Mechanistic Pathways to Oxidation Kinetics of Acrylic Acid by Quinolinium Fluorochromate

Abstract

The pathway for the oxidation of acrylic acid by quinolinium fluorochromate (QFC) has been investigated in acetic acid-water mixtures at 308K. The oxidation displays a first order dependence on [QFC] and [acrylic acid] each. The reaction is also first order with respect to [$HClO_4$]. The reaction has 1:1 stoichiometry. The effects of varying the percentage of acetic acid on the reaction rate have been studied. There is no effect of addition of salt. The various activation parameters have been computed and a mechanism proposed to explain the observed results.

Keywords: Oxidation, Kinetics, Mechanism, Acrylic Acid, Ouinolinium Fluorochromate.

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Introduction

Recently a variety of chromium (VI) complexes have been prepared and tested to be effective oxidants[1-3]. Quinolinium fluorochromate (QFC)[4,5] is one of them. It has been employed for the oxidation study, in view of its ease of preparation, high stability mildness and selectivity. The compound is capable of acting as both electron transfer and oxygen atom transfer agent. Acrylic acid is industrially important compound. It is the simplest unsaturated carboxylic acid. Our interest in the mechanistic pathways of the oxidation reaction of unsaturated organic substrates[6] and reducing sugars[7] with modified Cr (VI) reagents promoted us to get an insight to the title reaction.

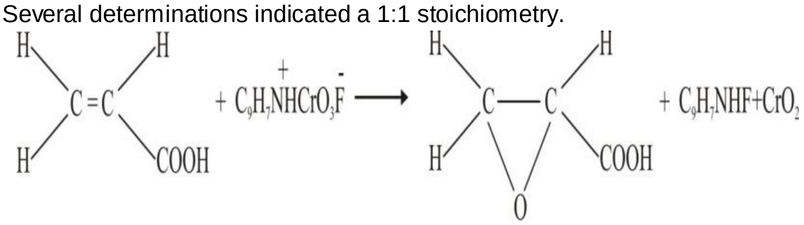
Experimental

Quinolinium fluorochromate[4] was safely prepared by the careful addition of quinoline (Loba-Chemie) to a solution of chromium trioxide in 40% hydrofluoric acid followed by filteration of the yellow orange crystal. Its purity was checked by estimating Cr (VI) iodometrically. Aqueous solution of acrylic acid (B.D.H.) was always freshly prepared. The ionic strength of the system was kept constant using a concentrated solution of sodium perchlorate (B.D.H). Other chemicals employed were of A.R. grade. Doubly distilled water was used for all the kinetic run.

All kinetic measurements were carried out in 50% acetic acid-50% water mixtures containing $HClO_4$ and $NaClO_4$ under pseudo-first order conditions by keeping large excess of acrylic acid over QFC at constant temperature (± 0.1K). The oxidation progress was followed by iodometric estimation of unreacted Cr (VI) after quenching the reaction. The pseudo-first order rate constants k_{obs} were computed from log [oxidant] against time.

Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined by allowing excess of oxidant to react with acrylic acid under kinetic conditions. The reaction mixture was kept for 24 h to ensure the completion of the reaction. The unreacted Cr (VI) was estimated by iodometric method.
Several determinations indicated a 1:1 stoichiometry.



The epoxide formed in the reaction mixture was identified by periodate test for epoxide[8].

Results and Discussion

Empirical Rate Law

The oxidation reaction is first order with respect to [QFC] as seen from the linearity of log [QFC] versus time plot. The k_{obs} is independent of initial concentration of QFC (Table 1).

Table 1

Dependence of the reaction rate on [oxidant]

$[QFC] \times 10^3$ ($mol\ dm^{-3}$)	2.0	3.2	4.0	6.0	6.4	8.0	10.0
$k_1 \times 10^5$ (s^{-1})	4.12	4.00	4.10	4.14	4.08	4.06	4.04

Solvent : acetic acid-water (50-50% v/v) ; [acrylic acid] = 2.0×10^{-2} mol dm^{-3} ; $[NaClO_4]$ - 2.0×10^{-1}mol dm^{-3} ; $[HClO_4]$ = 9.2×10^{-1}mol dm^{-3} ; temperature : 308K

The rate increases steadily with increase in [substrate]. (Table 2) and the result show that the order in [acrylic acid] is one. The bimolecular rate constants, k_2, in table 2 are simply the first order rate constant divided by [acrylic acid].

Table 2

Dependence of the Reaction Rate on [substrate]

[acrylic acid] $\times 10^2$ ($mol\ dm^{-3}$)	1.0	1.6	2.0	3.0	3.2	4.0	5.0
$k_1 \times 10^5 (s^{-1})$	2.00	3.22	4.12	6.20	6.40	8.30	10.30
$k_2 \times 10^3$ ($dm^3\ mol^{-1}\ s^{-1}$)	2.00	2.01	2.06	2.06	2.00	2.07	2.06

Solvent : acetic acid-water (50-50% v/v) ; [QFC] = 4.0×10^{-3}mol dm^{-3} $[NaClO_4]$ = 2.0×10^{-1}mol dm^{-3} ; $[HClO_4]$ = 9.2×10^{-1}mol dm^{-3} ; temperature : 308K

Table 3

Dependence of rate on $[HClO_4]$

$[HClO_4]$ ($mol\ dm^{-3}$)	0.23	0.46	0.92	1.38	1.84	2.30
$k_1 \times 10^5$ (s^{-1})	1.05	2.04	4.12	6.20	8.14	10.48
$k_2 \times 10^5$ ($dm^3\ mol^{-1}\ s^{-1}$)	4.56	4.43	4.48	4.49	4.42	4.56

The increase in $[HClO_4]$ increases rate and shows a first order dependence on $[HClO_4]$ (Table 3.). The linear increase in the rate with the acidity suggested the involvement of protonated form of QFC in the rate determining step. There have been earlier reports on the involvement of protonated chromium species in Cr (VI) oxidation[9] occuring in acid media[10]. Consequently, the empirical rate law is described as follows:

$$-\frac{d[QFC]}{dt} = k_{obs}\ [QFC]\ [substrate]\ [H^+]$$

Salt Effect on The Reaction Rate

Addition of $NaClO_4$ has no appreciable effect on the rate of reaction. Similar observations were also reported in the oxidation of unsaturated alcohol[11] by QFC.

Test For Free Radicals

Addition of vinyl monomer, acrylonitrile in the reaction mixture has no effect on oxidation of acrylic acid and no visible polymerisation occurs during the reaction. This does not rule out the formation of free radical intermediates since it may be due to the high rate of oxidation of the free radicals.

Effect of Solvent Composition

The course of reaction has been studied under varying composition of acetic-acid water mixture. The reaction rate increases with increase in acetic acid content of the reaction mixture. A plot of log k_{obs} against inverse of dielectric constant is linear with positive slope. This implies the occurrence of an interaction of an ion-dipole type[12], which provides convincing evidence that QFC is protonated.

Activation Parameters

The reaction was studied at different temperatures to determine the activation parameters (Table 4.). Based on the Arrhenius plot, the activation parameters, Ea, $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ were computed using usual relationships. The entropy of activation is largely negative as expected for bimolecular reaction.

Table 4 Effect of Temperature on the Oxidation Rate

Solvent : Acetic-Water (50-50% v/v) ; [Acrylic Acid] = 2.0×10^{-2}mol dm^{-3} ; [QFC] = 4.0×10^{-3}mol dm^{-3} ; $[NaClO_4]$ = 2.0×10^{-1}mol dm^{-3} ; $[HClO_4]$ = 9.2×10^{-1}mol dm^{-3}.

Temperature (K)	$k_1 \times 10^5$ (s^{-1})	Ea ($kJ\ mol^{-1}$)	$\Delta H^\#$ ($kJmol^{-1}$)	$\Delta G^\#$ ($kJ\ mol^{-1}$)	$-\Delta S^\#$ ($JK^{-1}\ mol^{-1}$)
293	1.38	-	53.09	98.99	156.66
298	1.98	53.28	53.05	99.83	156.98
303	2.84	55.92	53.01	100.64	157.18
308	4.12	57.39	52.97	101.38	157.19
313	5.88	-	52.93	102.15	157.24

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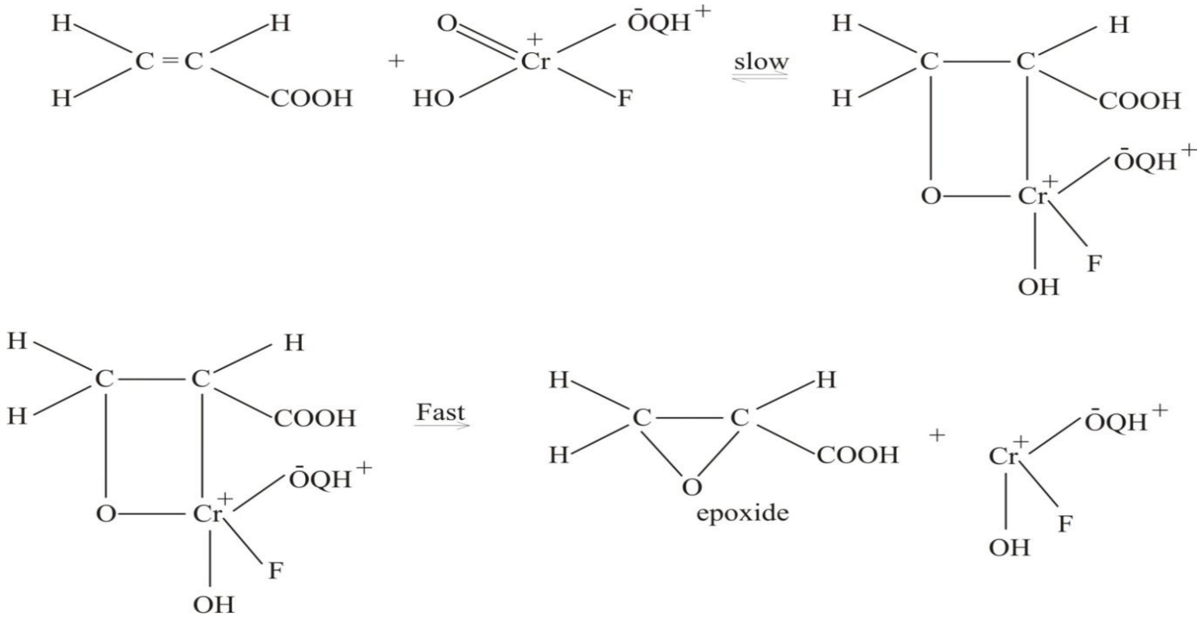
Mechanism

The epoxide is the only reaction product observed. The formation of product and other observed data may be explained by a mechanism proposed in scheme 1.

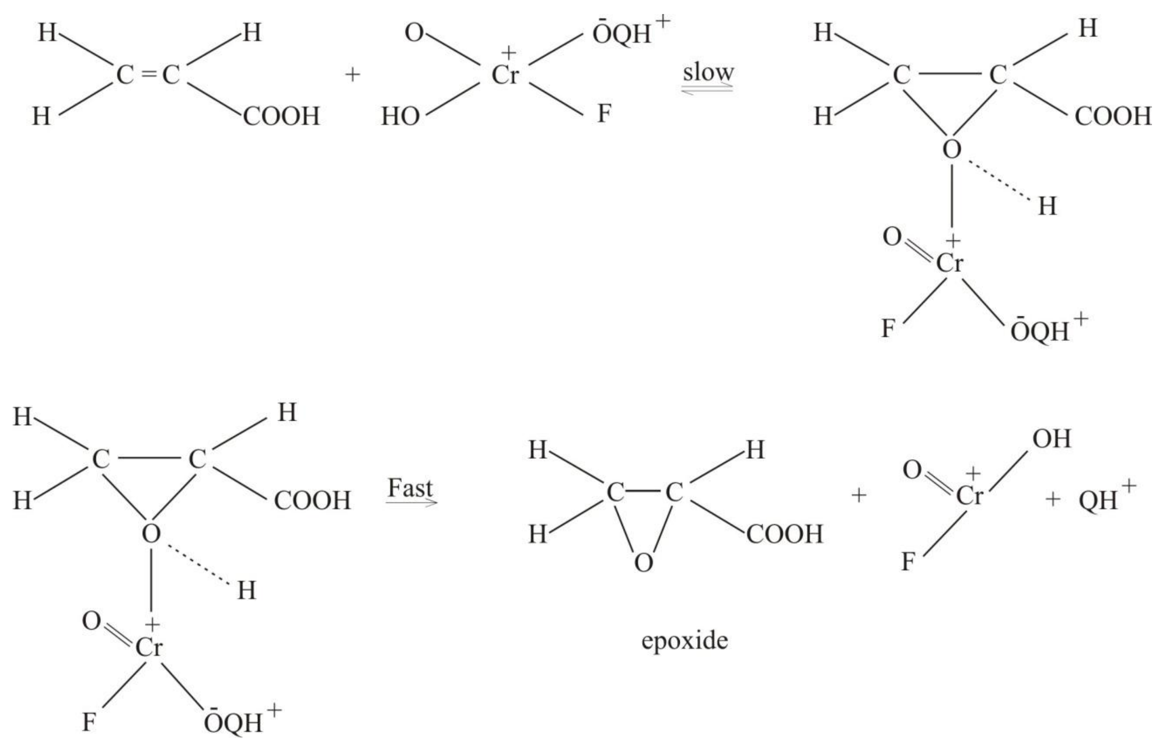
The rate determining step may be loose complex formation between the protonated QFC and acrylic acid. An electrophilic attack of Cr (VI) (Chromium being positively changed in the protonated QFC) on the double bond leads to the four centered transition state which rearranges to give the epoxide in the final step.

Scheme 1



In the proposed mecahnism (Scheme 1.) a direct chromium to carbon bond does not account for the insensitivity to steric effects very often observed in the oxidation of olefins by Cr (VI)[13]. Thus the most favourable reaction path may be the three center type addition as depicted in Scheme 2.

Scheme 2



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