

# Kinetics and Mechanism of Oxidation of Malic Acid by Benzyltrimethylammonium Fluorochromate in Aqueous Acetonitrile Medium

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**Abstract:** Kinetics of oxidation of malic acid by benzyltrimethylammonium fluorochromate (BTMAFC) in acetonitrile-water solvent mixture at 298 K in the presence of perchloric acid has been followed spectrophotometrically. The reaction is first order with respect to both malic acid and BTMAFC and is catalyzed by H<sup>+</sup> ion. Hydrogen ion dependence shows the form  $k_{\text{obs}} = a + b[\text{H}^+]$ . The reaction rate is not affected by changes in ionic strength of the reaction medium or by the addition of acrylonitrile. However, addition of manganese sulphate causes a decrease in the rate of reaction. An increase in the water content of the solvent mixture decreases the rate of reaction. The reaction has been studied at four different temperatures and activation parameters,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  have been evaluated using Arrhenius and Eyring equations. Based on these findings, a suitable mechanism involving a direct hydride ion transfer from substrate to oxidant has been proposed.

**Keywords:** Oxidation, Kinetics, Mechanism, Malic acid, Chromium(VI)

## Introduction

There are continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic compounds under mild conditions. Organic substrates containing different functional groups have been oxidised using a variety of chromium(VI) reagents. Chromium(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic<sup>1</sup>. Some of the entries in the list of modified Cr(VI) reagents are pyridinium chlorochromate<sup>2</sup>, caffeinium chlorochromate<sup>3</sup>, quinolinium fluorochromate<sup>4</sup>, triphenylmethylphosphonium chlorochromate<sup>5</sup>, quinolinium chlorochromate<sup>6</sup>, imidazolium fluorochromate<sup>7</sup>, tributylammonium chlorochromate<sup>8</sup>, prolinium chlorochromate<sup>9</sup>, tripropylammonium fluorochromate<sup>10</sup>, tetrahexylammonium chlorochromate<sup>11</sup>, etc. Benzyltrimethylammonium fluorochromate (BTMAFC) is more efficient for quantitative oxidation of several organic substrates and has certain advantages

over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. The phase-transfer catalytic nature of ammonium ions perhaps makes the BTMAFC a more efficient and stronger oxidizing agent. A survey of literature shows that mechanistic studies with BTMAFC are very few<sup>12</sup>. However, no detailed kinetic study of oxidation of malic acid with BTMAFC has so far been attempted. We have investigated the kinetics of oxidation of malic acid in acetonitrile-water mixture by BTMAFC to get a clear picture of mechanism of oxidation. Further, this reagent does not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

## Experimental

All the chemicals used were of AR Grade. BTMAFC was prepared by literature method<sup>12</sup> and its purity was checked by determining Cr(VI) concentration iodometrically. Analar grade malic acid (Aldrich) was used as such. All the solutions used in the study were made in distilled acetonitrile or doubly distilled water.

### *Kinetic measurements*

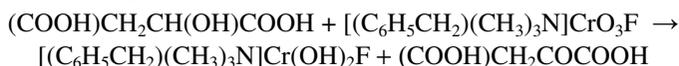
The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over BTMAFC. The kinetic runs were carried out in 50% acetonitrile-50% water (v/v) solvent mixture. The reactions were followed spectrophotometrically by monitoring the decrease in absorption of BTMAFC at 372 nm for up to 3 half-lives. No attempts were made to keep the ionic strength of the reaction medium constant as the reactions were not influenced by changes in ionic strength. The pseudo-first order rate constants,  $k_{\text{obs}}$ , were determined by least square method from the linear plots of  $\log[\text{BTMAFC}]$  versus time. Replicate runs showed that the rate constants were reproducible to within  $\pm 3\%$ . The second order rate constants,  $k_2$ , were calculated as  $k_{\text{obs}}/[\text{substrate}]$ . All kinetic runs, other than those for studying the effect of hydrogen ions, were carried out in absence of perchloric acid.

### *Product analysis*

In a typical experiment, solutions of malic acid and BTMAFC in 2:1 molar ratio were mixed and kept aside in dark for about 24 h to ensure completion of reaction. It was then treated with 50 mL of a saturated solution of 2,4-dinitrophenyl hydrazine and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenyl hydrazone (DNP) was filtered off, dried and recrystallised from ethanol. The product was identical to an authentic sample of DNP (melting point and mixed melting point) of the corresponding keto acid. The oxidation state of chromium in completely reduced reaction mixtures, as determined iodometrically, was  $3.89 \pm 0.29$ .

### *Stoichiometry*

In a typical experiment, a reaction mixture containing 10 times excess of BTMAFC over malic acid was prepared and allowed to react overnight. Then the unreacted BTMAFC was estimated iodometrically, which established a 1:1 stoichiometry between BTMAFC and malic acid, as represented in the following scheme.



**Scheme 1**

## Results and Discussion

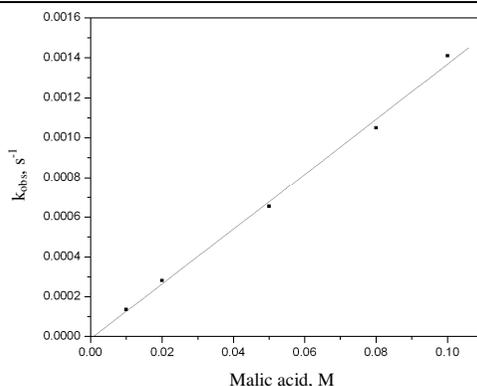
Oxidation of malic acid by BTMAFC has been conducted in 50% acetonitrile and 50% water medium at 298 K, under pseudo first-order conditions and the results obtained were

discussed in the following paragraphs. As it was found that ionic strength of the reaction medium had no significant effect on reaction rate, constancy of ionic strength was not maintained throughout the present study.

The values of  $k_{\text{obs}}$  were calculated for different concentrations of BTMAFC by maintaining other parameters at constant values. The data in Table 1 show that the pseudo first order rate constant ( $k_{\text{obs}}$ ) remains almost constant on varying the concentration of BTMAFC, revealing that the reaction follows first-order kinetics with respect to [BTMAFC]. The  $k_{\text{obs}}$  values calculated for different concentrations of malic acid by keeping the concentration of BTMAFC at a constant value are also included in Table 1. The data establish that the rate increases with increase in [malic acid] in a first-order fashion. Further, the plot of  $k_{\text{obs}}$  versus [malic acid] is excellently linear passing through origin (Figure 1;  $r = 0.999$ ). Also, the  $k_2$  values remain constant when [malic acid] is varied (Table 1); this result, coupled with the nearly unit slope value of the double logarithmic plot between  $k_{\text{obs}}$  and [malic acid] ( $r = 0.999$ ; slope =  $0.996 \pm 0.021$ ) confirms the first-order nature of the reaction with respect to [malic acid].

**Table 1.** Pseudo first-order and second-order rate constants for the oxidation of malic acid by BTMAFC in 50:50 acetonitrile-water (v/v) mixture at 298 K

$10^3$ [BTMAFC] M	[Malic acid] M	$10^3$ [H <sup>+</sup> ] M	$10^4 k_{\text{obs}}, \text{s}^{-1}$	$10^2 k_2^c, \text{M}^{-1} \text{s}^{-1}$
0.5	0.01	-	$1.35 \pm 0.12$	$1.35 \pm 0.12$
0.5	0.02	-	$2.81 \pm 0.29$	$1.41 \pm 0.15$
0.5	0.05	-	$6.54 \pm 0.64$	$1.27 \pm 0.13$
0.5	0.08	-	$10.5 \pm 1.0$	$1.31 \pm 0.13$
0.5	0.10	-	$14.1 \pm 1.3$	$1.41 \pm 0.13$
1.0	0.01	-	$1.38 \pm 0.11$	$1.38 \pm 0.11$
2.0	0.01	-	$1.42 \pm 0.10$	$1.42 \pm 0.10$
3.0	0.01	-	$1.43 \pm 0.11$	$1.43 \pm 0.11$
5.0	0.01	-	$1.46 \pm 0.12$	$1.46 \pm 0.12$
0.5	0.01	0.01	$1.92 \pm 0.15$	$1.92 \pm 0.15$
0.5	0.01	0.02	$3.38 \pm 0.31$	$3.38 \pm 0.31$
0.5	0.01	0.04	$4.89 \pm 0.42$	$4.89 \pm 0.42$
0.5	0.01	0.06	$6.45 \pm 0.60$	$6.45 \pm 0.60$
0.5	0.01	0.10	$9.22 \pm 0.88$	$9.22 \pm 0.88$



**Figure 1.** Direct plot of  $k_{\text{obs}}$  versus [Malic acid] for the oxidation of malic acid with BTMAFC

The values of  $k_{\text{obs}}$  were calculated at different concentrations of  $\text{H}^+$  by keeping the [BTMAFC] and [Malic acid] at constant values. The  $k_{\text{obs}}$  value increases linearly with increase in  $[\text{H}^+]$  (Table 1), establishing the catalytic behavior of perchloric acid and the hydrogen ion dependence obeys the equation  $k_{\text{obs}} = a + b[\text{H}^+]$ . The values of  $a$  and  $b$  for malic acid are  $1.57 \pm 0.22 \times 10^{-4} \text{ s}^{-1}$  and  $6.66 \pm 0.40 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  ( $r = 0.995$ ). Similar results with respect to [oxidant], [substrate] and  $[\text{H}^+]$  acid-catalytic behaviour have been reported in the oxidation of hydroxy acids and alcohols by quinolinium fluorochromate<sup>13,14</sup>, tripropylammonium fluorochromate<sup>15,16</sup> and morpholinium chlorochromate<sup>17,18</sup>.

The effect of ionic strength on the reaction rate was studied by varying the ionic strength of the medium by adding different quantities of  $\text{NaClO}_4$ , maintaining other parameters constant (Table 2). The data reveal that variation of ionic strength of the medium has no significant effect on reaction rate. This result shows the participation of a neutral species as a reactant in the rate-determining step. The kinetic runs carried out in the presence of acrylonitrile (Table 2) establish that the reaction fails to initiate the polymerisation of added acrylonitrile. Absence of any effect of added acrylonitrile on the reaction discounts<sup>19</sup> the possibility of formation of free radicals during the course of the reaction as a result of a one-electron oxidation.

**Table 2.** Influence of ionic strength (I) and acrylonitrile (AN) on reaction rate for the oxidation of malic acid by BTMAFC in 1:1 acetonitrile-water (v/v) mixture at 298 K<sup>a</sup>

[I], M	$10^4 k_{\text{obs}}, \text{ s}^{-1}$	$10^3$ , AN, M	$10^4 k_{\text{obs}}, \text{ s}^{-1}$
0.01	$1.35 \pm 0.12$	0	$1.35 \pm 0.12$
0.03	$1.31 \pm 0.11$	1.0	$1.28 \pm 0.10$
0.06	$1.41 \pm 0.13$	3.0	$1.31 \pm 0.11$
0.10	$1.43 \pm 0.12$	6.0	$1.34 \pm 0.11$

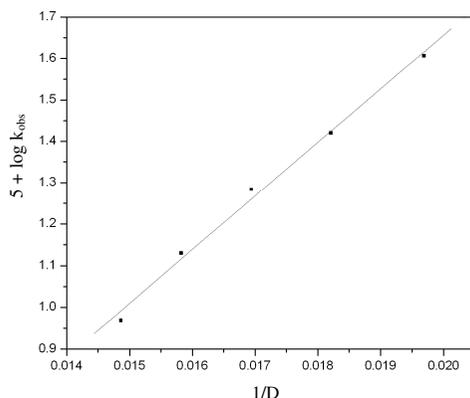
<sup>a</sup>General conditions: [BTMAFC] = 0.0005 M; [Malic acid] = 0.01 M

The rate constant values measured for the oxidation of malic acid with BTMAFC in presence of differing amounts of  $\text{MnSO}_4$  are listed in Table 3. The data show that the rate of reaction decreases significantly with increasing concentration of added  $\text{MnSO}_4$ . This result reveals<sup>15,20</sup> a direct two electron reduction of Cr(VI) to Cr(IV). The effect of the solvent composition on the reaction rate was studied by varying the acetonitrile content in the solvent mixture from 40% to 80% and the measured  $k_{\text{obs}}$  values (Table 3) show that the rate of reaction increases remarkably with increase in the percentage proportion of acetonitrile in the solvent medium, establishing that the reaction between malic acid and BTMAFC is favoured by a solvent of low dielectric constant. The plot of  $\log k_{\text{obs}}$  versus  $1/D$  (Amis plot) is linear (Figure 2;  $r = 0.997$ ; slope = 129.31), with a positive slope, indicating<sup>21</sup> that the rate-determining step involves an interaction between a cation and a dipole.

**Table 3.** Influence of added manganous sulphate and solvent polarity on reaction rate for the oxidation of malic acid by BTMAFC at 298 K<sup>a</sup>

$10^3$ , $\text{Mn}^{2+}$ , M	$10^4 k_{\text{obs}}, \text{ s}^{-1}$	% $\text{CH}_3\text{CN}$ , v/v <sup>b</sup>	$10^4 k_{\text{obs}}, \text{ s}^{-1}$
0	$1.35 \pm 0.12$	40	$0.93 \pm 0.08$
0.50	$1.21 \pm 0.10$	60	$1.92 \pm 0.15$
0.80	$1.09 \pm 0.19$	70	$2.63 \pm 0.23$
1.20	$0.95 \pm 0.10$	80	$4.04 \pm 0.38$

<sup>a</sup>General conditions: [BTMAFC] = 0.0005 M; [Malic acid] = 0.01 M; Solvent = 1:1 acetonitrile-water (v/v) mixture unless otherwise stated. <sup>b</sup>Rest was water

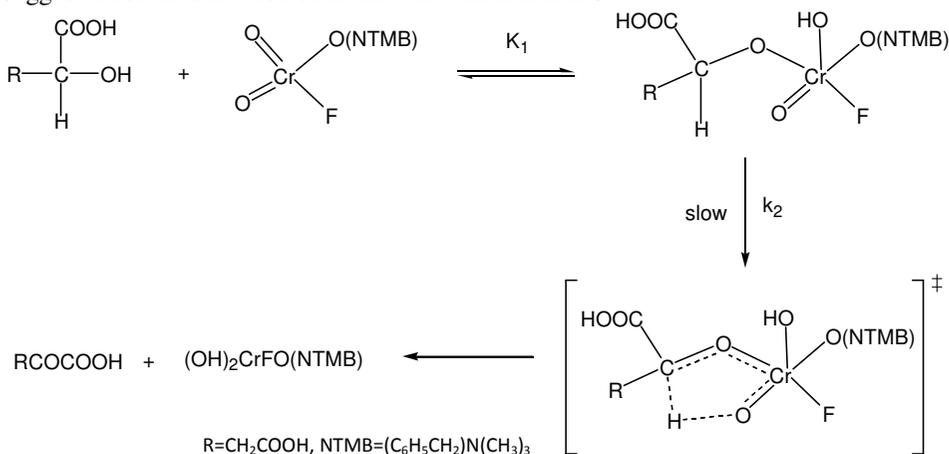


**Figure 2.** Plot of  $\log k_{\text{obs}}$  versus  $1/D$  for the oxidation of malic acid with BTMAFC

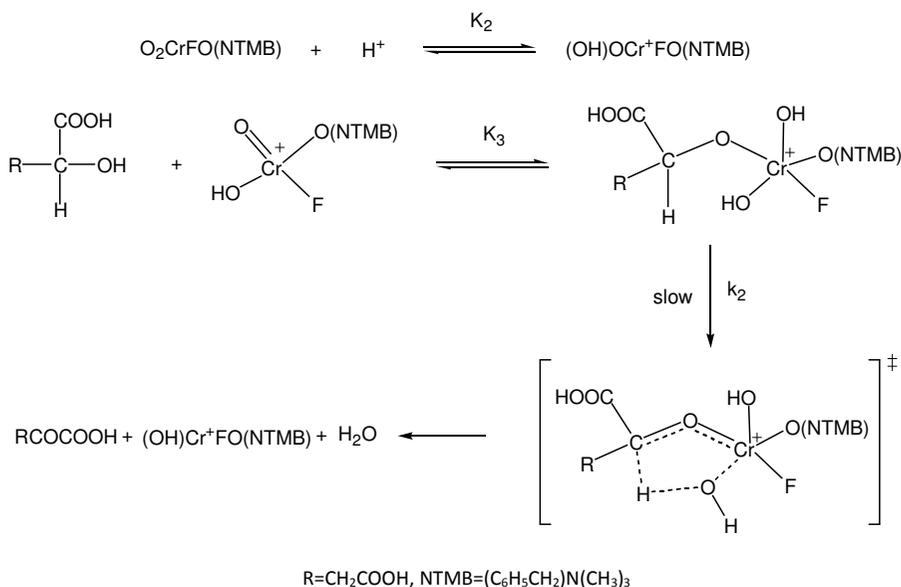
The reaction was carried out at three other temperatures (303, 313 and 323 K) keeping other experimental conditions constant. The values of  $k_2$  ( $\text{M}^{-1}\text{s}^{-1}$ ) are 0.0135, 0.0223, 0.0517 and 0.112 at 298, 303, 313 and 323 K, respectively. From the Arrhenius and Eyring plots, the thermodynamic parameters for the oxidation of malic acid were found to be  $E_a = 67.4 \pm 1.3$  kJ/mol,  $\Delta H^\ddagger = 64.8 \pm 1.3$  kJ/mol,  $\Delta G^\ddagger$  (298 K) =  $83.6 \pm 1.8$  kJ/mol and  $\Delta S^\ddagger = -63.2 \pm 1.8$   $\text{JK}^{-1}\text{mol}^{-1}$ .

### Mechanism

Absence of any effect of added acrylonitrile and the retarding effect of added  $\text{MnSO}_4$  on the reaction indicate a two-electron oxidation. The solvent effect points to an interaction between a cation and a dipole in the rate-determining step and supports a transition state, which is more polar than the reactant state. Retardation of the rate of oxidation by the added  $\text{Mn}^{2+}$  ion implies a two-electron transfer in the rate-determining step. The hydrogen ion dependence can be explained by assuming a rapid reversible protonation of the oxidant to give a protonated BTMAFC, which may function as an effective electrophile. Based on the above kinetic observations, two mechanistic pathways (Schemes 2 & 3), acid-dependent and acid-independent, involving hydride-ion transfer from O–H group to BTMAFC have been suggested for the oxidation of malic acid with BTMAFC.



**Scheme 2.** Acid independent path

**Scheme 3.** Acid dependent path

The rate law can be given as

$$\text{Rate} = \frac{K_2 K_3 k_2 [\text{BTMAFC}] [\text{Malic acid}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}$$

This rate law explains the first-order dependence of the reaction on [BTMAFC], [Malic acid] and fractional-order dependence on [H<sup>+</sup>]. The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, resulting in loss of entropy<sup>22</sup>.

## Conclusion

The BTMAFC oxidation of malic acid involves a direct hydride ion transfer from the substrate to oxidant, resulting in the formation of oxo acid and Cr(IV) as products. This mechanism is supported by the experimental data such as the reaction stoichiometry, the effect of solvent polarity, the effect of added Mn<sup>2+</sup> and the activation parameters.

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