Epoxidation of Acrylic Acid by Tetraethylammonium Chlorochromate in an Aquo-Acetic Acid-A Kinetic Study

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Tetraethylammonium chlorochromate oxidised acrylic acid in aqueous acetic acid (50 % v/v) medium in presence of perchloric acid to the epoxide as the oxidation product. The rate of the reaction was dependent on the first power of the concentration of oxidant, substrate and acid. Ionic strength variation has no effect on the reaction rate. The reaction does not induce polymerization. The reaction rate increased with increasing amount of acetic acid in the mixture. Thermodynamic and activation parameters for the reaction have been computed from the data on the temperature dependence. A suitable mechanism consistent with the observed kinetic results has been postulated.

Key Words: Kinetics, Oxidation, Mechanism, Acrylic acid, Tetraethylammonium chlorochromate.

INTRODUCTION

There has been continued interest in the development of new Cr(VI) reagents which function as mild oxidants and found wide use in synthetic and kinetic studies[1-4]. We have been interested in kinetics and mechanism of the oxidation of organic substrates by Cr(VI) oxidants and have reported the oxidation kinetics of some reducing sugars[5,6] and unsaturated substrates[7,8] by quinolinium chlorochromate (QCC). A new reagent, tetraethylammonium chlorochromate (TEACC), is reported recently[9]. There seems to be only few studies on the oxidation reaction of tetraethylammonium chlorochromate[9,10]. Hence the present investigation is undertaken to focus on the kinetics and mechanism of the epoxidation of acrylic acid by tetraethylammonium chlorochromate in acetic acid-water mixtures (50 % v/v).

EXPERIMENTAL

Tetraethylammonium chlorochromate was prepared by careful addition of tetraethylammonium hydroxide (20 %, Fluka) to a solution of chromium trioxide dissolved in 6 M HCl followed by the filtration of the yellow orange crystal[9]. Its purity was checked by the iodometric method. Aqueous solution of acrylic acid (Loba) was always freshly prepared. The ionic strength of the system was kept constant using a concentrated solution of sodium perchlorate (BDH). Perchloric acid (E. Merck) and all other chemicals employed were of A.R. grade. Doubly distilled water was used for all the kinetic runs.

Kinetic measurements: All the 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 an excess of substrate over tetraethylammonium chlorochromate at constant temperature (± 0.1 K). The progress of the reaction was followed by estimating the unreacted oxidant iodometrically after quenching the reaction. The pseudo first-order rate constants, k$_{obs}$, were determined from the linear plot of log [oxidant] *versus* time. Replicate runs showed that the rate constants were reproducible to within ± 3 % error.

Product analysis and stoichiometry: The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [tetraethylammonium chlorochromate] largely in excess over [acrylic acid]. The reaction mixture was kept for 24 h to ensure the completion of the reaction. The estimation of unreacted tetraethylammonium chlorochromate iodometrically showed that 1 mol of acrylic acid reacts with 1 mol of tetraethylammonium chlorochromate.

Therefore, the stoichiometry of the reaction can be represented as follows:
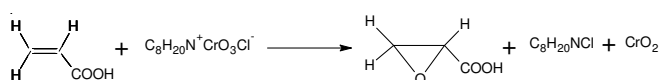
The epoxide formed in the reaction mixture was identified by periodate test for epoxide[11].

RESULTS AND DISCUSSION

Empirical rate law: The reaction is first order with respect to tetraethylammonium chlorochromate (TEACC) as seen from the linearity of log [tetraethylammonium chlorochromate] *versus* time plot. Further, the pseudo first-order rate constants, k_{obs}, do not depend on the initial concentration of tetraethylammonium chlorochromate (Table-1).

TABLE-1
DEPENDENCE OF THE REACTION RATE ON [OXIDANT]
Solvent: Acetic acid-water (50-50 % v/v); [acrylic acid]
= 2×10^{-2} mol dm⁻³ [NaClO₄] = 2×10^{-1} mol dm⁻³; [HClO₄]
= 9.2×10^{-1} mol dm⁻³; temperature = 303 K

[TEACC] × 10³ (mol dm⁻³)	2.0	3.2	4.0	6.0	6.4	8.0
$k_1 \times 10^6$ (s⁻¹)	4.30	4.45	4.36	4.23	4.32	4.43

The oxidation is first order in the substrate, the pseudo-first order rate constant increased with the increase in acrylic acid (Table-2) and a plot of log k_{obs} *versus* log [acrylic acid] was linear with a slope of unity. The bimolecular rate constants, k_2 in Table-2 are simply the first order rate constants divided by [acrylic acid].

TABLE-2
DEPENDENCE OF THE REACTION RATE ON [SUBSTRATE]
Solvent: Acetic acid-water (50-50 % v/v); [TEACC*]
= 2×10^{-3} mol dm⁻³, [NaClO₄] = 2×10^{-1} mol dm⁻³; [HClO₄]
= 9.2×10^{-1} mol dm⁻³; temperature = 303 K

[Acrylic acid] × 10² (mol dm⁻³)	1.0	1.6	2.0	3.0	3.2	4.0	5.0
$k_1 \times 10^6$ (s⁻¹)	2.19	3.35	4.30	6.63	7.02	8.69	11.00
$k_2 \times 10^4$ (dm³ mol⁻¹ s⁻¹)	2.19	2.09	2.15	2.21	2.19	2.17	2.20

*Tetraethylammonium chlorochromate.

The k_{obs} values varied with variation in the initial concentration of HClO₄ and dependence on acid was also observed to be unity, as seen from linear plot of log k_{obs} *versus* log [HClO₄] (Table-3).

TABLE-3
DEPENDENCE OF THE REACTION RATE ON [HClO₄]
Solvent: Acetic acid-water (50-50 % v/v); [TEACC*]
= 2×10^{-3} mol dm⁻³; [NaClO₄] = 2×10^{-1} mol dm⁻³; [acrylic acid]
= 2×10^{-2} mol dm⁻³; temperature = 303 K

[HClO₄] (mol dm⁻³)	0.23	0.46	0.92	1.38	1.84	2.30
$k_1 \times 10^6$ (s⁻¹)	1.11	2.12	4.30	6.55	8.61	11.07
$k_2 \times 10^6$ (dm³ mol⁻¹ s⁻¹)	4.83	4.61	4.67	4.75	4.68	4.81

*Tetraethylammonium chlorochromate.

Catalysis by perchloric acid suggests the probable involvement of protonated Cr(VI) species in the rate-determining step. The participation of protonated chromium species in Cr(VI) oxidations[12] is well known in acid media[13].

Consequently, the empirical rate law is described as follows

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

Effect of ionic strength: Variation of ionic strength of the medium by the addition of NaClO₄ had no pronounced effect on the rate. Similar observations were also reported in the oxidation of unsaturated substrates by QCC[7,8].

Induced polymerisation: The reaction mixture failed to initiate polymerization of acrylonitrile, indicating the absence of formation of free radical species in the reaction sequence.

Effect of solvent composition: The course of the reaction has been studied in 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} *versus* 1/D was linear with positive slope. This implies the occurrence of an interaction of an ion-dipole type[14], which provides convincing evidence that tetraethylammonium chlorochromate is protonated.

Effect of temperature: Activation and thermodynamic parameters were computed by using the Arrhenius and Eyring equations (Table-4), the entropies of activation are largely negative as expected for bimolecular reaction.

TABLE-4
DEPENDENCE OF THE REACTION RATE ON TEMPERATURE
Solvent: Acetic acid-water (50-50 % v/v); [acrylic acid]
= 2×10^{-2} mol dm⁻³; [NaClO₄] = 2×10^{-1} mol dm⁻³; [TEACC*]
= 2×10^{-3} mol dm⁻³; [HClO₄] = 9.2×10^{-1} mol dm⁻³

Temperature (K)	$k_1 \times 10^6$ (s⁻¹)	Ea (kJ mol⁻¹)	ΔH# (kJ mol⁻¹)	ΔG# (kJ mol⁻¹)	ΔS# (kJ mol⁻¹)
293	2.17	–	50.91	103.5	179.50
298	3.22	50.49	0.87	104.33	179.41
303	4.30	53.36	0.83	105.40	180.09
308	6.48	56.20	0.79	106.13	179.67
313	8.77	–	50.75	107.11	180.05

*Tetraethylammonium chlorochromate.

Mechanism: It was found that the epoxide is the only product of epoxidation of maleic acid with tetraethylammonium chlorochromate. To explain the formation of the product and other observed data, the mechanism in **Scheme-I** is proposed.

Scheme-I
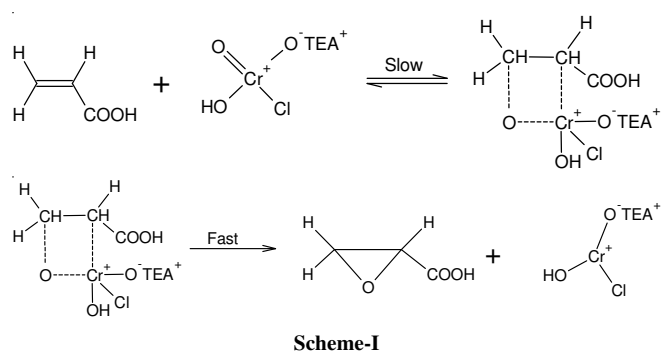
The first step in the mechanism is the electrophilic attack of Cr(VI) (chromium being positively charged in tetraethylammonium chlorochromate) on the double bond of the substrate producing a four-membered transition state which can yield the epoxide in the fast step. The rate-determining step may be the loose complex formation between the protonated tetraethylammonium chlorochromate and substrate.

In the proposed mechanism (**Scheme-I**), 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)[15]. Thus the most favourable reaction path may be the three centre type addition as depicted in **Scheme-II**.
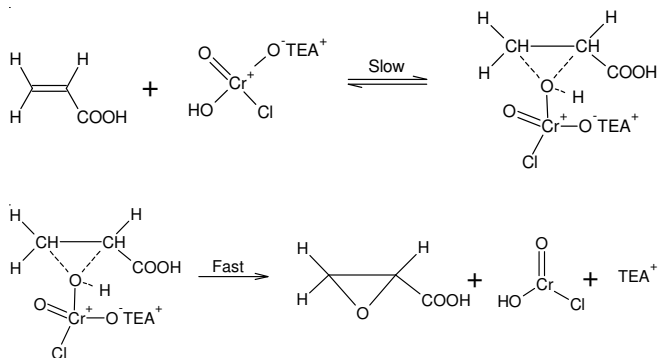
Scheme-II

Both scheme envisages an oxygen atom transfer from the oxidant. This is in accord with the earlier observations made for unsaturated alcohols[16,17].

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