

HOMOGENEOUS CATALYSIS OF MANGANESE(II) IN ACID BROMATE OXIDATION OF OLEFINIC ACIDS

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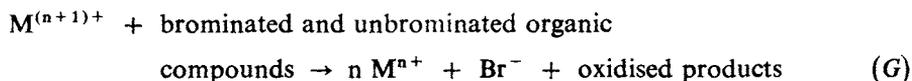
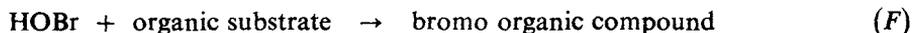
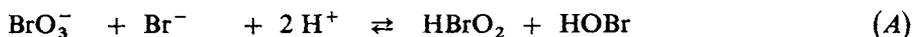
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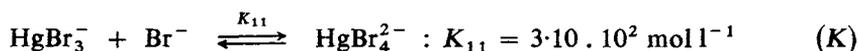
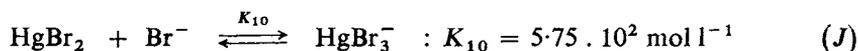
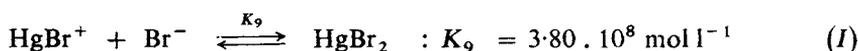
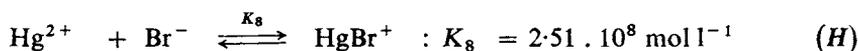
Manganese(II)-catalysed acid bromate oxidation of acrylic *trans*-crotonic and *trans*-cinnamic acids, in the presence of mercury(II), a bromide ion scavenger, exhibits first order in concentration of bromate, and reaches an upper limit with increase in substrate as well as catalyst concentration. Oxidation rate increases with acidity and is not altered when deuterium replaces either α or β proton of the olefinic acid. The catalytic effect of Mn(II) is displayed by its complex forming ability and the proposed mechanism assumes the oxidation of the formed Mn(II)-substrate π complex to Mn(III)-substrate π complex by acid bromate which further converts to products. The formation of a π complex between Mn(II) and the olefinic bond of the substrate is assumed for the first time.

The ion Mn(II) has been employed as a catalyst by many workers in chromium(VI) (refs¹⁻⁵), thallium(III) (ref.⁶), vanadium(V) (ref.⁷) and cerium(IV) (refs⁸⁻¹⁰) oxidations. A survey through the existing literature reveals that Mn(II)-catalysed acid bromate oxidation of organic compounds did not receive the attention of kineticists so far. However, Mn(II) has been used in many B-Z (Belousov-Zhabotinsky) reactions and the essential features of the mechanism are:



An important characteristic of the mechanism suggested for the B-Z system is the key role attributed to bromide ion, an intermediate of the reaction. According to mechanism by Noyes and coworkers^{11,12}, in the catalysed and uncatalysed bromate oscillatory reactions, bromide ions have a controlling functions. It was also realised that for an oscillation to occur the reaction set must have an autocatalytic reaction sub-set.

On the other hand, it has been demonstrated recently^{13,14} that in the presence of mercury(II), a bromide ion scavenger, the auto-catalytic reaction is switched off, both temporal and spatial oscillations vanish and the system tends to decay rather than amplify. This added mercury(II) plays a dual role by complexing Br⁻ ion as non-ionised mercury(II)-bromo complexes¹⁵.



Thus the Br₂ production and its subsequent addition to the ethylenic bond¹⁶ is eliminated and also oscillations are inhibited. In the presence of mercury(II), the reaction mechanism should be totally different to that of B-Z reaction. Therefore in the present work, in order to test the mechanism of the hitherto unreported reaction, the substrates acrylic, *trans*-crotonic and *trans*-cinnamic acids, which can easily add bromine, have been used.

EXPERIMENTAL

KBrO₃, MnSO₄ · 2H₂O, Hg(OCOCH₃)₂ were of AR purity. Acrylic, *trans*-crotonic and *trans*-cinnamic acids were of LR grade and used after purification. *trans*-α-[²H]-Cinnamic acid (m.p. 135°C), *trans*-β-[²H]-cinnamic acid, (m.p. 136°C) were obtained from Isotopes, Inc. (U.S.A.) and were checked for purity by IR and ¹H NMR spectroscopy. All other chemicals of AR grade (BDH, Fluka of Merck) were used as received. Solutions of the substrates were prepared either in redistilled water or in purified acetic acid.

A large excess (10 to 100-fold) of substrate was used for all kinetic measurements. The reactions were allowed to run in nitrogen atmosphere and in dark, their kinetics were followed by estimating bromate iodometrically. The reaction obeyed good first-order kinetics. Pseudo first-order rate constants (*k*'₁) were calculated from the slopes of the plots of ln[BrO₃⁻] vs time. Manganese(III) acetate was prepared by the procedure given elsewhere¹⁷ and its kinetics was also followed iodometrically. The rate constants obtained from multiple determinations were within ± 3% of each other. A Shimadzu multipurpose recording double beam spectrophotometer model MPS-5000 equipped with a temperature controller was used for absorption studies.

RESULTS

The kinetic complexity either observed or anticipated is eliminated by employing mercuric acetate which behaves only as a bromo complex forming metal ion (Table I). In the presence of Hg(II) (0.001–0.05 mol l⁻¹) the kinetic data fitted very well the integrated form of the empirical rate expression: $-d[\text{BrO}_3^-]/dt = k_1'[\text{BrO}_3^-]$.

The variation in the k_{obs} with the concentration of the substrate was investigated at different temperatures in solutions of H₂SO₄. The rates were found to follow the Michaelis–Menten type of correlation (Fig. 1). The value of k'_{obs} increased with an increase in acid concentration (Table II) and followed Hammett acidity function (H_0). A change in salt concentration had no effect (Table III) but k_1' decreased as the dielectric constant of the medium increased and was varied by changing the composition of acetic acid–water medium (Table IV).

TABLE I

Dependence of rate on bromate concentration at $40 \pm 0.1^\circ\text{C}$, [substrate] = 0.01 mol l⁻¹; [Mn(II)] = $1.0 \cdot 10^{-4}$ mol l⁻¹; [acid] = 1.0 mol l⁻¹; [Hg(OAc)₂] = 0.005 mol l⁻¹; CH₃COOH–H₂O = 30–70% (v/v). The values in parentheses were obtained with 0.05 mol l⁻¹ mercuric acetate

$10^4 \cdot [\text{Br(V)}]$ mol l ⁻¹	$10^4 \cdot k_1', \text{s}^{-1}$					
	acrylic acid		crotonic acid		cinnamic acid	
	H ₂ SO ₄	HClO ₄	H ₂ SO ₄	HClO ₄	H ₂ SO ₄	HClO ₄
2.5	3.84 (3.83)	3.76 (3.74)	2.54 (2.55)	2.74 (2.17)	2.30 (2.32)	2.25 (2.25)
5.0	3.84 (3.86)	3.77 (3.75)	2.57 (2.54)	2.15 (2.13)	2.33 (2.31)	2.26 (2.25)
10.0	3.83 (3.84)	3.75 (3.75)	2.54 (2.54)	2.17 (2.14)	2.31 (2.31)	2.25 (2.24)
15.0	3.84 (3.84)	3.76 (3.73)	2.55 (2.56)	2.15 (2.16)	2.32 (2.30)	2.24 (2.26)
20.0	3.85 (3.83)	3.76 (3.73)	2.55 (2.55)	2.16 (2.15)	2.32 (2.32)	2.25 (2.25)
25.0	3.84 (3.83)	3.76 (3.75)	2.56 (2.55)	2.16 (2.17)	2.31 (2.30)	2.24 (2.26)

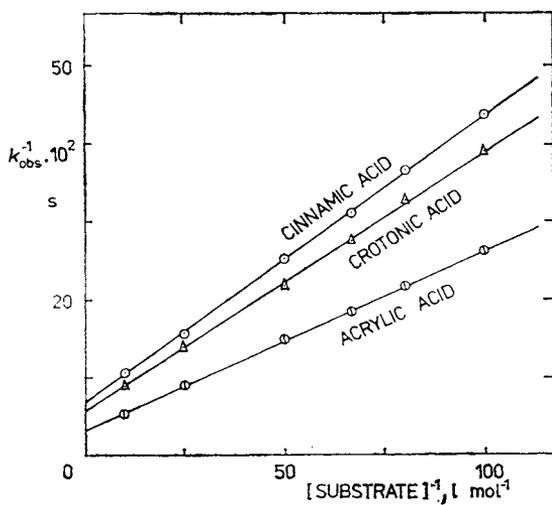


FIG. 1

Representative Michaelis-Menten plots for olefinic acids at $40 \pm 0.01^\circ\text{C}$. Other conditions as in Tables I and II

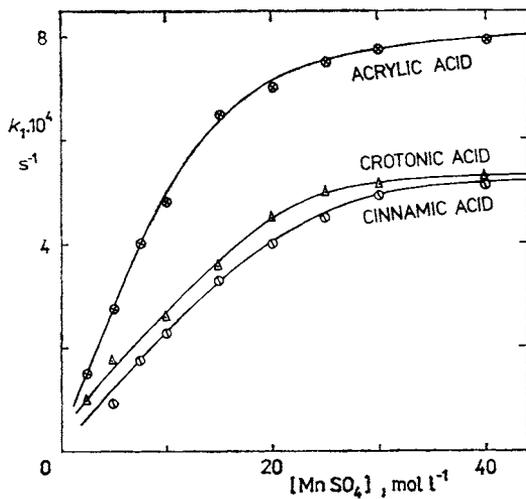


FIG. 2

Dependence of rate on Mn(II) concentration. Concentration of reactants as in Tables I and II

The oxidation rate was not altered when deuterium replaced either α or β proton of cinnamic acid ($k_H/k_D = 1.02 \pm 0.01$). The general features of manganese(II)

TABLE II

Dependence of rate on acid concentration. $[KBrO_3] = 0.001 \text{ mol l}^{-1}$ and other conditions as in Table I

[acid] mol l^{-1}	$10^4 \cdot k_1, \text{s}^{-1}$					
	acrylic acid		crotonic acid		cinnamic acid	
	H_2SO_4	HClO_4	H_2SO_4	HClO_4	H_2SO_4	HClO_4
0.25	0.93	0.87	0.61	0.59	0.50	0.49
0.50	1.34	1.13	0.90	0.72	0.96	0.92
1.00	3.83	3.75	2.55	2.17	2.30	2.25
1.50	7.22	6.93	5.11	4.28	4.30	4.18
2.00	16.89	12.85	10.74	9.95	8.96	8.64
2.50	28.02	22.16	17.92	16.30	15.35	14.89
n^a	1.00	1.01	1.10	1.00	1.00	1.01

^a Slopes obtained from Hammett plot.

TABLE III

Effect of added salt on the rate of reaction

[salt] mol l^{-1}	$k_1 \cdot 10^4, \text{s}^{-1} \text{ }^a$			[salt] mol l^{-1}	$k_1' \cdot 10^4, \text{s}^{-1} \text{ }^a$		
	AA	CRA	CA		AA	CRA	CA
	[NaClO ₄]				$10^3 \cdot [\text{Na}_4\text{P}_2\text{O}_7]$		
0.25	3.83	2.55	2.31	1.0	3.84	2.55	2.30
0.50	3.85	2.55	2.33	5.0	3.85	2.57	2.31
1.00	3.84	2.53	2.30	50.0	3.83	2.55	2.32
1.50	3.83	2.57	2.31	100.0	3.85	2.56	2.33
	[NaHSO ₄]				$10^3 \cdot [\text{LiF}]$		
0.25	3.83	2.57	2.30	1.0	3.83	2.56	2.30
0.50	3.85	2.57	2.31	5.0	3.86	2.57	2.33
1.00	3.85	2.55	2.32	10.0	3.85	2.56	2.32
1.50	3.84	2.56	2.31	50.0	3.84	2.55	2.30

^a AA Acrylic acid, CRA crotonic acid, CA cinnamic acid.

TABLE IV
Rate dependence on dielectric constant

H ₂ O-HOAc % (v/v)	Dielectric constant	10 ⁴ · k ₁ , s ⁻¹ ^a		
		AA	CRA	CA
90-10	66.6	1.22	1.15	0.98
80-20	59.9	2.41	1.66	1.42
70-30	53.2	3.84	2.56	2.32
60-40	46.5	5.26	3.60	3.61
50-50	39.8	8.96	6.04	7.15
40-60	33.1	16.13	11.79	12.68
30-70	26.4	34.58	23.47	27.78

^a AA Acrylic acid, CRA crotonic acid, CA cinnamic acid.

TABLE V
Thermodynamic parameters at 40°C; experimental conditions as in Tables I and II (values in parentheses were obtained in 1 mol l⁻¹ perchloric acid)

Substrate	k ₁ · 10 ⁵ s ⁻¹	ΔH [*] kJ mol ⁻¹	-ΔS [*] J deg ⁻¹ mol ⁻¹	ΔG [*] kJ mol ⁻¹
Bromate-Mn(II)-olefinic acid reaction				
Acrylic acid	38.32 (37.53)	39.75 (42.02)	184 (167)	98.26 (97.82)
<i>trans</i> -Crotonic acid	25.55 (21.71)	44.33 (44.62)	176 (173)	98.36 (98.74)
<i>trans</i> -Cinnamic acid	23.03 (22.56)	68.22 (66.78)	97 (101)	98.61 (98.62)
Bromate-olefinic acid reaction				
Acrylic acid	4.60	51.13	165	102.78
<i>trans</i> -Crotonic acid	2.88	54.69	158	104.00
<i>trans</i> -Cinnamic acid	2.11 (2.06)	82.47 (80.64)	72 (77)	104.80 (104.87)
Manganese(III)-olefinic acid reaction				
Acrylic acid	5.89	58.79	138	102.14
<i>trans</i> -Crotonic acid	6.14	56.18	146	101.88
<i>trans</i> -Cinnamic acid	42.15	79.06	57	97.01

catalysis are depicted in Fig. 2. The activation parameters evaluated from Arrhenius plot are given in Table V.

Polymerization of monomer like acrylamide or acrylonitrile confirms the production of free radicals in the system. However, no detectable polymer was observed when the monomer was added to separate solutions of Br(V)-Mn(II), Br(V)-olefinic acid and Mn(II)-olefinic acid systems.

DISCUSSION

The reduction of bromate with excess of olefinic acid is autocatalytic in nature. In acid solutions, Br₂ resulting from an autocatalytic reaction ($\text{BrO}_3^- + 5 \text{Br}^- + 6 \text{H}^+ \xrightleftharpoons{K} 3 \text{Br}_2 + 3 \text{H}_2\text{O}$; $K = 10^{33}$) reacts rapidly and irreversibly with the unsaturated acids. To avoid such reaction, the Br⁻ ions were trapped by employing mercury(II) which binds the Br⁻ ions. Added mercuric acetate served only as a bromo complex forming metal ion. In the presence of mercury(II), the bromine liberation was totally suppressed, the kinetic data and product analysis also confirmed it.

The Mn(II) catalysis could be explained in two alternate ways one of them is the application of Field, Koros and Noyes¹¹ theory of oxidation of organic substrates by Mn(III) ions resulted from bromate-Mn(II) reactions (A)-(G).

If the mechanism suggested by Noyes and coworkers^{11,18} is applied to the oxidation of Mn(II) with no Br⁻ ion involved, the set of elementary reactions (C), (D) and (L) is obtained, where $\dot{\text{Br}}\text{O}_2$ is a radical species which in turn is responsible for the oxidation of Mn(II). An autocatalytic reaction for bromous acid is obtained from reactions (C) and (D):



Thus, the initial rate of Mn(III) formation is considered to be twice that of bromate consumption.

Attempts to correlate the present results with Mn(III) oxidation of unsaturated acids failed because the Mn(III) solution added to reaction mixture coagulates, preventing further work. (Unstable Mn(III) undergoes disproportionation $2 \text{Mn(III)} \rightleftharpoons \text{Mn(II)} + \text{Mn(IV)}$ to give Mn(IV) which precipitates as MnO₂.) To prevent the precipitation of MnO₂, Mn(II) was employed. In the presence of Mn(II) (equal to the Mn(III) concentration) initially there is no heterogeneous phase in the reaction mixture. However, as the reaction proceeded a fine coating of the oxidant was observed on the surface of the reaction vessel. When the experiments were carried out at different temperatures under these conditions, a plot of $\ln k$ vs $1/T$ gave a curve which proved that homogeneous and heterogeneous reactions proceeded simultaneously. At higher Mn(II) concentrations ($\text{Mn(II)}/\text{Mn(III)} \geq 10$) the reaction was

homogeneous up to 50% conversion. Under these conditions, the reaction exhibited 1.0 order in Mn(III) and 0.5 ± 0.1 order in substrate concentrations. The oxidation rate of cinnamic acid was found to be faster (Table V) than that of crotonic and acrylic acid at all temperatures and oxidant to substrate ratio.

Runs were made with a tenfold molar excess of pyrophosphate over Br(V) to ensure that any Mn(III), if formed, should be prevented from disproportionation. If Mn(III) forms in the reaction mixture, it is readily trapped by pyrophosphate¹⁹ and the pyrophosphato-manganese(III) formed can be recognized by its spectrum. Surprisingly Mn(III) was not observed at any time during the oxidation.

With this negative observation of Mn(III), it was assumed that soluble Mn(IV) may be responsible for the oxidation as suggested by Simándi and Jaky²⁰ in permanganate oxidation of cinnamic acid. The Mn(IV) species may not be formed via disproportionation of Mn(III) but directly from Mn(II). Its disappearance might have occurred via reaction with the organic intermediate or possibly with unsaturated acid but skipping of the Mn(III) state.

Adamčíková and Ševčík²¹ recently studied the bromate-Mn(II) reaction and noticed an induction period, followed initially by a rapid, and then a continuous gradual increase of Mn(III) concentration. Manganese(IV) was not at all produced under any circumstances. The duration of the induction period increased with decrease in bromate and acid concentrations and was independent of Mn(II) concentration.

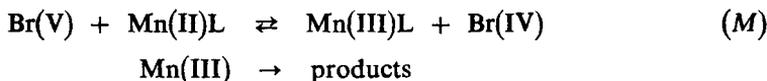
On the other hand, in the present study with mercury(II), the reaction exhibited first order in bromate, no induction period was observed over a wide range of bromate, substrate, acid and catalyst concentrations. Again concentrated mixtures of Br(V) and Mn(II), stored for several hours at 60°C, produced no detectable quantities of either Mn(III) or Mn(IV) ions. The reaction controlling ability of pyrophosphate and fluoride ions (Table III) also strongly suppressed the production of Mn(III) or Mn(IV).

The obtained data discard the route through the Field, Koros and Noyes¹¹ mechanism. The other possibility is the attribution of a direct oxidation of Mn(III)-olefinic acid complex to an Mn(III)-olefinic acid complex which subsequently decomposes to products.

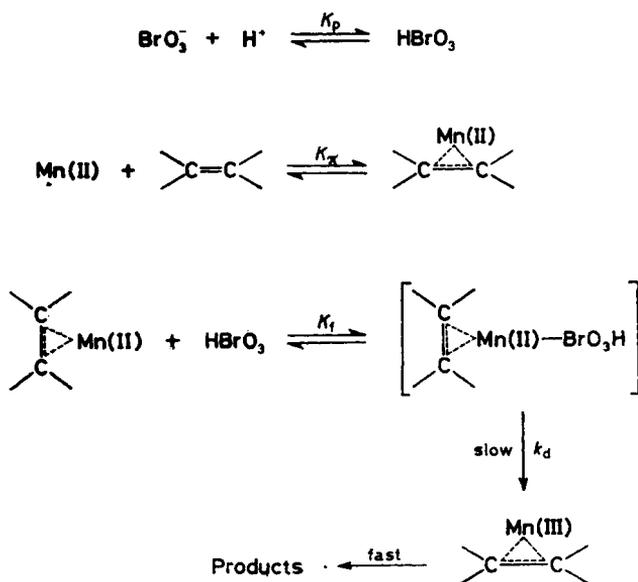
Figure 1 and 2 show that the oxidation of acrylic, crotonic and cinnamic acids has a dependence on Mn(II) concentration, consistent with the Michaelis-Menten kinetics; the reversible formation of a manganese(II) complex with one molecule of the substrate must precede the rate-determining oxidation. Furthermore, the UV spectra of the reaction mixture of crotonic and cinnamic acids at 275 nm compared to the spectra of the pure compounds show π complex formation with high molar extinction coefficient.

The marked lowering of the activation energies (Table V) of manganese(II)-catalysed reactions (compared to either Br(V) or Mn(III) oxidation) show that the

balance of the equilibrium in Eq. (M)



to which the catalysis is evidently due, depends on the fact that all the three substrates can form π complexes with manganese(II) ions in which the redox potential for Mn(III)/Mn(II) is decidedly less than for Mn(III) (aq)/Mn(II) (aq). If such complexing is not present, a similar manganous ion catalytic efficiency should be observed with all the three substrates, and moreover, other organic compounds oxidation by acid bromate, e.g. that of alcohols, diols, and carbonyl compounds should exhibit similar catalysis; but this is not the case. Based on the aforesaid arguments the mechanism shown in Scheme 1 is proposed.



SCHEME 1

The acid substrates dissociate slightly and it is probable that manganous ion in H_2SO_4 or HClO_4 medium forms complex prevailingly with the undissociated substrate molecules. For all the three substrates, the slow oxidation process may involve the transfer of an electron to Br(V) from a π complex of Mn(II) followed by a much faster breakdown of the Mn(III) π complex, for this never attains a spectroscopically detectable concentration.

Products analysed by TLC indicate that the double bond is certainly cleaved giving formaldehyde, acetaldehyde and benzaldehyde as major products (70–75%) in the case of acrylic, crotonic and cinnamic acids, respectively.

The derived rate law for the above mechanism is

$$k_1 = \frac{k_d K_p K_\pi K_f [\text{substrate}] [\text{Mn(II)}] [\text{H}^+]}{1 + K_p [\text{H}^+] + K_p K_\pi K_f [\text{H}^+] [\text{substrate}] [\text{Mn(II)}]}, \quad (1)$$

where K_p is the protonation constant for the bromate and is 0.51 mol^{-1} (refs^{22–24}), k_d denotes decomposition constant, K_f formation constant of the adduct $\text{Br(V)}-\text{Mn(II)}-\text{substrate}$ and K_π π complex formation constant.

At 1.0 mol l^{-1} acid concentration the above equation reduces to:

$$\frac{1}{k_1} = \frac{1}{1.5 K_f K_\pi k_d [\text{substrate}] [\text{Mn(II)}]} + \frac{1}{k_d}. \quad (2)$$

The above equation accords with the kinetic findings, and can explain why the apparent activation energy for the catalysed oxidation of acrylic, crotonic and cinnamic acids is much less than that for the direct reaction between manganese(III) and olefinic acids.

According to Eq. (2), the plots of k_{obs}^{-1} vs $[\text{substrate}]^{-1}$ and k_{obs}^{-1} vs $[\text{Mn(II)}]^{-1}$ should be linear with definite intercept. This supports the proposed mechanism. The mechanism is further corroborated by the solvent influence on the reaction rate. The intermediate complex $\{\text{substrate}-\text{Mn(II)}-\text{Br(V)}\}$ is less polar than the reactants due to dispersal of charge, hence, decreasing polarity of the solvent is expected to stabilize the bromate complex in preference to the reactants thereby enhancing the rate. Such a solvent influence has actually been observed (Table IV).

From the intercept and slope data (Eq. (2)), the decomposition constant k_d , formation constant K_f and π complex formation constant K_π can be calculated and are recorded in Table VI.

TABLE VI
Values of parameters in Eqs (1) and (2)

Acid	$k_d \cdot 10^3, \text{ s}^{-1}$	$K_\pi K_f \cdot 10^{-4}$
<i>trans</i> -Cinnamic	1.43	11.65
<i>trans</i> -Crotonic	1.67	11.92
Acrylic	2.99	9.67

Catalysis by manganese(II) could of course reach an upper limit when the maximum concentration of complexed ion has been formed. Finally a comparison of cinnamic acid with acrylic and crotonic acids indicate that unlike Mn(III) oxidation, phenyl conjugation does not accelerate the reaction rate. Although polar effects cannot be fully excluded, the drop of the reactivity upon methyl or phenyl substitution in acrylic acid seems to be mainly due to steric reasons.

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