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KINETICS AND MECHANISM OF THE EPOXIDATION OF SOME UNSATURATED ORGANIC COMPOUNDS WITH TETRAETHYLAMMONIUM CHLOROCHROMATE

J. V. SINGH

Department of Chemistry, Nehru College Chhibramau-209721, Kannauj (U.P.) India

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The kinetics of oxidation of unsaturated organic compounds viz. crotonaldehyde and maleic acid by tetraethylammonium chlorochromate (TEACC) have been investigated in acetic acid-water mixture (50% v/v) in presence of perchloric acid. The reaction is of first order each in oxidant, substrate and acid for both substrates. Increase in dielectric constant of the medium decreases the rate, while variation in ionic strength has no significant effect on the rate. The reaction does not induce polymerisation of acrylonitrile. The reaction rate have been determined at different temperature and the activation and thermodynamic parameters have been computed. Mechanism consistent with the observed results has been discussed.

KEYWORDS: Oxidation, Kinetics, Mechanism, Tetraethylammonium, Chlorochromate, Unsaturated Organic Compounds, Epoxide.

INTRODUCTION

The development of new Cr(VI) reagents for the effective and selective oxidation of organic substrates under mild condition has been going on because Cr(VI) is a versatile oxidant for the oxidation of many types of organic substrates and also due to advancement in the synthesis of complex organic molecules under different reaction conditions [1-4]. Tetraethylammonium chlorochromate (TEACC) adds to the select list of newer Cr(VI) reagents as the most significant oxidant for the effective and selective oxidation of organic substrates under mild conditions [5]. There seems to be no reports on the kinetic and mechanistic aspects of oxidation of unsaturated organic compounds viz. crotonaldehyde and maleic acid by TEACC. Hence the present investigation is undertaken and the kinetic results of oxidation of both substrates with TEACC in acetic acid-water (1 : 1 v/v) solvent are reported in this paper.

EXPERIMENTAL

Materials: Tetraethylammonium chlorochromate (TEACC) was safely prepared by careful addition of tetraethylammonium hydroxide (20% Fluca) to a solution of chromium trioxide dissolved in 6 M HCl followed by the filteration of yellow orange crystal [5]. Solutions of crotonaldehyde (Fluka) and maleic acid (Loba) were always freshly prepared.

The ionic strength was kept constant using a concentrated solution of sodium perchlorate (B.D.H.). Perchloric acid (E. Merck) and all other chemicals (A.R., B.D.H.) were used without further purification. Doubly distilled water was used for all kinetic run.

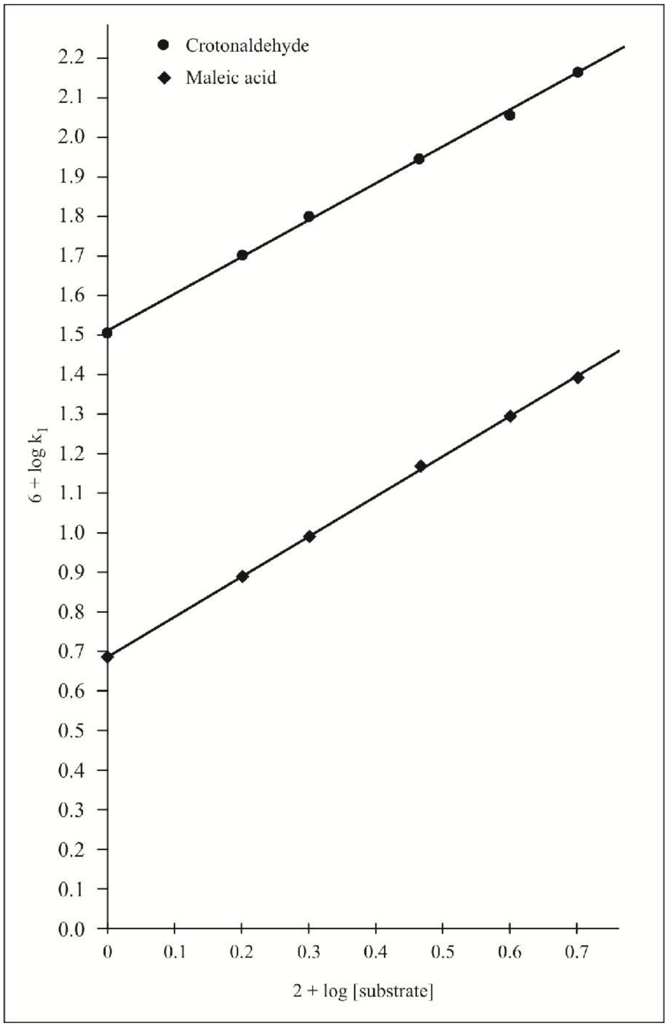


Fig. 1. Plot of log k_1 vs log [unsaturated compound]

[TEACC] = 2.0×10^{-2} mol dm^{-3}; [$HClO_4$] = 0.92 mol dm^{-3}; [$NaClO_4$] = 2.0×10^{-1} mol dm^{-3}; Solvent : AcOH-H_2O (50-50% v/v); Temperature : 303 K.

Kinetic measurements: All the kinetic measurements were carried out in 50% acetic acid-50% water mixture containing $HClO_4$ and $NaClO_4$ under pseudo first order conditions by keeping an excess of substrate over tetraethylammonium chlorochromate (± 0.1 K). The progress of the reaction was followed by estimating unreacted oxidant iodometrically after quenching the reaction. The pseudo-first order rate constant k_{obs}, were determined from the linear plot of log [oxidant] versus time. Replicate runs showed that the rate constant were reproducible to within ± 3% error.

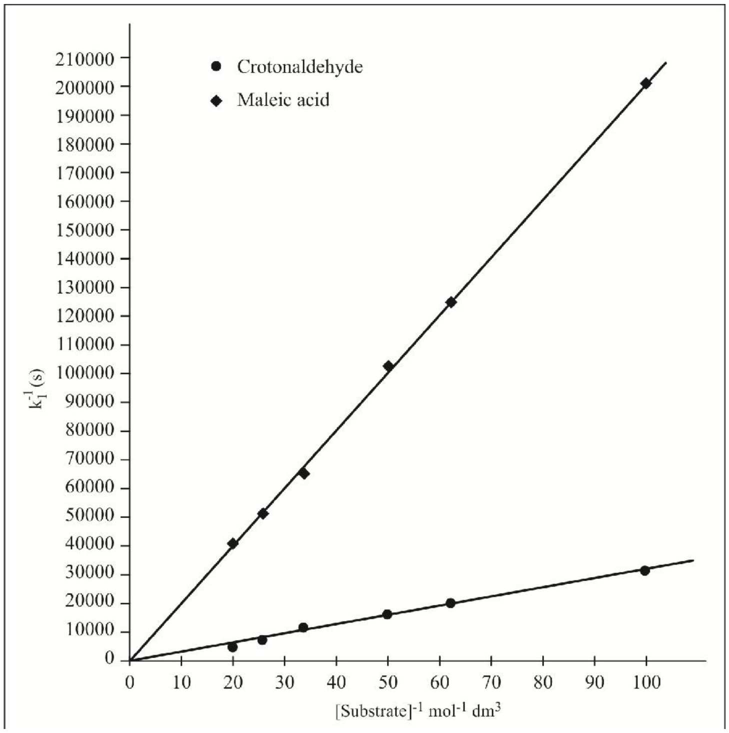
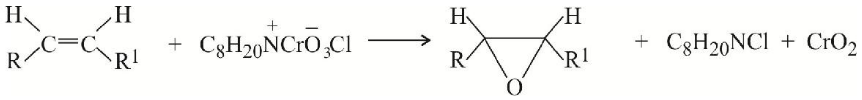


Fig. 2. Plot of log k_1^{-1} vs [substrate]$^{-1}$

[TEACC] = 2.0 × 10^{-2} mol dm^{-3}; [$HClO_4$] = 0.92 mol dm^{-3}; [$NaClO_4$] = 2.0 × 10^{-1} mol dm^{-3};
Solvent : AcOH-H_2O (50-50% v/v); Temperature : 303 K.

Stoichiometry and product analysis: Stoichiometry of the reaction for both the substrates was found to be 1 : 1 as determined by carrying out several sets of experiments with varying amounts of [TEACC] largely in excess over [substrate]. The reaction mixture was kept 24 hr to ensure the completion of the reaction. The unreacted tetraethylammonium chlorochromate was estimated iodometrically.



where, R=CH_3 and R^1 = CHO for crotonaldehyde and R = R^1= COOH for maleic acid

Product analysis under kinetic conditions gave only the expoxide in each case of study, which was identified by periodate test [6].

RESULTS AND DISCUSSION

In each case, the oxidation followed a first order kinetics both with respect to [substrate] and [oxidant]. Plots of log [TEACC] versus time were linear upto at least 80% completion of the reaction. The pseudo-first order rate constants, k_{obs}, do not depend on initial concentration of TEACC (Table 1), establishing first order dependence of the rate on [TEACC] in both the cases. At constant [TEACC] the rate increases steadily with increase in [substrates] (Table 1) and the plots of log k_{obs} versus log [substrate] are linear with unit slope (Fig. 1), showing first order dependence of the rate on [substrate]. The second order rate constants $k_2=k_1/[\text{substrate}]$ give the concordant values. The plots of $1/k_1$ against 1/[substrate] give a straight line passing through origin (Fig. 2). This confirms first order kinetics with respect to substrate and suggests that no intermediate complex is formed between substrate and oxidant. UV-visible spectral studies did not show any evidence for the formation of TEACC-substrate complex (Fig. 3).

Table 1: Dependence of rate on [reactants] at 303 K

Solvent : AcOH-H_2O (50-50% v/v)

$[NaClO_4] = 2.0 \times 10^{-1}$ mol dm^{-3}

[TEACC] × 10^3 (mol dm^{-3})	[Crotonaldahyde] × 10^2 (mol dm^{-3})	[Maleic acid] × 10^2 (mol dm^{-3})	[$HClO_4$] (mol dm^{-3})	Crotonaldehyde $k_1 \times 10^5$ (s^{-1})	Maleic acid $k_1 \times 10^6$ (s^{-1})
2.0	2.0	2.0	0.92	6.34	9.84
3.2	2.0	2.0	0.92	6.50	9.75
4.0	2.0	2.0	0.92	6.40	9.72
6.0	2.0	2.0	0.92	6.48	9.87
6.4	2.0	2.0	0.92	6.34	9.95
8.0	2.0	2.0	0.92	6.52	9.90
2.0	1.0	1.0	0.92	3.20	4.98
2.0	1.6	1.6	0.92	5.10	7.89
2.0	2.0	2.0	0.92	6.34	9.84
2.0	3.0	3.0	0.92	9.30	14.78
2.0	4.0	4.0	0.92	12.20	19.75
2.0	5.0	5.0	0.92	15.45	24.65
2.0	2.0	2.0	0.23	1.58	2.49
2.0	2.0	2.0	0.46	3.18	4.98
2.0	2.0	2.0	0.92	6.34	9.84
2.0	2.0	2.0	1.38	9.54	14.45
2.0	2.0	2.0	1.84	12.69	19.23
2.0	2.0	2.0	2.30	15.86	24.13

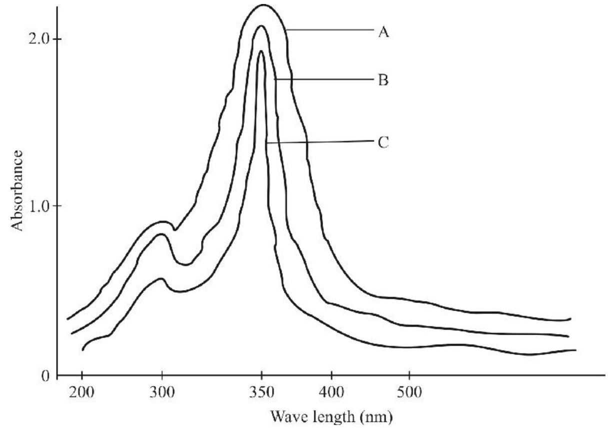


Fig. 3. Electronic spectra of TEACC in aqueous acetic acid (50% v/v) (A) without substrate (B) with crotonaldahyde (C) with maleic acid

The direct proportionality between k_1 values and [$HClO_4$] indicate first order kinetics with respect to [H^+] (Table 1). The plots of log k_1 versus log [H^+] gave straight line with a slope of unity (Fig. 4)

The linear increase in the rate with acidity suggests the involvement of protonated Cr(VI) species in the rate determining step. The participation of protonated chromium species in Cr(VI) oxidations [7] is well known in acid media [8].

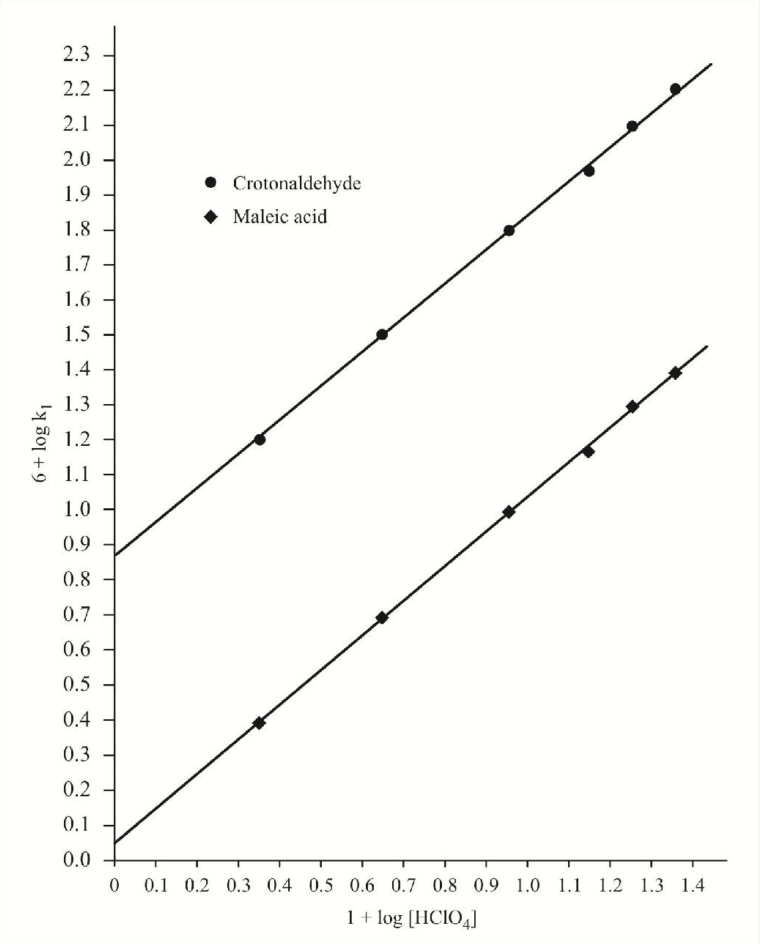


Fig. 4. Plot of log k_1 vs log [H^+]

[TEACC] = 2.0 × 10^{-3} mol dm^{-3}; [unsaturated organic compound] = 2.0 ×10^{-2} mol dm^{-3}; [$NaClO_4$] = 2.0 × 10^{-1} mol dm^{-3}; Solvent : AcOH-H_2O (50 : 50 v/v); Temperature : 303 K.

Effect of ionic strength : Variation of ionic strength of the medium by the addition of $NaClO_4$ has no pronounced effect on the rate. Similar observations were also reported in the oxidation of unsaturated substrates by QCC [9, 10].

Induced Polymerisation: 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 oxidation of crotonaldehyde and maleic acid were studied in the solvent containing different proportions of acetic acid and water. The reaction rate increases with increase in acetic acid content of the reaction mixture. The plots of log k_1 against 1/D were linear with positive slope. This implies the occurrence of an interaction of an ion-dipole type [11] which confirms the involvement of protonated oxidant species in the rate determining step.

Effect of temperature: The rate increases with the rise in temperature. The reaction between unsaturated organic compounds and TEACC were studied at five different temperatures in the range 293K-313K and the activation and thermodynamic parameters plots were computed by standard procedure (Table 2). The Arrhenius of log k_1 versus 1/T were linear (Fig. 5). The entropy of activation are largely negative as expected for bimolecular reaction. The constancy of free energy of activation for both substrates may signal the operation of similar mechanism.

Table 2. Activation and thermodynamic parameters

Unsaturated Organic Compounds	Ea (kJ mol^{-1})	ΔH# (kJ mol^{-1})	ΔG# (kJ mol^{-1})	– ΔS# (JK^{-1} mol^{-1})
Crotonaldehyde	53.20	50.73	98.62	158.04
Maleic acid	53.32	50.89	103.31	173.01

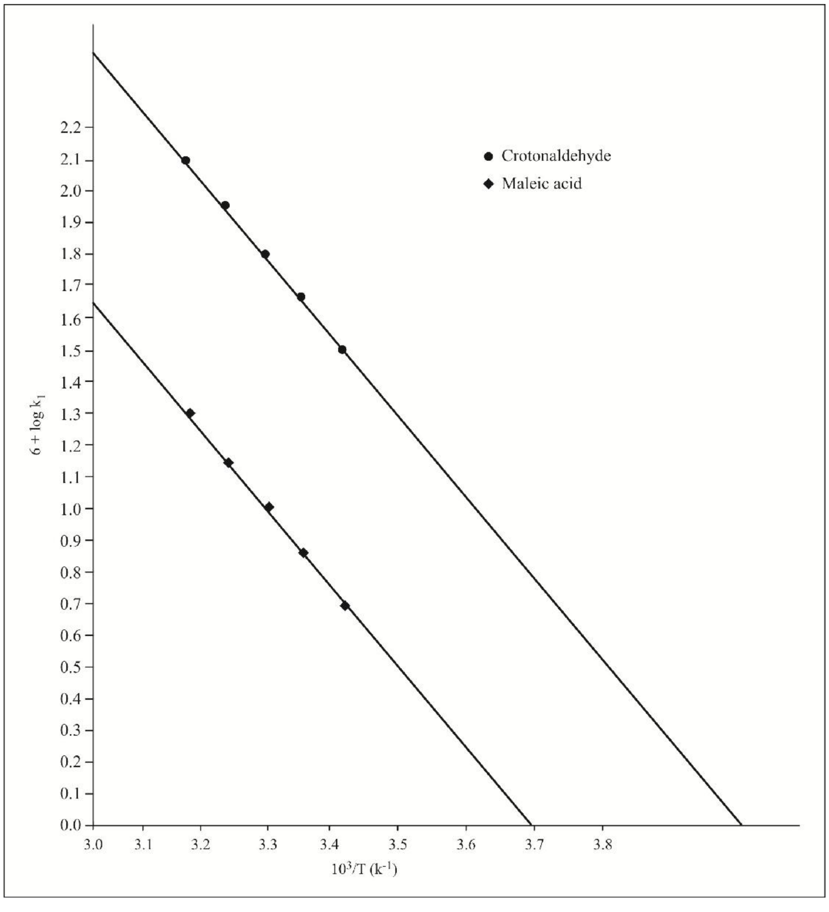
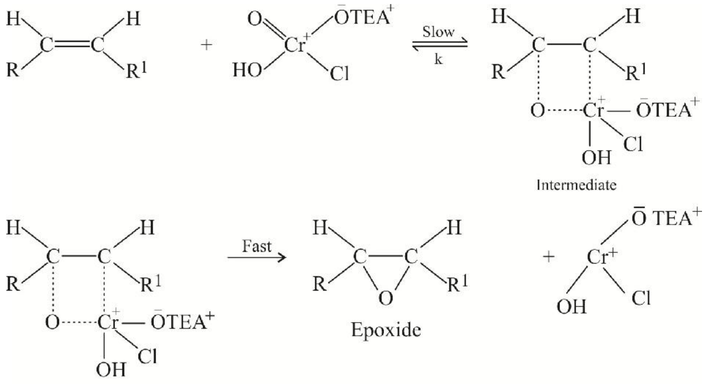


Fig. 5. Plot of log k_1 vs 1/T

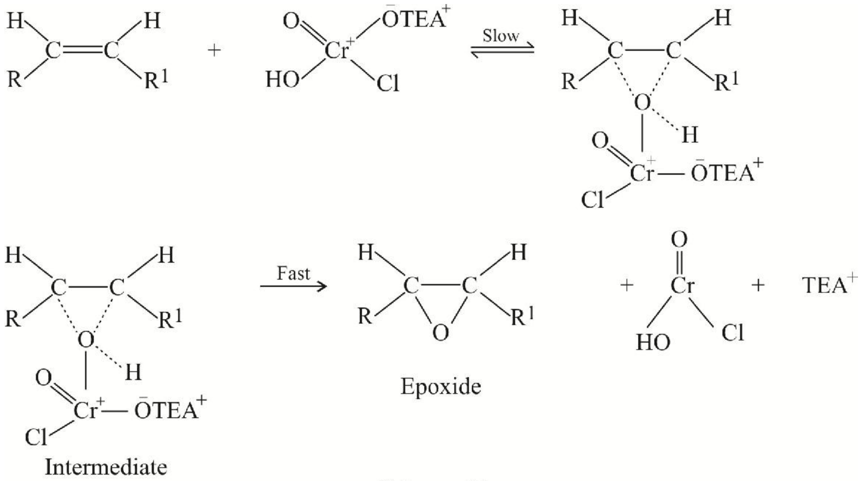
[TEACC] = 2.0 × 10^{-3} mol dm^{-3}; [unsaturated organic compound] = 2.0 × 10^{-2} mol dm^{-3}; [HClO$_4$] = 0.92 mol dm^{-3}; [NaClO$_4$] = 2.0 × 10^{-1} mol dm^{-3}; Solvent : AcOH : H$_2$O (50-50% v/v)

Mechanism: It was found that epoxide is the only product of epoxidation of unsaturated organic compound with TEACC. To explain the formation of product and other observed data, the mechanism in scheme I is proposed



Scheme I

The rate determining step may be the loose complex formation between the protonated TEACC and substrate. An electrophilic attack of Cr(VI), being positively charged in the protonated TEACC on the double bond of the substrate produce a four-membered transition state which can yield the epoxide in the fast step. 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) [12]. Thus the most favourable path may be the three centre type addition as depicted in scheme II.



Scheme II

where, R = CH_3 and R^1 = CHO for crotonaldehyde and R = R^1 = COOH for maleic acid

Both scheme envisage an oxygen atom transfer from the oxidant. This is in accord with the earlier observation made for unsaturated substrates [13, 14]. Consequently the rate law is described as follows:

$$\text{TEACC} + \text{H}^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \text{TEACCH}^+ \qquad \ldots(1)$$

$$\text{TEACCH}^+ + \text{S} \xrightarrow[\text{Slow (r.d.s)}]{k_1} \text{Intermediate} \qquad \ldots(2)$$

$$\text{Intermediate} \xrightarrow{\text{Fast}} \text{Product} \qquad \ldots(3)$$

$$\text{Rate} = -\frac{d[\text{TEACC}]}{dt} = k_1[\text{TEACCH}^+]\ [\text{S}] \qquad \ldots.(4)$$

By equation (1)

$$-\frac{d[\text{TEACC}]}{dt} = k_1\ K\ [\text{TEACC}]\ [\text{H}^+]\,[\text{S}] \qquad \ldots.(5)$$

$$-\frac{d[\text{TEACC}]}{dt} = k_{obs}\ [\text{TEACC}]\ [\text{H}^+]\,[\text{S}] \qquad \ldots.(6)$$

where, $k_1 K = k_{obs}$

The rate law is in accordance with the experimental kinetic findings.

The low rate of oxidation of maleic acid compared to crotonaldehyde could be due to the presence of two carboxylic groups on the same side in maleic acid, the cis attack by TEACC is prevented.

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