

Kinetic study of the oxidation of aliphatic aldehydes by *bis*(2,2'-bipyridyl) copper(II) permanganate

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Abstract. Kinetics of oxidation of aliphatic aldehydes, to the corresponding carboxylic acids, by *bis*(2,2'-bipyridyl) copper(II) permanganate (BBCP) has been studied. The reaction is first order with respect to BBCP. Michaelis–Menten type kinetics were observed with respect to the aldehyde. The formation constants for the aldehyde–BBCP complexes and the rates of their decomposition, at different temperatures, have been evaluated. Thermodynamic parameters for the complex formation and the activation parameters for their decomposition have also been determined. The reaction is catalysed by hydrogen ions; the acid-dependence being of the form: $k_{\text{obs}} = a + b[\text{H}^+]$. The oxidation of MeCDO exhibited a substantial kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 4.33$ at 303 K). The role of aldehyde hydrate in the oxidation process has been discussed. A mechanism involving formation of permanganate ester and its slow decomposition has been proposed.

Keywords. Aldehydes; *bis*(2,2'-bipyridyl)copper(II) permanganate; kinetics; mechanism; oxidation.

1. Introduction

Oxidation of organic compounds by aqueous potassium permanganate, a widely used oxidizing reagent, suffers from disadvantages which have been described earlier (Fieser and Fieser 1967). To minimize these, several permanganate derivatives, incorporating different counterions, have been prepared and used in oxidation of organic compounds (Firouzbadi *et al* 1984). One such reagent is *bis*(2,2'-bipyridyl) copper(II) permanganate (BBCP). It has been used for oxidation of thiols and alcohols to disulphides and carbonyl compounds respectively (Firouzbadi *et al* 1983). We have been unable to find any reports dealing with the kinetics of oxidations by BBCP in the literature. In continuation of our earlier work (Kothari 1991) on the oxidation of some thioacids, we report here the kinetics of oxidation of six aliphatic aldehydes by BBCP in aqueous perchloric acid. Mechanistic aspects are also discussed.

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2. Experimental

2.1 Materials

The aldehydes were commercial products and were purified by the methods described earlier (Sharma and Banerji 1985; Agarwal *et al* 1990). BBCP was prepared and purified by the reported method (Firouzbadi *et al* 1984). Perchloric acid (Merck) was used as the source of hydrogen ions. Deuterated acetaldehyde (MeCDO) was obtained from Sigma Chemicals.

2.2 Stoichiometry

In a typical reaction, acetaldehyde (4.4 g, 0.1 mol) and BBCP (12.3 g, 0.02 mol) were dissolved in 100 ml water, in the presence of 0.1 mol dm⁻³ perchloric acid. The reaction mixture was allowed to stand for ≈ 6 h to ensure completion of the reaction. It was rendered alkaline with NaOH, filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was acidified and extracted with ether (3 × 50 ml). The ether extract was dried (MgSO₄) and treated with thionyl chloride (10 ml). The solvent was allowed to evaporate. Dry methanol (7 ml) was added and the HCl formed was removed by a current of dry air. The residue was dissolved in ether (200 ml) and the ester content was determined colorimetrically as iron(III) hydroximate by the procedure of Hall and Schaefer (1954). The yield of acetic acid was 87% (0.15 g) based on the consumption of BBCP. Iodometric determination of the oxidation state of manganese, in the spent reaction mixture, showed that Mn(VII) had been reduced to Mn(IV). The overall reaction can, therefore, be written as,



2.3 Kinetic measurements

Reactions were studied under pseudo-first-order conditions by maintaining a large excess of the aldehyde over BBCP. The reactions were followed on a Hi-Tech model SFL-44 stopped-flow spectrophotometer coupled with an MCS-1 data processing system. The pseudo-first-order rate constant, k_{obs} , and the standard deviation therein were calculated by a computer program specially written for the equipment. The reaction was followed by monitoring the decrease in [BBCP] at 529 nm. For some kinetic runs, the reactions were also followed by monitoring the increase in [Mn(IV)] at 418 nm. For each run, 4–6 experiments were performed and it was found that the rate constants were reproducible to within ± 4%. Preliminary experiments showed that the reaction is not sensitive to changes in ionic strength (0.01 to 0.5 mol dm⁻³). Hence no attempt was made to keep the ionic strength constant. All kinetic measurements, except those to study the acid-catalysis, were performed in the absence of any added mineral acid.

3. Results

Computer generated plots indicated that the reaction is first order with respect to BBCP. Further, the rate constants are independent of the initial concentration of

Table 1. Rate constants of the oxidation of propionaldehyde by BBCP at 303 K.

[EtCHO] (mol dm ⁻³)	10 ³ [BBCP] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	k _{obs} (s ⁻¹)
0.020	1.0	0.0	1.23
0.035	1.0	0.0	2.00
0.043	1.0	0.0	2.45
0.069	1.0	0.0	3.57
0.087	1.0	0.0	4.58
0.150	1.0	0.0	6.25
0.245	1.0	0.0	8.10
0.430	1.0	0.0	10.4
0.245	2.0	0.0	8.17
0.245	4.0	0.0	8.24
0.245	8.0	0.0	7.91
0.150	1.0	0.01	9.67
0.150	1.0	0.02	13.0
0.150	1.0	0.05	23.5
0.150	1.0	0.08	34.0
0.150	1.0	0.12	47.1
0.150	1.0	0.16	61.2
0.150	1.0	0.20	74.5
0.150	1.0	0.20 ^a	75.0
0.150	1.0	0.00 ^b	6.11

^aContained 0.05 mol dm⁻³ CH₂=CHCN; ^bcontained 0.02 mol dm⁻³ 2,2'-bipyridine

BBCP. The rate increases with an increase in the concentration of the aldehyde, but the order is less than one (table 1). A plot of 1/k_{obs} versus 1/[aldehyde] is linear with an intercept on the rate-ordinate. This result is consistent with the following overall reaction scheme and leads to the rate law (4).



$$\text{rate} = k_{\text{ex}} K_{\text{ex}} [\text{aldehyde}] [\text{BBCP}] / (1 + K_{\text{ex}} [\text{aldehyde}]). \quad (4)$$

The variation in substrate concentration was studied at different temperatures and the values of K_{ex} and k_{ex} were calculated from the linear plots of 1/k_{obs} against 1/[aldehyde]. The thermodynamic and activation parameters were also calculated (tables 2 and 3).

Addition of perchloric acid increases the rate and the hydrogen ion dependence has the form: $k_{\text{obs}} = a + b[\text{H}^+]$. Addition of acrylonitrile and 2,2'-bipyridine did not affect the rate (table 1).

To ascertain the importance of the cleavage of the aldehydic C-H bond in the rate-determining step, the oxidation of deuterated acetaldehyde was studied. It was observed that the formation constant of the complex, K_{ex} , does not differ much in

Table 2. Formation constants and thermodynamic parameters of RCHO–BBCP complexes (acid-independent pathway).

R	$K_{ex}(\text{dm}^3 \text{mol}^{-1})$				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	283 K	293 K	303 K	313 K			
H	5.23 ± 0.5	4.63 ± 0.4	4.00 ± 0.4	3.38 ± 0.3	-13.2 ± 0.5	-24 ± 2	-6.1 ± 0.4
Me	4.72 ± 0.4	4.20 ± 0.5	3.65 ± 0.4	3.03 ± 0.4	-13.3 ± 0.7	-26 ± 2	-5.8 ± 0.6
Et	4.85 ± 0.6	4.37 ± 0.5	3.85 ± 0.2	3.15 ± 0.2	-12.9 ± 0.9	-24 ± 3	-5.9 ± 0.7
Pr	4.12 ± 0.6	3.43 ± 0.3	2.65 ± 0.6	2.01 ± 0.4	-20.2 ± 1.0	-51 ± 3	-5.2 ± 0.8
Pr ⁱ	4.63 ± 0.5	4.07 ± 0.6	3.27 ± 0.5	2.62 ± 0.4	-16.6 ± 1.0	-37 ± 3	-5.6 ± 0.8
ClCH ₂	3.89 ± 0.6	3.40 ± 0.5	2.89 ± 0.4	2.52 ± 0.4	-13.3 ± 0.3	-27 ± 1	-5.3 ± 0.2
MeCDO	4.80 ± 0.5	4.13 ± 0.6	3.25 ± 0.5	2.92 ± 0.3	-15.3 ± 0.8	-32 ± 3	-5.7 ± 0.6

Table 3. Rates of decomposition and activation parameters of RCHO–BBCP complexes (acid-independent pathway).

R	$k_{ex}(\text{s}^{-1})$				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	283 K	293 K	303 K	313 K			
H	0.30 ± 0.04	0.73 ± 0.08	1.42 ± 0.1	3.02 ± 0.2	53.4 ± 1.1	-66 ± 4	72.9 ± 0.9
Me	3.21 ± 0.2	6.10 ± 0.3	11.0 ± 0.5	23.2 ± 0.8	45.3 ± 1.6	-75 ± 5	67.7 ± 1.3
Et	4.30 ± 0.2	8.72 ± 0.4	17.4 ± 0.8	36.3 ± 1.1	49.6 ± 1.0	-58 ± 3	66.7 ± 0.8
Pr	5.04 ± 0.3	9.63 ± 0.5	18.4 ± 0.7	38.4 ± 1.0	47.0 ± 1.4	-66 ± 5	66.5 ± 1.1
Pr ⁱ	7.06 ± 0.4	13.3 ± 0.6	25.3 ± 1.0	52.0 ± 1.5	46.3 ± 1.4	-66 ± 4	65.7 ± 1.1
ClCH ₂	0.023 ± 0.003	0.068 ± 0.006	0.14 ± 0.02	0.29 ± 0.03	58.9 ± 2.3	-68 ± 7	78.9 ± 1.8
MeCDO	0.65 ± 0.05	1.30 ± 0.1	2.53 ± 0.1	5.66 ± 0.3	50.1 ± 1.7	-72 ± 6	71.4 ± 1.4

the oxidation of MeCDO and MeCHO. The rates of decomposition of the complex, however, exhibited a substantial kinetic isotope effect ($k_H/k_D = 4.35$ at 303 K).

When the whole of BBCP had been reduced, the reaction mixture had a red–brown colour. A determination of the oxidation state of reduced manganese species by iodometric titration showed its oxidation state to be 4.05 ± 0.16 . This indicated that the Mn(VII) is being reduced to Mn(IV). To confirm that Mn(IV) is indeed formed as a result of oxidation of aldehydes by BBCP, rates were determined at 418 nm also (Freeman and Kappos 1985; Lee and Perez-Benito 1988). The results showed that the rates of decay at 529 nm and of increase at 418 nm agreed within $\pm 12\%$. It was also observed that BBCP has virtually no absorption at 418 nm.

4. Discussion

Not much is known about the structure of BBCP, particularly about the nature of bonding of the two permanganate residues with the central copper atom. However, in the corresponding iodo complex, one iodine atom is linked by a covalent bond and the other, being present as an iodide ion, by an electrovalent bond (Barclay *et al* 1963). By similar analogy, BBCP can be represented as $[\text{bpy}_2 \text{Cu(II)MnO}_4]\text{MnO}_4$.

Aliphatic aldehydes are hydrated to varying extents in aqueous solution and the equilibrium constant of the following reaction has been reported (Bell 1964),



From the values of K_d and k_{obs} two sets of formation constants of the intermediate complex and rates of their decomposition were calculated. One set was calculated assuming that only the hydrate form of the aldehyde participates in the reaction,

$$\text{rate} = k_{\text{Hy}} K_{\text{Hy}} [\text{BBCP}] [\text{RCH(OH)}_2] / (1 + K_{\text{Hy}} [\text{RCH(OH)}_2]) \quad (6)$$

Similarly, another set was calculated assuming that only the free carbonyl form takes part in the oxidation process

$$\text{rate} = k_A K_A [\text{BBCP}] [\text{RCHO}] / (1 + K_A [\text{RCHO}]) \quad (7)$$

It is observed that the rates of decomposition of the complexes do not depend on the nature of the reactive species, while the formation constants vary to a large extent (table 4). This suggests that the nature of the intermediate complex is independent of the reactive form of the reductant. A comparison of the values of K_A and K_{Hy} of different aldehydes showed that the K_{Hy} values are of the same order for all the aldehydes but the K_A of formaldehyde and chloroacetaldehyde are very high as compared to those of other aldehydes. This large difference in the values of K_A cannot be explained by any polar or steric effect of the substituent. Therefore, it is unlikely that the free carbonyl form of the aldehydes participates in the oxidation process. Similar conclusions have been drawn in many other oxidations of aliphatic aldehydes (Rocek and Ng 1973; Jain and Banerji 1983; Sharma and Banerji 1985). Though no definite reason for this observation can be given, it may be due to the higher reactivity of a gem-diol containing two easily oxidisable hydroxyl groups. Secondly, most aliphatic aldehydes exist predominantly in the hydrate form in aqueous solutions.

The rate of decomposition of the complexes exhibited an excellent correlation with Taft's σ^* values (Wiberg 1963) with negative reaction constants (table 5). The negative reaction constants point to an electron-deficient carbon centre in the transition state.

The absence of any effect of the radical scavenger on the reaction rate points against a one-electron oxidation giving rise to free radicals. The following mechanism accounts

Table 4. Formation constants and rate constants of oxidation of hydrate form and free carbonyl form.

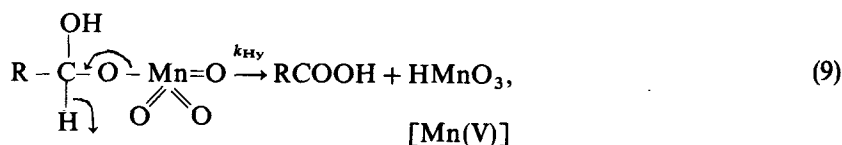
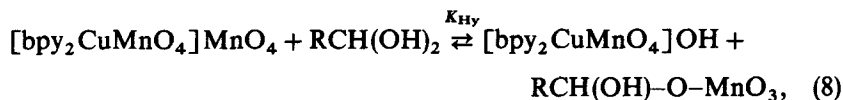
Aldehyde	K_d^a	K_{ex}	k_{ex}	K_{Hy}	K_A
HCHO	6.9×10^{-4}	4.00 ± 0.3	1.42 ± 0.1	4.00 ± 0.3	4820 ± 290
MeCHO	0.77	3.65 ± 0.4	11.0 ± 0.5	4.32 ± 0.6	8.53 ± 1.0
EtCHO	1.7	3.85 ± 0.2	17.4 ± 0.8	10.4 ± 0.4	6.10 ± 0.3
PrCHO	2.6	2.65 ± 0.6	18.4 ± 0.7	9.2 ± 1.2	3.61 ± 0.9
Pr'CHO	2.8	3.27 ± 0.5	25.3 ± 1.0	12.1 ± 0.9	4.50 ± 0.7
ClCH ₂ CHO	0.032	2.89 ± 0.4	0.14 ± 0.02	2.92 ± 0.2	102 ± 14

^aData from the compilation by Bell (1964).

Table 5. Temperature dependence of the reaction constant.

T(K)	283	293	303	313
ρ	-2.00 ± 0.03	-1.85 ± 0.05	-1.80 ± 0.06	-1.72 ± 0.05
r	0.9996	0.9985	0.9990	0.9978
sd	0.03	0.07	0.05	0.10

for the observed data,



The observed acid-catalysis may well be due to a protonation of the hydroxyester prior to its decomposition,



It is of interest to compare here the mechanisms of oxidation of the aldehydes by potassium permanganate and BBCP. In the oxidation by potassium permanganate (Jain and Banerji 1983), the reaction is first order with respect to the aldehydes and there is no acid-independent pathway. Permanganic acid has been postulated as the reactive oxidizing species. An intermolecular hydride-ion transfer from the aldehyde hydrate to permanganic acid has been proposed for that reaction.

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