion **A** which would be stabilized by the phenyl group. The intermediate formed reacts with a nucleophile (water) in the reaction mixture to form an intermediate **B**, which could be converted to the chromate ester **C**. This ester could then be cleaved to give the observed products. The sequence of reactions is shown in Scheme 1.

Efforts to isolate the intermediate **I** during the course of the reaction were not successful. Independent kinetic experiments performed in this laboratory have shown that 2,3-dihydroxy-3-phenyl propinoic acid, (**I**), underwent a rapid reaction with QDC in acid medium under a nitrogen atmosphere to give benzaldehyde and glyoxylic acid as the products. The oxidative cleavage of 1,2-diols to yield aldehydes has been established in earlier investigations.[16,17]

The proposed mechanism is supported by the values of the thermodynamic parameters (Table 3). The fairly high positive values of the enthalpies of activation ($\Delta H^{\neq}$) indicated that the transition state was highly solvated. The negative values of the entropies of activation ($\Delta S^{\neq}$) suggested that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecules. The constancy of the $\Delta G^{\neq}$ values indicated a common mechanism for the oxidation of all of the substrates. Using Exner's criterion,[18] the plot between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ was linear ($r=0.990$), and the isokinetic temperature was 350 K. The linear trend between enthalpies and entropies of activation showed that the reaction was controlled by both parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$).

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