Oxidation of Maleic Acid by Tetraethylammonium Chlorochromate in an Aquo-Acetic Acid Medium- A Kinetic and Mechanistic Study

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The oxidation of maleic acid by tetraethylammonium chlorochromate (TEACC) was studied, in the presence of perchloric acid and in acetic acid-water mixtures (50 % v/v). The reaction is first order with respect to maleic acid, tetraethylammonium chlorochromate and acid. Ionic strength changes have no significant effect on the reactivity. The reaction does not induce polymerization of acrylonitrile. The reaction rates were determined at different temperatures and the activation parameters were computed. The reaction rate increased with increasing amount of acetic acid in the mixture. A suitable mechanism consistent with the observed kinetic results has been proposed.

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

INTRODUCTION

Many studies on oxidation reactions involving Cr(VI)-based oxidants and organic substrates have been reported[1-4]. We have been interested in the kinetics of oxidations by modified Cr(VI) oxidants and have reported the oxidation kinetics of some reducing sugars[5,6] and unsaturated substrates[7,8]. A new reagent, tetraethylammonium chlorochromate is reported recently[9]. There seems to be no reports on the kinetic and mechanistic aspects of oxidation reactions by tetraethyl-ammonium chlorochromate, except those of benzyl alcohol[9] and crotonaldehyde[10]. Hence the present investigation is undertaken and the kinetic results of oxidation of maleic acid with tetraethylammonium chlorochromate in acetic acid-water (50 % v/v) are reported in this paper.

EXPERIMENTAL

Tetraethylammonium chlorochromate was safely 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] and its purity was checked by the iodometric method. Aqueous solution of maleic 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 ($\pm$ 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 $\pm$ 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 [maleic 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 maleic acid reacts with 1 mol of tetraethylammonium chlorochromate. Therefore, the stoichiometry of the reaction can be represented as follows:
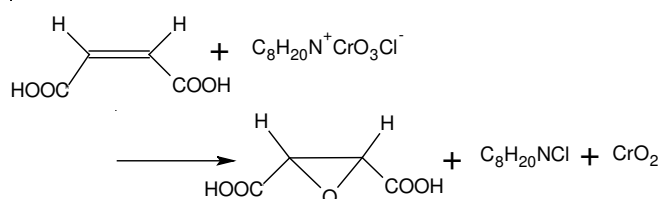
The epoxide formed in the reaction mixture was identified by periodate test for epoxide[11].

RESULTS AND DISCUSSION

Empirical rate law: The reaction is first order with respect to tetraethylammonium chlorochromate 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 tetraethyl-ammonium chlorochromate (Table-1).

TABLE-1
DEPENDENCE OF THE REACTION RATE ON [OXIDANT]
Solvent: Acetic acid-water (50-50 % v/v); [maleic acid] $= 2 \times 10^{-2}$ mol dm^{-3}; [NaClO$_4$] $= 2 \times 10^{-1}$ mol dm^{-3}; [HClO$_4$] $= 9.2 \times 10^{-1}$ mol dm^{-3}; temperature = 303 K

[TEACC*] $\times 10^3$ (mol dm^{-3})	2.00	3.20	4.00	6.00	6.40	8.00
$k_1 \times 10^6$ (s^{-1})	9.84	9.75	9.72	9.87	9.95	9.90

*Tetraethylammonium chlorochromate.

The oxidation is first order in the substrate, the pseudo-first order rate constant increased with the increase in maleic acid (Table-2) and a plot of log k_{obs} *versus* log [maleic 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 [maleic acid].

TABLE-2
DEPENDENCE OF THE REACTION RATE ON [SUBSTRATE]
Solvent: Acetic acid-water (50-50 % v/v); [TEACC*] $= 2 \times 10^{-3}$ mol dm^{-3}; [NaClO$_4$] $= 2 \times 10^{-1}$ mol dm^{-3}; [HClO$_4$] $= 9.2 \times 10^{-1}$ mol dm^{-3}; temperature = 303 K

[Maleic acid] $\times 10^2$ (mol dm^{-3})	1.0	1.6	2.0	3.0	3.2	4.0	5.0
$k_1 \times 10^6$ (s^{-1})	4.98	7.89	9.84	14.78	15.81	19.75	24.65
$k_2 \times 10^4$ (dm^3 mol^{-1} s^{-1})	4.98	4.93	4.92	4.93	4.94	4.94	4.93

*Tetraethylammonium chlorochromate.

The k_{obs} values varied with variation in the initial concentration of HClO$_4$ and dependence on acid was also observed to be unity, as seen from linear plot of log k_{obs} *versus* log [HClO$_4$] (Table-3).

TABLE-3
DEPENDENCE OF THE REACTION RATE ON [HClO$_4$]
Solvent: Acetic acid-water (50-50 % v/v); [TEACC*] $= 2 \times 10^{-3}$ mol dm^{-3}; [NaClO$_4$] $= 2 \times 10^{-1}$ mol dm^{-3}; [maleic acid] $= 2 \times 10^{-2}$ mol dm^{-3}; temperature = 303 K

[HClO$_4$] (mol dm^{-3})	0.23	0.46	0.92	1.38	1.84	2.30
$k_1 \times 10^6$ (s^{-1})	2.49	4.98	9.84	14.45	19.23	24.13
$k_2 \times 10^6$ (dm^3 mol^{-1} s^{-1})	10.83	10.83	10.70	10.47	10.45	10.49

*Tetraethylammonium chlorochromate.

Catalyzed 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:

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

Effect of ionic strength: Variation of ionic strength of the medium by the addition of NaClO$_4$ had no pronounced effect on the rate. Similar observations were also reported in the oxidation of unsaturated substrates by QCC[7,8].

Induced polymerization: The reaction mixture failed to initiate polymerisation 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); [maleic acid] $= 2 \times 10^{-2}$ mol dm^{-3}; [NaClO$_4$] $= 2 \times 10^{-1}$ mol dm^{-3}; [TEACC*] $= 2 \times 10^{-3}$ mol dm^{-3}; [HClO$_4$] $= 9.2 \times 10^{-1}$ mol dm^{-3}

| Temperature (K)	$k_1 \times 10^6$ (s^{-1})	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})
293	4.95	–	50.97	101.49	172.44
298	7.40	50.72	50.93	102.27	172.28
303	9.84	53.32	50.89	103.31	173.01
308	14.88	56.20	50.85	104.00	172.56
313	20.07	–	50.81	104.95	172.97

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.
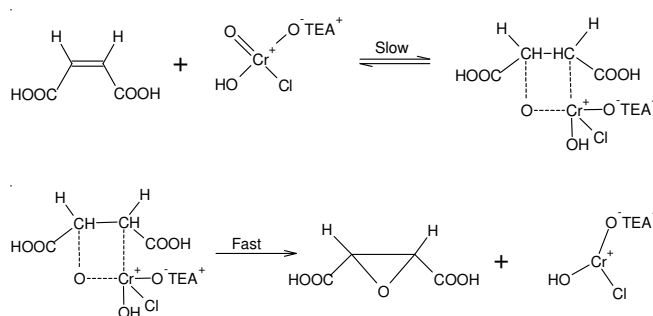
Scheme-I

The first step in the mechanism is the electrophilic attack of Cr(VI) (chromium being positively charged in tetraethyl-ammonium 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 proto-nated 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**.
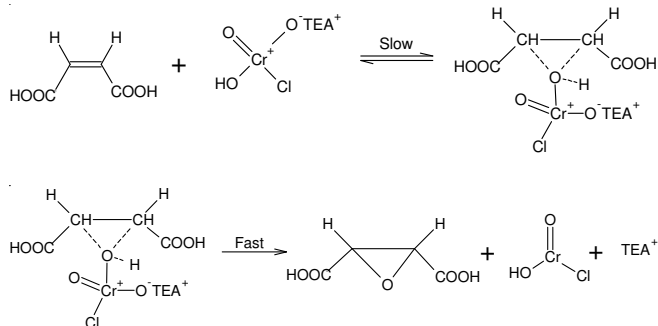
Scheme-II

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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