

Kinetics and mechanism of the oxidation of formic and oxalic acids by quinolinium fluorochromate

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Abstract. Kinetics and mechanism of oxidation of formic and oxalic acids by quinolinium fluorochromate (QFC) have been studied in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first-order with respect to QFC. Michaelis–Menten type of kinetics were observed with respect to the reductants. The reaction is acid-catalysed and the acid dependence has the form: $k_{\text{obs}} = a + b[\text{H}^+]$. The oxidation of α -deuterioformic acid exhibits a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 6.01$ at 303 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate-determining step. Suitable mechanisms have been proposed.

Keywords. Oxidation of acids; organic acids; quinolinium fluorochromate; halochromate (VI).

1. Introduction

Quinolinium fluorochromate (QFC) has been used as a mild and selective oxidizing reagent in synthetic organic chemistry¹. Though few reports on the mechanistic aspects of oxidation reactions of QFC are available in the literature², there seem to be no reports on the kinetics of oxidation of oxalic acid (OA) and formic acid (FA) by QFC. We have been interested in the kinetics of the reactions of complexed Cr(VI) species and have reported the kinetics and mechanism of the oxidation of oxalic and formic acids by pyridinium fluorochromate (PFC), pyridinium chlorochromate (PCC) and pyridinium bromochromate (PBC)^{3–5}. It was observed that the oxidations by PFC and PCC presented different kinetic pictures. In this paper, we study the kinetics of oxidation of oxalic and formic acids by QFC in dimethylsulphoxide (DMSO). Mechanistic aspects are discussed.

2. Experimental

2.1 Materials

QFC and α -deuterioformic acid (DCO_2H or DFA) were prepared by the reported methods^{1,6}. Due to the non-aqueous nature of the medium, toluene-*p*-sulphonic acid

*For correspondence

(TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar solvent like DMSO it is likely to be completely ionised. Solvents were purified by the usual methods⁷.

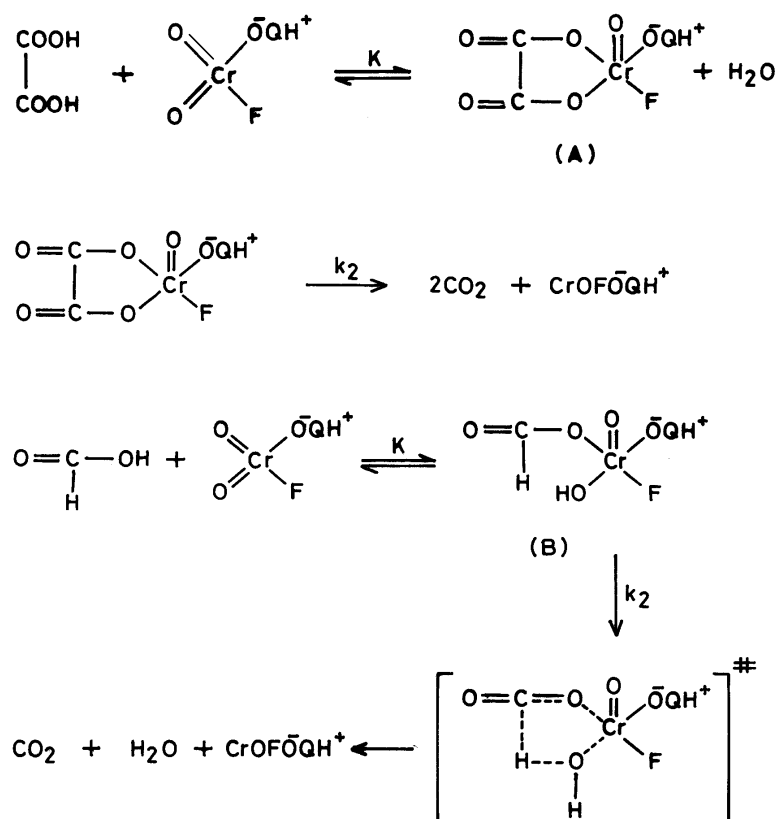
2.2 Stoichiometry

To determine the stoichiometry, an excess of QFC ($\times 5$ or greater) was reacted with the organic acid in DMSO (100 ml) and the amount of residual QFC after the completion of reaction was measured spectrophotometrically at 365 nm. The results indicated 1:1 stoichiometry. No quantitative determination of carbon dioxide formed was carried out.

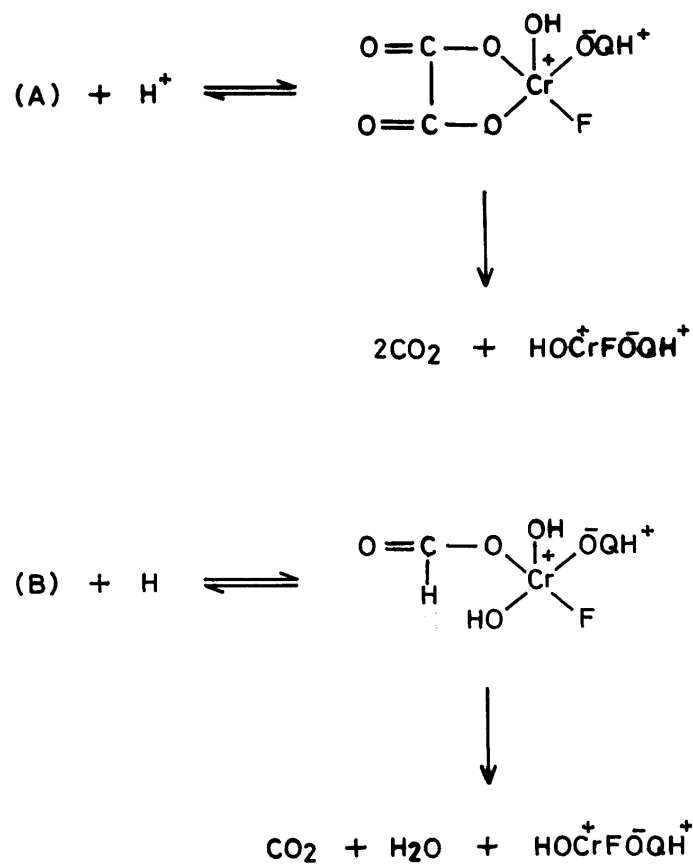
The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, was 3.98 ± 0.35 .

2.3 Kinetic measurements

The reactions were followed under pseudo-first-order conditions by maintaining a large excess ($\times 15$ or greater) of the organic acid over QFC. The temperature was kept constant to $\pm 0.1\text{K}$. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of QFC spectrophotometrically at 365 nm for up to 80% of the reaction. No other reactant or product has any significant



Scheme 1.



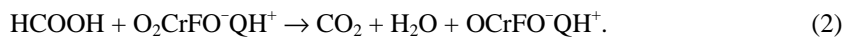
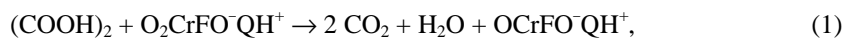
Scheme 2.

absorption at this wavelength. The pseudo-first-order rate constants, k_{obs} , were evaluated from the linear ($r = 0.995\text{--}0.999$) plots of $\log [\text{QFC}]$ against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 4\%$.

3. Results

3.1 Stoichiometry

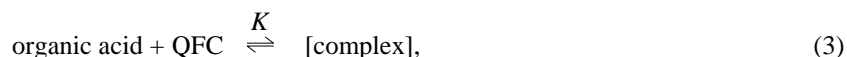
The oxidation of organic acids leads to the formation of carbon dioxide. The stoichiometric determination indicated the following overall reactions,



QFC undergoes a two-electron change. This is in accord with our earlier observations with both PFC³ and QFC².

3.2 *Rate laws*

The reactions were found to be first-order with respect to QFC. The reactions exhibited Michaelis–Menten type kinetics with respect to the organic acids (table 1). A plot of $1/[\text{organic acid}]$ vs $1/k_{\text{obs}}$ is linear with an intercept on the rate ordinate (figure 1). This indicates the following overall mechanism [(3) and (4)] and the rate law (5),



$$-d[\text{QFC}]/dt = k_2 K[\text{QFC}] [\text{organic acid}]/(1 + K[\text{organic acid}]). \quad (5)$$

The dependence of the reaction rate on reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic and activation parameters, at 298 K, were also calculated from the values of K and k_2 respectively, at different temperatures (tables 2 and 3).

3.3 *Induced polymerization of acrylonitrile*

The oxidation of organic acids by QFC, in an atmosphere of nitrogen, fails to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile has no effect on the rate (table 1).

Table 1. Rate constants for the oxidation of organic acids by QFC in DMSO at 303 K.

10^3 (QFC) (mol dm ⁻³)	(Acid) (mol dm ⁻³)	$10^5 k_{\text{obs}}$ (s ⁻¹)	
		Oxalic acid	Formic acid
1.0	0.01	103	2.02
1.0	0.02	138	3.88
1.0	0.04	168	7.20
1.0	0.12	196	16.8
1.0	0.36	207	30.3
1.0	0.48	209	33.6
1.0	0.60	210	36.1
1.0	0.12	198 ^a	16.3 ^a
2.0	0.02	141	4.01
4.0	0.02	136	3.73
6.0	0.02	139	4.11
8.0	0.02	140	3.94
10.0	0.02	137	3.80

^aContained 0.001 mol dm⁻³ acrylonitrile

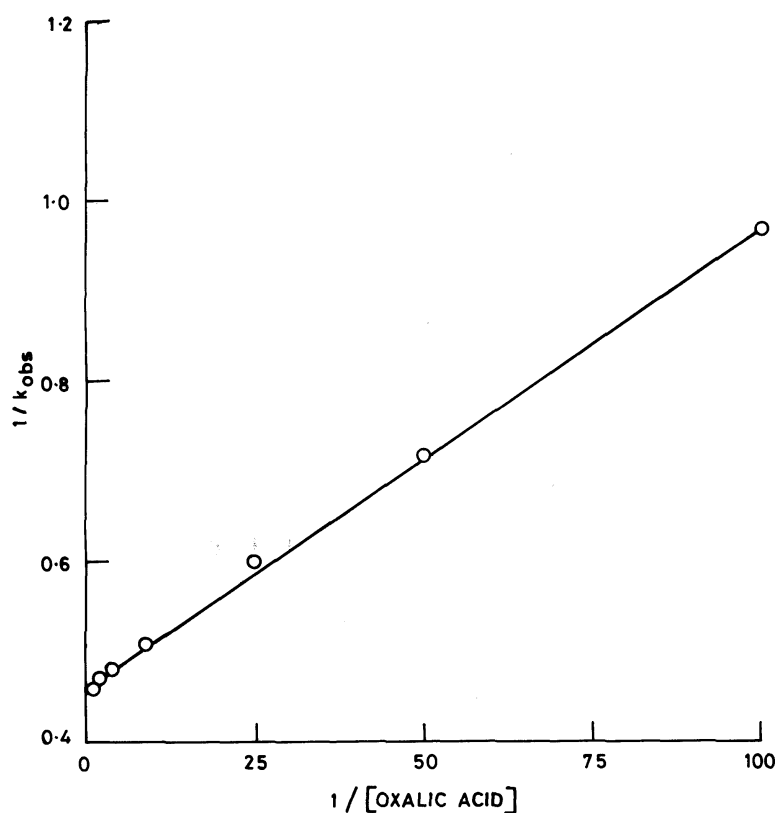


Figure 1. Plot of $1/(\text{oxalic acid})$ vs $1/k_{\text{obs}}$. Reaction conditions are described in table 1.

Table 2. Formation constant and thermodynamic parameters for the organic acid-QFC complexes in DMSO.

Acid*	K ($\text{dm}^3 \text{mol}^{-1}$) at				ΔH (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔG (kJ mol^{-1})
	303 K	308 K	313 K	318 K			
OA	92.2	25.7	6.95	1.92	-209 ± 2	-645 ± 7	-17.2 ± 2.0
FA	4.16	3.35	2.68	2.10	-38.9 ± 0.7	-107 ± 2	-6.7 ± 0.6
DFA	4.28	3.45	2.78	2.25	-36.8 ± 0.3	-102 ± 1	-6.7 ± 0.2

*Abbreviations: OA – oxalic acid; FA – formic acid; DFA – deuterioformic acid

3.4 Effect of acidity

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the following form (table 4),

$$k_{\text{obs}} = a + b [\text{H}^+]. \quad (6)$$

Table 3. Rate constants and activation parameters of the oxidation of organic acids by QFC in DMSO.

Acid	$10^4 k_2$ (dm ³ mol ⁻¹ s ⁻¹) at				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	303 K	308 K	313 K	318 K			
OA	21.4	31.0	43.6	62.2	54.2 ± 0.5	-118 ± 1	89.2 ± 0.4
FA	5.05	7.11	10.2	13.6	50.9 ± 0.9	-141 ± 3	92.7 ± 0.9
DFA	0.84	1.22	1.80	2.47	55.6 ± 0.8	-140 ± 3	97.2 ± 0.7
k_H/k_D	6.01	5.82	5.66	5.50			

Abbreviations as in table 2

Table 4. Dependence of the reaction rate on hydrogen-ion concentration. [OA] and [FA] = 0.02 mol dm⁻³, [QFC] 0.001 mol dm⁻³; temperature 303 K; solvent: DMSO

Acid	at (TsOH)/(mol dm ⁻³)						
	$10^5 k_{\text{obs}}$ (s ⁻¹)	0.10	0.20	0.40	0.60	0.80	1.00
OA		186	237	325	437	526	610
FA		5.23	6.66	9.15	12.3	14.8	17.1

The values of a and b for oxalic acid, are $1.41 \pm 0.06 \times 10^{-3} \text{ s}^{-1}$ and $4.76 \pm 0.09 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($r^2 = 0.9984$). The corresponding values for the oxidation of formic acid are $3.97 \pm 0.20 \times 10^{-5} \text{ s}^{-1}$ and $1.34 \pm 0.03 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ($r^2 = 0.9981$).

3.5 Kinetic isotope effect

To ascertain the importance of the cleavage of the $\alpha\text{-C-H}$ bond in the rate-determining step, the oxidation of DFA was studied. The results, recorded in tables 2 and 3, show that while the formation constant K , for the ordinary and deuteriated formic acids have almost identical values, the rate constant for the decomposition of the complex, k_2 , exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 6.01$ at 303 K).

3.6 Solvent effect

The oxidation of formic acid was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of K and k_2 are recorded in table 5.

4. Discussion

4.1 Solvent effect

The formation constant of the intermediate complex, K , did not vary much with the solvent but the rate constant, k_2 , showed much variation in values with different solvents.

Table 5. Formation constants and rate constants for the decomposition of formic acid–QFC complex in different solvents at 303 K.

Solvents	K (dm mol ⁻¹)	$10^5 k_2$ (s ⁻¹)	Solvents	K (dm mol ⁻¹)	$10^5 k_2$ (s ⁻¹)
Chloroform	4.03	15.8	Acetic acid	4.66	3.98
1,2-Dichloromethane	4.05	14.5	Cyclohexane	4.83	0.22
Dichloromethane	4.27	16.2	Toluene	4.96	2.63
DMSO	4.16	50.5	Acetophenone	3.60	15.4
Acetone	5.00	11.2	THF	4.33	4.89
DMF	4.58	24.5	<i>t</i> -Butyl alcohol	5.17	6.46
Butanone	4.12	8.13	1,4-Dioxane	4.82	5.50
Benzene	5.14	3.24	Carbon disulphide	4.14	1.17
Ethylacetate	3.66	3.98	1,2-Dimethoxyethane	4.37	2.75
Nitrobenzene	3.82	17.4			

The rate constants, k_2 , in eighteen solvents (CS₂ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship of Kamlet *et al.*⁸,

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha. \quad (7)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α . The results of correlation analyses in terms of (7), a biparametric equation involving π^* and β , and separately with π^* and β are given below.

$$\log k_2 = -5.56 + 2.03 (\pm 0.20) \pi^* + 0.13 (\pm 0.17) \beta + 0.40 (\pm 0.16) \alpha, \quad (8)$$

$$R^2 = 0.8933; \text{sd} = 0.19; n = 18; \psi = 0.26,$$

$$\log k_2 = -5.47 + 1.88 (\pm 0.23) \pi^* + 0.27 (\pm 0.18) \beta, \quad (9)$$

$$R^2 = 0.8440; \text{sd} = 0.22; n = 18; \psi = 0.30,$$

$$\log k_2 = -5.41 + 1.96 (\pm 0.22) \pi^*, \quad (10)$$

$$r^2 = 0.8217; \text{sd} = 0.22; n = 18; \psi = 0.31,$$

$$\log k_2 = -5.63 + 0.61 (\pm 0.42) \beta, \quad (11)$$

$$r^2 = 0.1181; \text{sd} = 0.49; n = 18; \psi = 0.83.$$

Here n is the number of data points and ψ is the Exner statistical parameter⁹.

Kamlet's⁸ triparametric equation explains $\approx 89\%$ of the effect of solvent on the oxidation. However, by Exner's criterion⁹ the correlation is not even satisfactory (cf. (8)). The major contribution is of solvent polarity. It alone accounts for $\approx 82\%$ of the data. Both β and α play relatively minor roles.

Data on the solvent effect were also analysed in terms of Swain's equation¹⁰ of the cation- and anion-solvating concept of the solvents

$$\log k_2 = aA + bB + C. \quad (12)$$

Here, A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A + B)$ is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of (12), separately with both A and B and with $(A + B)$.

$$\log k_2 = 1.54 (\pm 0.02) A + 1.83 (\pm 0.01) B - 5.79, \quad (13)$$

$$R^2 = 0.9992; \text{sd} = 0.02; n = 19; \psi = 0.02,$$

$$\log k_2 = 1.28 (\pm 0.60) A - 4.54, \quad (14)$$

$$r^2 = 0.2107; \text{sd} = 0.49; n = 19; \psi = 0.76,$$

$$\log k_2 = 1.71 (\pm 0.27) B - 5.29, \quad (15)$$

$$r^2 = 0.6978; \text{sd} = 0.30; n = 19; \psi = 0.42,$$

$$\log k_2 = 1.73 \pm 0.04 (A + B) - 5.78, \quad (16)$$

$$r^2 = 0.9918; \text{sd} = 0.05; n = 19; \psi = 0.07.$$

The rates of decomposition of the complex in different solvents showed excellent correlation in Swain's equation (cf. (13)) with the cation-solvating power playing the major role. In fact, cation-solvation alone accounts for $\approx 70\%$ of the data. Correlation with the anion-solvating power was very poor. Solvent polarity, represented by $(A + B)$, also accounted for $\approx 99\%$ of the data. In view of the fact that solvent polarity is able to account for $\approx 99\%$ of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of \log (rate) against the inverse of the relative permittivity is not linear ($r^2 = 0.5949$; $\text{sd} = 0.39$; $\psi = 0.49$).

5. Mechanism

The presence of a substantial kinetic isotopic effect confirmed that an α -C-H bond is cleaved in the rate-determining step. The observed kinetics indicate the formation of an intermediate complex in a rapid pre-equilibrium. However, the highly unfavourable entropy term obtained in the complex formation of oxalic acid-QFC reaction suggests that oxalic acid acts as a bidentate ligand and forms a cyclic intermediate complex. In the chromic acid oxidation also, the formation of a cyclic anhydride intermediate, oxalyl chromate, has been postulated¹¹. The value of formation constant, $9.5 \text{ dm}^3 \text{ mol}^{-1}$, reported by Hassan and Rocek¹¹ compares favourably with the values obtained in this investigation. The absence of any effect of a radical scavenger, acrylonitrile, indicates that a hydrogen abstraction mechanism, giving rise to free radicals, is unlikely.

In formic acid oxidation, the cation-solvating power of the solvents plays a relatively more important role. Therefore, formation of an electron-deficient carbon centre in the transition state is indicated. Thus the decomposition of QFC–formic acid complex may involve hydride ion transfer via an anhydride intermediate.

Involvement of a concerted cyclic process is supported by a study of the temperature dependence of the kinetic isotope effect¹². The data for protio- and deuterio-formic acids when fitted in the familiar expression $k_H/k_D = A_H/A_D \exp(-\Delta H^*/RT)$ show direct correspondence with the properties of a symmetrical transition state in which the differences in the activation energies for the protio and deuterio compounds are equal to the differences in the zero point energies of the corresponding C–H and C–D bonds ($\approx 4.5 \text{ kJ mol}^{-1}$) and the entropies of the activation of the respective reactions are almost equal^{13,14}.

The observed dependence on the hydrogen-ion concentration in both the reactions shows there is an additional acid-catalysed pathway. This may be attributed to rapid reversible protonation of the anhydride, with the protonated anhydride decomposing at a rate higher than the decomposition of the unprotonated anhydride.

In the oxidation of these acids by QFC, PFC³ and PBC⁵, Michaelis–Menten-type kinetics, with respect to the reductants, are obtained, but with PCC⁷ the reactions are first-order. It is possible that the values of formation constants for the reductant–PCC complexes are very low. This results in the observation of second-order kinetics. No explanation of the difference is available presently. Kinetic isotope effects, solvent effects and dependence on hydrogen ion concentration are similar in all these reactions, for which essentially similar mechanisms have been proposed.

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