

Quinolinium Dichromate Oxidations. Kinetics and Mechanism of the Oxidative Cleavage of Styrenes

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Received January 20, 1993

The kinetics of oxidation of styrene and substituted styrenes by quinolinium dichromate (QDC) in dimethyl formamide, in the presence of acid, has been investigated. The rate of the reaction is dependent on the first powers of the concentrations of substrate, oxidant, and acid. A small inverse kinetic isotope effect has been observed ($k_H/k_D = 0.80$). Correlation with σ yielded a ρ value of -4.0 , suggesting the formation of a cationic intermediate in the rate-determining step of the reaction. Subsequent cleavage of the carbon-carbon bond yielded benzaldehyde and formaldehyde.

Introduction

Styrene has been converted to phenylglyoxylic acid by alkaline permanganate, with the hydroxy ketone as the probable intermediate.¹ The periodate-permanganate cleavage of alkenes was used as a means of determining the position of double bonds in unsaturated compounds.² The reaction of styrene and substituted styrenes with thallium(III) acetate in methanol and in acetic acid was studied by Kabbe³ and by Ouellette et al.⁴ The oxidation of styrene by chromyl chloride in carbon tetrachloride solution had involved a rate-determining attack of the oxidant on the carbon-carbon double bond.^{5,6} Other studies pertaining to the oxidation of styrene have included oxidants such as thallium(III) nitrate in methanol,⁷ Pb(IV),⁸ Ce(IV),⁹ Co(III),¹⁰⁻¹² and peracetic acid.¹³

We have already reported the results of the kinetic investigations of oxidations by quinolinium dichromate (QDC) involving diverse kinds of organic substrates such as benzyl alcohols,¹⁴ diphenylamines,¹⁵ arylalkanes,^{16a} polynuclear aromatic hydrocarbons,^{16b} fluorene,^{16c} toluene, and substituted toluenes,^{16d,17} and amino acids.¹⁸ In our continuing efforts to exploit QDC as a versatile oxidizing agent, we have now focused our attention on the oxidation of unsaturated systems (styrene and substituted styrenes) and have looked at the possibility of cleaving the carbon-carbon double bond of styrene to give identifiable products.

Experimental Section

(a) **Materials.** Styrene was a SISCO sample and was distilled. The fraction distilling at 145 °C was collected. The purity of this sample was checked by IR and UV analyses, which were found to correspond to that of the styrene monomer.¹⁹ Substituted styrenes were obtained from the Aldrich Chemical Co. and were purified by distillation, and their purity was checked from physical constants. Quinolinium dichromate (QDC) was prepared by the reported method,²⁰ and its purity was checked by estimating Cr(VI) iodometrically. Dimethylformamide (DMF) was a BDH sample and was distilled under reduced pressure before use. Sulfuric acid (E. Merck) was used as such after a check of its physical constants. Styrene glycol (1-phenylethane-1,2-diol) was prepared by the standard method²¹ and was obtained as white needles (mp 65 °C). Dehydration of 1-phenylethanol-1-*d* with potassium hydroxide gave α -deuteriostyrene (bp 60 °C, 30 Torr), while the dehydration of 2-phenylethanol-1,1-*d*₂ with potassium hydroxide yielded β,β -dideuteriostyrene (bp 54 °C, 30 Torr). The purity of the deuterated compounds thus prepared was checked by ¹H-NMR spectroscopy.

(b) **Kinetic Measurements.** The reactions were performed under pseudo-first-order conditions, maintaining a large excess of the styrenes with respect to QDC. The reactions were carried out at constant temperature (± 0.1 K) and were followed by monitoring the absorption band at 440 nm, spectrophotometrically, as described in an earlier paper.¹⁴ All the reactions were performed under a nitrogen atmosphere. The rate constants were evaluated from the linear ($r > 0.992$) plots of $\log [QDC]$ against time. The values reported were the mean of two or more runs and were reproducible to within $\pm 3\%$. The solvent was DMF or a DMF-water mixture. The reaction mixtures remained homogeneous in the solvent systems used.

(c) **Product Analysis.** Using the same experimental conditions as were used for kinetic determinations, a solution of the reaction mixture was kept under a nitrogen atmosphere for 24 h, until the reaction had gone to completion. The solution was extracted with chloroform and the organic layer washed with water, dried over anhydrous MgSO₄, and then concentrated. Spotting on TLC plates showed two spots. The two products were separated on a silica gel column, eluted with varying proportions (100:0-70:30, v/v) of hexane and chloroform, concentrated, and then identified as follows:

For the first product, an IR spectrum exhibited a carbonyl band at 1700 cm⁻¹ and certain other bands below 900 cm⁻¹ that were characteristic of benzaldehyde. The second product was characterized as formaldehyde, which existed in water largely as the hydrate [CH₂(OH)₂]. IR analysis did not show any carbonyl band. On evaporation of the aqueous solution of formaldehyde, a solid residue was left behind, which on recrystallization from ether gave crystalline needles of 1,3,5-trioxane (mp 62 °C). The

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Table I. Stoichiometry of the Oxidation of Styrene by QDC. Concentration of Styrene = 0.005 M

[H ₂ SO ₄]/M	10 ² [QDC]/M	Δ[QDC]/Δ[styrene]
0.0	2.5	1.33
0.10	2.60	1.36
0.25	2.70	1.30
0.50	2.80	1.33

Table II. Dependence of the Reaction Rate on Oxidant Concentration ([Styrene] = 0.01 M; [H₂SO₄] = 1.5 M; T = 313 K)

10 ⁴ [QDC]/M	10 ⁴ k ₁ /s ⁻¹	10 ⁴ [QDC]/M	10 ⁴ k ₁ /s ⁻¹
1.0	1.38	10.0	1.46
5.0	1.40	15.0	1.37
7.5	1.41	20.0	1.45

Table III. Dependence of the Reaction Rate on Substrate Concentration ([QDC] = 0.001 M; [H₂SO₄] = 1.5 M; T = 313 K)

10 ² [styrene]/M	1.0	5.0	7.5	10.0	15.0	20.0
10 ⁴ k ₁ /s ⁻¹	1.46	7.35	11.0	14.8	22.1	30.0
10 ² k ₂ /M ⁻¹ s ⁻¹	1.46	1.47	1.47	1.48	1.47	1.50

Table IV. Dependence of Reaction Rate on Acidity ([Styrene] = 0.01 M; [QDC] = 0.001 M; T = 313 K)

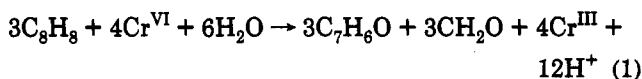
[H ₂ SO ₄]/M	10 ⁴ k ₁ /s ⁻¹	[H ₂ SO ₄]/M	10 ⁴ k ₁ /s ⁻¹
1.0	0.95	2.0	1.92
1.25	1.22	3.0	2.95
1.50	1.46	4.0	3.86
1.75	1.71		

percentage yields of benzaldehyde and formaldehyde were 80–85% and 6–10%, respectively.

Results

The oxidation of styrene by QDC, in dimethyl formamide (DMF), resulted in the formation of benzaldehyde and formaldehyde. Under the present experimental conditions, there was no further oxidation of benzaldehyde.

Stoichiometry. The stoichiometry experiments were carried out under nitrogen at 313 K, under the conditions of [QDC]₀ > [styrene]₀, at varying acid concentrations. The disappearance of Cr(VI) was followed until the absorbance values became constant. The [QDC]_∞ was estimated. A stoichiometric ratio, Δ[QDC]/Δ[styrene], of 1.33 was observed (Table I), which conformed to the overall equation



Kinetic Data. Under pseudo-first-order conditions, the individual kinetic runs were first order with respect to QDC. Further, the pseudo-first-order rate constants did not alter appreciably with changing QDC concentration (20-fold range), at constant styrene concentration (large excess). This indicated a first-order dependence on QDC (Table II). The reaction was of first order with respect to the concentration of styrene; this was further confirmed by the constancy of *k*₂, the second-order rate constant (Table III). The reaction was catalyzed by acid, and the catalyzed reaction showed a first-order dependence on acidity (Table IV). These data suggest the following rate law:

$$-d[QDC]/dt = k[\text{styrene}][QDC][H^+] \quad (2)$$

Effect of Solvent Composition. The acid-catalyzed oxidation of styrene was studied in solutions containing

Table V. Dependence of Reaction Rate on Solvent Composition ([Styrene] = 0.01 M; [QDC] = 0.001 M, T = 313 K)

DMF:H ₂ O (% v/v)	100:0	95:5	90:10	85:15	80:20
<i>D</i>	37.6	39.7	41.8	43.9	46.1
10 ⁴ k ₁ /s ⁻¹	1.46	1.22	1.08	0.89	0.77

Table VI. Kinetic Isotope Effect ([Substrate] = 0.01 M; [QDC] = 0.001 M; [H₂SO₄] = 1.5 M; T = 313 K)

substrate	10 ⁴ k ₁ /s ⁻¹	k _H /k _D
styrene	1.46	
α-deuteriostyrene	1.49	0.98
β,β-dideuteriostyrene	1.83	0.80

Table VII. Rate Constants for the Oxidation of Styrenes by Quinolinium Dichromate (10⁴k₁/s⁻¹) in the Presence of Acid

substituent	303 K	308 K	313 K	318 K	323 K
H	0.56	0.92	1.46	2.40	3.51
<i>m</i> -Me	1.01	1.82	2.88	4.47	6.92
<i>p</i> -Me	3.09	4.79	7.60	10.96	15.85
<i>p</i> -OMe	7.24	12.02	20.01	31.62	47.86
<i>p</i> -Cl	0.04	0.07	0.14	0.23	0.39
<i>m</i> -Cl		0.02	0.04	0.07	0.12

varying proportions of DMF and water (Table V). It was observed that an increase in the dielectric constant of the medium reduced the rate of the reaction.

Kinetic Isotope Effect. The oxidation of α-deuteriostyrene gave a negligible secondary kinetic deuterium isotope effect (*k*_H/*k*_D = 0.98), while the oxidation of β,β-dideuteriostyrene gave an inverse secondary kinetic deuterium isotope effect (*k*_H/*k*_D = 0.80). The rate data are given in Table VI.

Linear Free Energy Relationship. The rates of oxidation of five ring-substituted styrenes were determined (Table VII). Correlation of the rate constants with σ substituent constants²² gave a value of ρ = -4.0 (*r* = 0.997).

Induced Polymerization. Since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was observed that there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride.²³ This indicated that a one-electron oxidation was quite unlikely. Control experiments were performed in the absence of styrene. The concentration of QDC did not show any appreciable change.

Effect of Temperature. The catalyzed oxidation of styrene was studied at different temperatures (Table VII). The activation parameters (303–323 K) were evaluated by the standard procedure.²⁴

Discussion

The rate of the reaction was dependent on the concentrations of substrate and oxidant. This kinetic behavior was consistent with a mechanism involving a rate-determining reaction between styrene and quinolinium dichromate. The linear increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement of such Cr(VI) species

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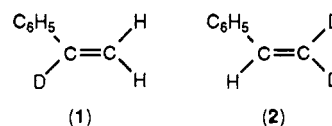
in chromic acid oxidation reactions.²⁵ Protonated Cr(VI) species have been observed in the presence of *p*-toluene-sulfonic acid in nitrobenzene-dichloromethane mixtures.²⁶ Moreover, the protonated Cr(VI) species would be a reactive electrophilic species and would be sufficiently reactive to attack the double bond of styrene and bring about the oxidative cleavage of the carbon-carbon double bond.

The dielectric constants for dimethyl formamide-water mixtures have been estimated from the dielectric constants of the pure solvents and have been recorded in Table V. A plot of $\log k_1$ against the inverse of the dielectric constant was linear ($r = 0.990$) with a positive slope. This suggested an interaction between a positive ion and a dipole²⁷ and was in consonance with the observation that in the presence of an acid the rate-determining step involved a protonated Cr(VI) species.

Olefins are nucleophilic substances, and modifications in structure would affect the rates of reactions of the olefins with electrophilic substances. When electron-releasing groups are attached to, or are in close proximity to, the double bond, the reaction rate is increased because of the increased electron density of the ethylenic system (e.g., styrene), which results in an increase in the nucleophilic properties of the double bond. When electron-attracting groups are present, the reaction rate is decreased because of a decrease in the nucleophilic properties of the double bond. The phenyl group acts as an electron-releasing group in styrene, since the specific reaction rate of styrene with QDC ($k_1 = 1.46 \times 10^{-4} \text{ s}^{-1}$ at 313 K) was greater than that of ethylene with QDC ($k_1 = 0.04 \times 10^{-4} \text{ s}^{-1}$ at 313 K). Inspection of Table VIII reveals that electron-releasing substituents accelerate the oxidation process and electron-attracting groups retard the process. Hence, a linear free energy relationship of the Hammett equation type should correlate the reactivity with the Hammett substituent constants.²² A plot of $\log k_1$ versus σ values of substituents was linear ($r = 0.997$), and the value of the reaction constant ρ was -4.0 . This suggested that the transition state possessed a large degree of carbonium ion character resulting from a large amount of positive charge developing at the carbon atom adjacent to the benzene ring (α -carbon atom). Earlier studies had shown that ρ values larger than -3 suggested a fairly large degree of carbonium ion character in the transition state.²⁸⁻³¹

Secondary kinetic deuterium isotope effects can be used to gain an insight into the changes in hybridization occurring at an isotopically substituted carbon atom, as the reactants proceed from the ground state to the transition state.³² The isotope effect data in Table VI show a clear distinction between the α and β carbons of styrene in the transition state. An inverse secondary kinetic deuterium isotope effect ($k_H/k_D < 1$) would indicate that one or more carbon atoms would undergo a change

in the state of hybridization from sp^2 to sp^3 between the ground state and the transition state.^{33,34} Electron abstraction from the double bond of 1 or 2,



accompanied by the development of a partial positive charge at the benzyl carbon atom (α -carbon), would give a negligible secondary deuterium isotope effect for the oxidation of 2. For the oxidation of 1, $k_H/k_D = 0.98$ is reasonable since the α -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. For the oxidation of 2, $k_H/k_D = 0.80$; this would indicate a change in the state of hybridization from sp^2 to sp^3 for the terminal carbon atom (β -carbon). Since the oxidation of styrene exhibited an inverse secondary deuterium isotope effect only at the β -carbon (Table VI), 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 implies that in the transition state there is substantial C_β -O bond formation, but negligible C_α -O bond formation, when QDC attacks the double bond of styrene.

A hydrogen abstraction mechanism is unlikely, in view of the failure to induce the polymerization of acrylonitrile and the reduction of mercuric chloride. In most hydrogen abstraction reactions, the reaction constants have small magnitude.³⁵ In the present investigation, the large negative value of the reaction constant ($\rho = -4.0$), together with the values of the kinetic isotope effects (Table VI), would suggest considerable carbonium ion character in the transition state. The kinetic data suggest the compatibility of an electrophilic attack of the protonated form of the oxidant (QDC) on the olefin (styrene) to form a carbonium ion A. This carbonium ion could be stabilized by the phenyl group. The intermediate formed reacts with a nucleophile (e.g., water) in the reaction mixture to form an intermediate such as B. In the presence of water and excess QDC, the intermediate B could be converted to the cyclic chromate ester C. This ester could then be cleaved to give the observed products. The sequence of reactions is shown in Scheme I.

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 styrene glycol, I, underwent a rapid reaction with QDC, in acid medium, under a nitrogen atmosphere, to yield benzaldehyde and formaldehyde as the products. The rate constants at 313 K were $2.19 \times 10^{-3} \text{ s}^{-1}$ (glycol = 0.01 M) and $2.25 \times 10^{-2} \text{ s}^{-1}$ (glycol = 0.10 M). Thus, the styrene glycol, I, when formed during the reaction, would be rapidly converted by QDC, in acid medium, to yield benzaldehyde and formaldehyde as the products. These two products have been isolated from the reaction mixture and have been characterized by spectral methods. The formation of these products would substantiate the mechanism of the oxidation reaction, wherein there was a cleavage of

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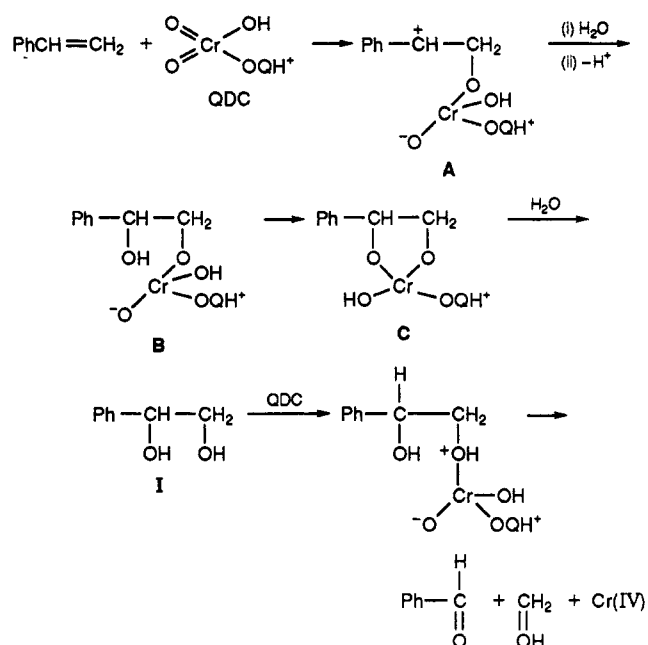
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Scheme I



the carbon-carbon bond in the final step of the reaction. The oxidative cleavage of the 1,2-glycols to yield aldehydes has been established in earlier investigations.³⁶⁻³⁹

In the oxidation of olefins by chromyl chloride, it had been shown that the reaction proceeded via a metallocycle intermediate.⁴⁰ Ab initio calculations on the energetics of these reactions had confirmed the intermediacy of the metallocyclohexane for the observed oxygen-containing products.⁴¹ This implied that for CrO_2Cl_2 the shift involved reaction with a strong metal-oxo triple bond, whereas for other metal oxides (KMnO_4 , OsO_4) the reactions were with an oxo double bond resulting in the conversion of a spectator oxo into an oxo triple bond. Such

Table VIII. Activation Parameters for the Oxidation of Styrenes by Quinolinium Dichromate in the Presence of Acid

substituent	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
H	72	-93	101.1
<i>m</i> -Me	67	-105	99.9
<i>p</i> -Me	60	-130	100.7
<i>p</i> -OMe	41	-190	100.5
<i>p</i> -Cl	79	-70	100.9
<i>m</i> -Cl	82	-60	100.8
error limits	$\Delta H^\ddagger \pm 3$ kJ mol ⁻¹	$\Delta S^\ddagger \pm 4$ J mol ⁻¹ K ⁻¹	$\Delta G^\ddagger \pm 3$ kJ mol ⁻¹

spectator oxo groups were observed to play a central role in stabilizing critical intermediates in these reactions and were suggested to be important in reactions of metal oxides such as MnO_4^{2-} , OsO_4 , RuO_4 , and supported transition metal oxides.⁴¹ In the present investigation, the reaction of styrene with QDC could be suggested to proceed via an intermediate wherein a spectator oxo could be converted into an oxo triple bond, similar to the type of intermediate suggested for the oxidation of olefins by KMnO_4 and OsO_4 .⁴¹

The proposed mechanism is supported by the values of the thermodynamic parameters (Table VIII). The fairly high positive values of the enthalpies of activation (ΔH^\ddagger) and the free energies of activation (ΔG^\ddagger) indicated that the transition state was highly solvated. The moderately large negative values of the entropies of activation (ΔS^\ddagger) suggested that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecules. The similarity in ΔG^\ddagger values for all the substrates arises due to changes in ΔH^\ddagger and ΔS^\ddagger values and emphasizes the probability that all of these reactions involve similar rate-determining steps. The activation enthalpies and entropies for the oxidation reaction were linearly related ($r = 0.991$). The correlation was tested and found to be valid by using Exner's criterion.⁴² The plot between ΔH^\ddagger and ΔS^\ddagger was linear, and the isokinetic temperature was 313 K. Although not much physical significance should be attached to isokinetic temperatures, it is sufficient to state that a linear correlation is usually a necessary condition for the validity of the Hammett equation. The linear trend between the enthalpies and entropies of activation showed that the reaction was controlled by both parameters (ΔH^\ddagger and ΔS^\ddagger).

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