

Kinetics of Oxidation of Benzaldehydes by Quinolinium Dichromate

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Quinolinium dichromate (QDC) in sulfuric acid oxidizes benzaldehydes to the corresponding acids in a 50% (v/v) acetic acid-water medium. The reaction is first order each in [QDC], [substrate] and $[H^+]$. The reaction rates have been determined at different temperatures and the activation parameters calculated. The rate decreases with an increase in the water content of the medium. The effects of substituents have been studied. A suitable mechanism is proposed.

Key words: Kinetic, Oxidation, Aromatic Aldehydes, Quinolinium Dichromate

Introduction

A number of reports on the mechanism of oxidation of several substrates by quinolinium dichromate are available. Quinolinium dichromate (QDC) is shown to oxidize primary and secondary alcohols to the corresponding aldehydes [1, 2], cyclic alcohols to the corresponding cyclic ketones [3], bicyclic alcohols [4] and benzyl alcohol [5]. The α -hydroxyacids [6] and α -ketoacids [7] are found to be oxidized with QDC and their reactions are studied kinetically. Quinolinium dichromate (QDC) oxidizes cinnamic and crotonic acids smoothly in N,N-dimethylformamide in the presence of an acid [8, 9] to give aldehydes. α , β -Unsaturated aldehydes [10], aliphatic dialdehydes [11] and heterocyclic aldehydes [12] are oxidized by QDC. Other substrates such as phenols [13], amino acids [14], methoxytoluenes [15], thallium(I) [16], styrenes [17] and diols [18] are also oxidized by QDC.

The present work reports the kinetics of oxidation of substituted benzaldehydes by QDC and evaluates the reaction constants. Mechanistic aspects are also discussed.

Experimental Section

Materials and methods

All benzaldehydes used were of A.R. grade (E Merck), the liquid benzaldehydes were used after distillation. The oxidant quinolinium dichromate (QDC, $[(C_9H_7N^+H)_2Cr_2O_7^{2-}]$) (Aldrich) was used. Acetic acid (A.R. grade) was distilled before use. Sulfuric acid (E. Merck) was used after a check of its physical constants.

Reactions were carried out under pseudo-first order conditions by maintaining a large excess of the aldehyde over [QDC]. The solvent was a 1:1 (v/v) acetic acid-water mixture. The reactions were carried out at constant temperatures (± 0.1 K) and were followed up to 80% completion. The amount of unreacted QDC was estimated iodometrically. The pseudo-first order rate constants (k_1) were computed from linear least squares plot of [QDC] vs. time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The second order rate constant was obtained from the relation, $k_2 = k_1/[\text{substrate}]$.

Product analysis

Benzaldehyde (0.2 mol) and QDC (0.4 mol) were mixed together with sulfuric acid (0.1 mol) in 50% (v/v) aqueous acetic acid (total volume 100 ml). The reaction mixture was set aside for about 24 h to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried. The residue was confirmed as benzoic acid by the m.p. 121°C , TLC and spectral analysis. The percentage yield was calculated to be 97%.

Results and Discussion

The oxidation of aromatic aldehydes by QDC resulted in the formation of the corresponding acids. Under the present experimental conditions, there was no further oxidation of the acids.

The stoichiometry of the reaction was determined [19]. Stoichiometric ratios, in the range of 0.65 to 0.68 were obtained, which conformed to the following overall equation:

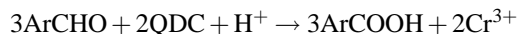


Table 1. Rate data for the oxidation of benzaldehyde at 303 K in 50% (v/v) acetic acid-water.

$10^2[\text{BA}]$ $\text{mol}\cdot\text{dm}^{-3}$	$10^3[\text{QDC}]$ $\text{mol}\cdot\text{dm}^{-3}$	$[\text{H}_2\text{SO}_4]$ $\text{mol}\cdot\text{dm}^{-3}$	$10^5 k_1$ s^{-1}
1.0	1.0	0.5	3.96
2.5	1.0	0.5	9.90
5.0	1.0	0.5	19.80
7.5	1.0	0.5	29.59
10.0	1.0	0.5	39.02
1.0	0.75	0.5	3.94
1.0	0.5	0.5	3.90
1.0	0.25	0.5	3.95
1.0	0.1	0.5	3.90
1.0	1.0	0.75	5.84
1.0	1.0	1.0	7.92
1.0	1.0	1.25	9.90
1.0	1.0	1.5	11.88

Table 2. Solvent effect for the oxidation of benzaldehyde by QDC at 303 K.

$\text{H}_2\text{O}:\text{AcOH}$ (%, v/v)	Dielectric constants D	$10^4 k$ s^{-1}	$\text{H}_2\text{O}:\text{AcOH}$ (%, v/v)	Dielectric constants D	$10^4 k$ s^{-1}
70:30	72.0	2.98	40:60	45.5	5.32
60:40	63.3	3.41	30:70	38.5	6.86
50:50	56.0	3.96			

$[\text{BA}] = 1 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{QDC}] = 1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol}\cdot\text{dm}^{-3}$.

Using pseudo-first-order conditions, individual kinetic runs were observed to be first order in QDC. The pseudo-first-order rate constants (k) were independent on the initial concentration of the oxidant (Table 1). The order of the reaction with respect to the substrate concentration was obtained by varying the aldehyde concentration and observing the effect on the rate at constant $[\text{QDC}]$ and $[\text{H}^+]$. The results are given in Table 1. The order with respect to the concentration of acid was obtained at constant aldehyde and QDC concentrations. The data given in Table 1 indicate a first order dependence on the concentration of the acid. Under the acid concentrations used in the present investigation, the protonation of the aldehydes would be less significant. The possibility of the aldehydes getting protonated can be ruled out on the basis that aldehydes are extensively hydrated in an aqueous medium, and are present as equilibrium mixtures of the carbonyl and hydrated forms. The formation constants are thus not dependent on the acidity or alkalinity [20].

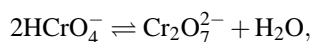
Hence, it would be justified to propose that in the range of acid concentrations used the oxidant QDC was converted to the protonated chromium(VI)

species. Earlier reports have established the involvement of protonated Cr(VI) species in chromic acid oxidation reactions [21, 22].

The oxidation of substrates was studied in solutions containing varying proportions of water and acetic acid. It was observed that there was an increase in the rate of the reaction with a decrease in the dielectric constant [23] of the medium (Table 2).

Mechanism and rate law

The kinetic results showed that the rate of oxidation of benzaldehydes was dependent on the first powers of the concentrations of each (substrate, oxidant and acid). The acid catalysis of the reaction must be related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentrations of the mineral acid used. Quinolinium dichromate (QDC) is an anionic condensed form of chromic acid. Aqueous solutions of chromic acid contain ions such as CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, besides other protonated species such as $\text{H}_2\text{Cr}_2\text{O}_7$, HCr_2O_7^- and H_2CrO_4 [11, 24]. The ionization constant for the HCrO_4^- ion was $3.0 \times 10^{-7} \text{ mol/l}$; hence, in dilute aqueous acid, the concentration of CrO_4^{2-} ions was negligible. This has been amply substantiated by Michel *et al.* [25], who examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate HCrO_4^- did not exist in aqueous solutions of Cr(VI) compounds. The ionization constant for the HCr_2O_7^- ion was 0.85 mol/l ; hence, in solutions where $\text{pH} = 1$, 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 would be HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. These ions are in equilibrium with each other according to the equation



with a 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 $\text{pH} = 11$, the Cr(VI) ion was only present in the form of the CrO_4^{2-} ion, whereas at $\text{pH} = 1.2$, it existed only as the $\text{Cr}_2\text{O}_7^{2-}$ ion [25]. Hence, at concentrations of acid larger than 0.05 M , the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, spectral studies have

shown that $\text{Cr}_2\text{O}_7^{2-}$ was the predominant species [26]. In the present investigation, since the concentrations of acid used were in the range of 0.5 to 1.5 M, 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.

The effect of a change in the solvent composition (water-acetic acid, %, v/v) on the rate of oxidation for the substrates was studied. It was observed that an increase in the water content of the medium showed a decrease in the rate of oxidation (Table 2). 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 the dielectric constant of the medium (increase in the acetic acid content) would favor the dichromate form over the chromate form. If ion pairs were to be formed in this medium, it would be expected that they have a higher ion-pair association constant for the dichromate ion, which would again favor the dichromate ion. Plots of $\log k$ versus $1/D$ were found to be linear, with positive slopes, which indicated that the reactions were of the ion-dipole type [27].

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed *via* the hydrate form [20, 28–33].

The sequence of reactions for the oxidation of benzaldehydes by QDC, in an acid medium is shown in Scheme 1. In an acid medium, the oxidant QDC is converted to the protonated bimetallic chromium(VI) species (PQ), in the acid range used for the present investigation, the protonated QDC would have the Cr(VI) existing mainly as $\text{Cr}_2\text{O}_7^{2-}$. The substrate (A) was converted to the hydrated form (HY). The reaction of the hydrated form (HY) of the substrate with the protonated QDC (PQ) resulted in the formation of the monochromate ester [11] which under decomposition in the rate determining step give the product.

Based on the mechanism shown in Scheme 1, the rate law has been derived as follows:

$$-d[\text{QDC}]/dt = k_3[\text{E}] = k_3[\text{HY}][\text{PQ}],$$

where

$$[\text{PQ}] = K_1 [\text{QDC}][\text{H}^+],$$

and

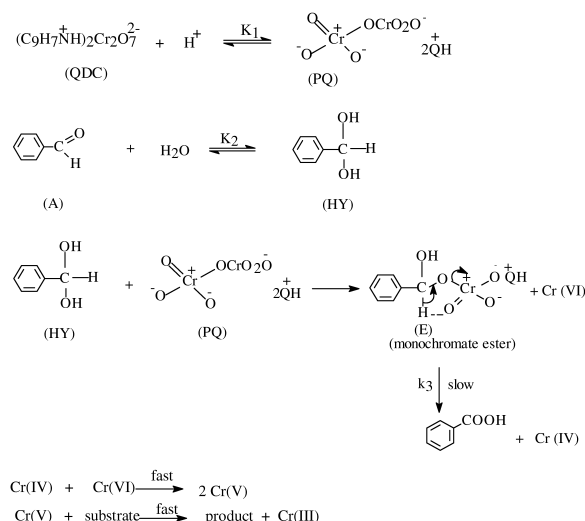
$$[\text{HY}] = K_2 [\text{A}][\text{H}_2\text{O}].$$

Substituting the values of [PQ] and [HY], the follow-

ing equation was obtained:

$$-d[\text{QDC}]/dt = K_1 K_2 k_3 [\text{A}] [\text{QDC}] [\text{H}^+].$$

From this rate expression, it is clear that the reaction exhibited a first-order dependence with respect to the concentrations of each (substrate, oxidant, and acid). This rate law explains all of the experimentally observed results.



Scheme 1.

Effect of substituents

Effect of substituents on the rate of oxidation has been studied with a number of *para*- and *meta*- substituted benzaldehydes. In general, the rate of reaction is accelerated by electron-withdrawing substituents and

Table 3. Temperature effect and thermodynamics for the oxidation of substituted benzaldehydes by QDC.

Subst.	$10^3 k_2 (\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$			$\Delta H^\#$ (kJ·mol ⁻¹)	$\Delta S^\#$ (J·K ⁻¹ ·mol ⁻¹)
	303 K	313 K	323 K		
H	3.96	6.51	9.92	35.0	175.60
<i>p</i> -CH ₃	1.35	2.51	4.31	44.91	151.80
<i>p</i> -OCH ₃	0.60	1.23	2.31	52.56	133.32
<i>p</i> -Cl	5.09	7.85	11.99	37.46	165.30
<i>p</i> -NO ₂	23.30	32.70	44.00	23.95	198.90
<i>p</i> -CN	17.32	24.30	34.70	25.85	193.50
<i>m</i> -CH ₃	2.81	4.87	7.80	39.20	164.58
<i>m</i> -OCH ₃	4.66	7.63	11.60	34.75	175.10
<i>m</i> -Br	7.50	11.50	17.20	35.58	168.34
<i>m</i> -NO ₂	15.00	21.20	28.70	23.99	200.80
<i>p</i> -Br	5.71	8.82	13.60	32.92	179.40

Substituents constants	ρ_I	ρ_R	R	SD	λ	f
<i>para</i> -substituted						
σ_I, σ_R^o	1.09	1.75	0.987	0.30	1.61	0.09
σ_I, σ_R^+	1.05	1.05	0.999	0.26	1.00	0.03
σ_I, σ_R^-	0.97	1.11	0.981	0.28	1.14	0.10
$\sigma_I, \sigma_R^{(AB)}$	1.12	1.50	0.978	0.29	1.34	0.06
<i>meta</i> -substituted						
σ_I, σ_R^o	0.530	0.463	0.996	0.38	0.873	0.04
σ_I, σ_R^+	0.563	0.281	0.994	0.25	0.499	0.07
σ_I, σ_R^-	0.501	0.405	0.858	0.21	0.808	0.03
$\sigma_I, \sigma_R^{(AB)}$	0.555	0.450	0.960	0.25	0.811	0.06

Table 4. Correlation of rates of oxidation of *para*- and *meta*-substituted benzaldehydes by QDC with substituent parameters at 303 K.

Temp (K)	ρ_I	ρ_R	R	SD	λ	f
<i>para</i> -substituted						
303	1.05	1.050	0.9998	0.27	1.00	0.03
313	0.998	0.997	0.9997	0.25	0.999	0.04
323	0.975	0.970	0.9995	0.2	0.995	0.05
<i>meta</i> -substituted						
303	0.530	0.463	0.9993	0.38	0.873	0.04
313	0.545	0.351	0.9983	0.38	0.644	0.04
323	0.521	0.383	0.9853	0.39	0.735	0.04

Table 5. Temperature dependence of the reaction constants.

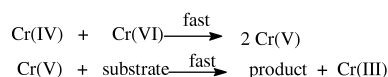
retarded by electron releasing ones (Table 3). A plot of $\log(k_2/k_2^o)$ vs σ gives a positive slope with ρ values of 1.269 ($r = 0.93$). Since the reaction rates failed to show a significant correlation with any single-parameter substituents constants, the rates have been analyzed in terms of the dual substituents parameter equation of Taft [34],

$$\log k = \log k_o + \sigma_I \rho_I + \sigma_R \rho_R.$$

The rates of oxidation of *para*- and *meta*-substituted benzaldehydes were separately correlated with σ_I and one of four σ_R values, viz. $\sigma_R^o, \sigma_R^{(AB)}, \sigma_R^+$ and σ_R^- . The results are summarized in Table 4, which are in good agreement with the results obtained by A. Jameel [35].

The results show that the rates of *para*-substituted benzaldehydes show excellent correlation with σ_I and σ_R^+ values. The correlation with the other three σ_R values are relative poor. The coefficient of multiple correlation (R), the standard deviation (SD), and f as the measure of the goodness of fit. f has been defined by Dayal *et al.* [34] as $f = \text{SD}/\text{RMS}$, where RMS is the root mean square of the data points (here $\log k/k_o$). The comparison of f values shows that f is smaller for σ_R^+ scale than those for other scales. Therefore, it is apparent that the rates of the oxidation *para*-substituted benzaldehydes by QDC correlate best with σ_I and σ_R^+ .

The rates of *meta*-substituted benzaldehydes show excellent correlation with σ_I and σ_R^o . The comparison of f values shows that f is smaller for σ_R^o scale than



those for other scales. This agrees with the observation of Ehrenson *et al.* [36] that the correlation of *meta*-substituted compounds is generally best with σ_R^o scale and *meta*-substituted compounds are less discriminating.

The reaction constants and the statistical data at different temperature are given in Table 5. The value of λ (*ca.* 0.983) shows that the oxidation of *para*-substituted benzaldehydes is more susceptible to the resonance effect than to the field effect. The selectivity of the reaction is decreased at higher temperature, but this decrease is of similar order for both the field and resonance effects resulting in the almost constant value of λ at different temperature.

In the oxidation of the *meta*-substituted compounds, the value of λ (*ca.* 0.751) indicates greater importance of the field effect. There is a small increase in the magnitude of the reaction constants with an increase in the temperature but this increase is of similar order for both the field and resonance effects, reflected in the almost constant value of λ at different temperatures.

Effect of temperature

The rate constants for the quinolinium dichromate oxidation of aromatic aldehydes at different tempera-

tures are listed in Table 3. The electron-withdrawing groups enhance and electron-releasing groups retard the oxidation rate. The activation parameters have been computed from a plot of $\log k$ vs. $1/T$ in the temperature range 303–323 K (Table 3). The activation enthalpies and entropies are linearly related by the equation [37]

$$\Delta H^\ddagger = \Delta H_o + \beta \Delta S^\ddagger,$$

where β is the isokinetic temperature and ΔH_o the enthalpy of activation when $\Delta S^\ddagger = 0$; usually ΔH_o has no physical significance. The isokinetic temperature obtained from the slope is 429.85 K ($r = 0.9916$). This linear correlation indicates that a single mechanism is operating throughout the series [38]. The negative values of ΔS^\ddagger provided support for the formation of a rigid activated complex.

- [1] K. Balasubramanian, V. Prathiba, *Indian J. Chem. Sect. B* **25**, 326 (1986).
- [2] S. Meenakshisundaram, M. Amutha, *Bull. Pol. Acad. Sci. Chem.* **49**, 165 (2001).
- [3] I. Nongkynrih, K. M. Mahanti, *Bull. Chem. Soc. Jpn.* **69**, 1403 (1996).
- [4] I. Nongkynrih, K. M. Mahanti, *Bull. Chem. Soc. Jpn.* **68**, 3325 (1995).
- [5] S. Kabilan, R. Girija, R. J. C. Reis, A. P. M. Segurado, *J. Chem. Soc. Perkin Trans. 2*, **6**, 1151 (2002).
- [6] K. Aruna, P. Manikyamba, V. E. Sundaram, *Coll. Czech. Chem. Commun.* **58**, 1624 (1993).
- [7] S. Das, G. S. Chaubey, M. K. Mahanti, *Kinetics and Catalysis* **43**, 794 (2002).
- [8] I. Nongkynrih, K. M. Mahanti, *Bull. Chem. Soc. Jpn.* **67**, 2320 (1994).
- [9] K. Aruna, P. Manikyamba, *Indian J. Chem. Sect. A: Inorg., Bio-Inorg., Phys., Theor. Anal. Chem.* **34**, 822 (1995).
- [10] G. S. Chaubey, S. Das, M. K. Mahanti, *Can. J. Chem. / Rev. Can. Chim.* **81**, 204 (2003).
- [11] G. S. Chaubey, S. Das, M. K. Mahanti, *Kinetics and Catalysis* **43**, 789 (2002).
- [12] G. S. Chaubey, S. Das, M. K. Mahanti, *Bull. Chem. Soc. Jpn.* **75**, 2215 (2002).
- [13] K. Aruna, P. Manikyamba, *Int. J. Chem. Kinet.* **29**, 437 (1997).
- [14] E. Karim, M. K. Mahanti, *Pol. J. Chem.* **66**, 1471 (1992).
- [15] J. Raha, G. C. Sarma, M. K. Mahanti, *Bull. Soc. Chim. Fr.* **4**, 487 (1991).
- [16] A. S. Chimatadar, S. B. Koujalagi, S. T. Nandibewoor, *Trans. Met. Chem.* **27**, 704 (2002).
- [17] I. Nongkynrih, K. M. Mahanti, *J. Org. Chem.* **58**, 4925 (1993).
- [18] K. Bernadette, T. Enboklin, D. Abhjit, K. M. Mahendra, *J. Org. Chem.* **61**, 8875 (1996).
- [19] B. Kuotsu, E. Tiewsoh, A. Debroy, M. K. Mahanti, *J. Org. Chem.* **61**, 8875 (1996).
- [20] R. P. Bell, *Adv. Phys. Org. Chem.* **4**, 1 (1964).
- [21] K. B. Wiberg, *Oxidation in Organic Chemistry* (Part A), p. 69, Academic Press, New York (1965).
- [22] K. K. Banerji, *Indian J. Chem., Sect. A* **17**, 300 (1979).
- [23] "Handbook of Chemistry and Physics," R. C. Weast (ed.), CRC Press, Ohio (1978).
- [24] N. Bailey, A. Carrington, K. A. K. Lott, M. C. R. Symons, *J. Chem. Soc.* 290 (1960).
- [25] G. Michel, R. Machiroux, *J. Raman Spectrosc.* **14**, 22 (1983).
- [26] M. Creslak-Golonka, *Coord. Chem. Rev.* **109**, 223 (1991).
- [27] E. S. Amis, *Solvent Effects on Reaction Rates and Mechanisms*, p. 42, Academic Press, New York (1967).
- [28] R. Bieber, G. Trumpler, *Helv. Chim. Acta* **30**, 1860 (1947).
- [29] L. C. Gruen, P. T. McTigue, *J. Chem. Soc.* 5217 (1963).
- [30] S. Kandlikar, B. Sethuram, T. N. Rao, *Indian J. Chem., Sect. A* **17**, 264 (1979).
- [31] A. L. Jain, K. K. Banerji, *J. Chem. Res. (M)*, 678 (1983).
- [32] K. K. Banerji, *Tetrahedron* **43**, 5949 (1987).
- [33] V. K. Sharma, K. Sharma, N. Mishra, *Oxid. Commun.* **16**, 33 (1993).
- [34] S. K. Dayal, S. Ehrenson, R. W. Taft, *J. Am. Chem. Soc.* **94**, 9113 (1972).
- [35] A. A. Jameel, *J. Indian Chem. Soc.* **75**, 439 (1998).
- [36] S. Ehrenson, R. T. C. Brownlee, R. W. Taft, *Prog. Phys. Org. Chem.* **10**, 1 (1973).
- [37] J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).
- [38] K. Bowden, N. B. Chapman, J. Shorter, *J. Chem. Soc.* 3370 (1964).