

Kinetic study of oxidation of some thioacids by *bis*(2,2'-bipyridyl) copper(II) permanganate

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Abstract. Oxidation of thioglycollic, thiolactic and thiomalic acids, to the corresponding disulphide dimers, by *bis*(2,2'-bipyridyl) copper(II) permanganate (BBCP) is first order with respect to BBCP and exhibits Michaelis–Menten type kinetics with respect to the thioacid. The reaction is catalysed by hydrogen ions. The rate decreases with an increase in the amount of acetic acid in the solvent. There is no effect of added bipyridine and acrylonitrile. A mechanism involving formation of a sulphenium cation in the rate-determining step has been proposed.

Keywords. Thioacid; *bis*(2,2'-bipyridyl) copper(II) permanganate; Michaelis–Menten kinetics; sulphenium cation.

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 the 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 the dimerization of thiols to disulphides (Firouzbadi *et al* 1983). There seems to be no report on the kinetics of oxidations by BBCP. In this paper, the kinetics of oxidation of thioglycollic acid (TGA), thiolactic acid (TLA) and thiomalic acid (TMA) by BBCP in aqueous acetic acid are reported.

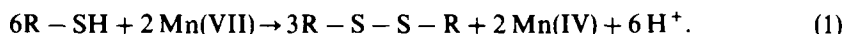
2. Experimental

2.1 Materials

The thioacids used were commercial products (Fluka) and were used as such. Dithiodiglycollic acid was supplied by Evans Chemicals (USA). Dithiodimalic and dithiodilactic acids were prepared by oxidation of the corresponding thiols by ferric alum (Leussing and Kolthoff 1953). The aqueous solutions of the thioacids were freshly prepared in water which had been purged with nitrogen. The solutions were standardised by titrating them against a standard solution of iodine (Krammer 1952; Leussing and Kolthoff 1953). BBCP was prepared by the reported method (Firouzbadi *et al* 1984). Acetic acid was refluxed with CrO₃ for 6 h and then fractionated. Perchloric acid (Merck) was used as a source of hydrogen ions.

2.2 Stoichiometry

Stoichiometric determinations, as well as the characterization of products were carried out polarographically (Kapoor *et al* 1969, 1972), using an automatic system (Heyrovsky LP55A). It was found that the cathode wave given by a known sample of the disulphide dimer coincided with the wave given by the final product of oxidation. 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 thioacid over BBCP. The solvent was 1:1 (*v/v*) acetic acid – water, unless specified otherwise. 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 programme 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 $\pm 4\%$.

3. Results

3.1 Rate laws

The 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 BBCP (table 1). The reaction exhibited Michaelis–Menten type kinetics with respect to the thioacid (figure 1). This indicates the following overall mechanism and leads to the rate law as below.



$$\text{Rate} = k_2 K [\text{thioacid}] [\text{BBCP}] / (1 + K [\text{thioacid}]) \quad (4)$$

The variation in substrate concentration was studied at different temperatures and the values of K and k_2 were calculated from the linear plots of $1/k_{obs}$ against $1/[\text{thioacid}]$. The thermodynamic and activation parameters were also calculated (tables 2 and 3). Addition of acrylonitrile and 2,2'-bipyridine did not affect the rate (table 1).

Table 1. Rate constants of the oxidation of thioacids by BBCP at 298 K.

[Thioacid] (mol dm ⁻³)	10 ³ [BBCP] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	<i>k</i> _{obs} /(s ⁻¹)		
			TGA	TMA	TLA
0.1	2.0	0.0	0.82	3.28	1.85
0.2	2.0	0.0	1.35	5.41	3.00
0.4	2.0	0.0	2.20	7.90	4.29
0.8	2.0	0.0	3.00	10.4	5.61
1.0	2.0	0.0	3.14	11.1	6.00
1.5	2.0	0.0	3.60	12.3	6.41
2.0	2.0	0.0	3.81	12.7	6.78
1.0	4.0	0.0	3.20	11.0	5.93
1.0	8.0	0.0	3.12	11.1	5.97
1.0	12.0	0.0	3.11	11.3	6.10
1.0	2.0 ^a	0.0	3.15	11.4	6.07
1.0	2.0 ^b	0.0	3.21	11.2	6.12
0.4	2.0	0.1	3.65	10.7	7.32
0.4	2.0	0.2	5.30	13.7	10.1
0.4	2.0	0.3	6.70	16.2	13.6
0.4	2.0	0.5	10.0	22.0	19.3
0.4	2.0	0.7	12.5	27.2	25.7
0.4	2.0	1.0	17.5	36.4	34.0
0.4	2.0	1.3	22.0	44.6	43.4

^a Contained 0.05 mol dm⁻³ acrylonitrile; ^b contained 0.02 mol dm⁻³ 2,2'-bipyridyl

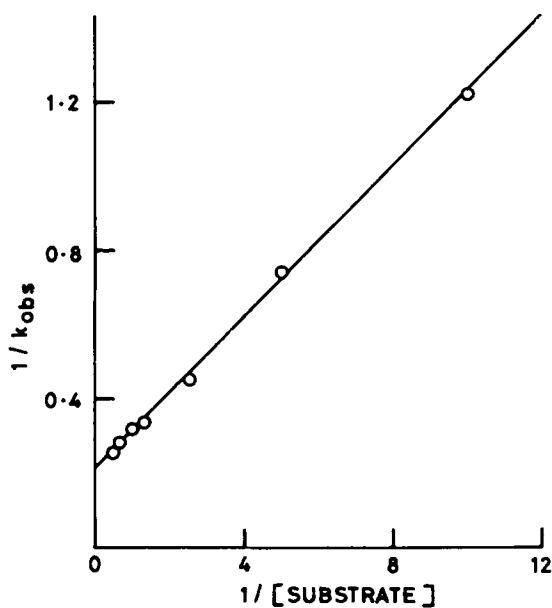


Figure 1. Dependence of the rate on the concentration of thioglycollic acid (reaction conditions are given in table 1).

Table 2. Formation constants and thermodynamic parameters of thioacid-BBCP complexes.

Acid	$K/(\text{dm}^3 \text{mol}^{-1})$				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
TGA	2.35 ± 0.2	2.10 ± 0.2	1.93 ± 0.1	1.72 ± 0.1	-7.8 ± 0.2	-20 ± 1	-1.8 ± 0.2
TMA	3.12 ± 0.3	2.80 ± 0.2	2.45 ± 0.3	2.03 ± 0.2	-10.7 ± 0.8	-28 ± 3	-2.5 ± 0.4
TLA	3.52 ± 0.3	3.07 ± 0.3	2.68 ± 0.2	2.25 ± 0.2	-11.2 ± 0.5	-29 ± 2	-2.8 ± 0.4

Table 3. Rates of decomposition and activation parameters of thioacid-BBCP complexes.

Acid	$k_2/(\text{s}^{-1})$				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
TGA	1.35 ± 0.04	2.82 ± 0.08	5.25 ± 0.11	10.5 ± 0.5	49.1 ± 0.7	-72 ± 3	70.5 ± 0.6
TMA	6.72 ± 0.22	12.6 ± 0.3	21.4 ± 0.9	30.7 ± 1.3	36.3 ± 1.6	-103 ± 5	66.9 ± 1.3
TLA	3.52 ± 0.14	6.30 ± 0.32	9.33 ± 0.5	16.2 ± 0.6	35.3 ± 1.3	-112 ± 4	68.6 ± 1.0

Table 4. Effect of solvent on the oxidation of thioglycollic acid by BBCP.

[TGA] = 0.4 mol dm⁻³, [BBCP] = 0.002 mol dm⁻³, T = 298 K.

% AcOH (v/v)	0.0	25.0	40.0	50.0	60.0	72.0
$k_{\text{obs}}/(\text{s}^{-1})$	52.5	12.9	4.70	2.20	0.97	0.32

3.2 Effect of acidity

Addition of perchloric acid increases the rate and the hydrogen ion dependence has the form

$$k_{\text{obs}} = a + b[\text{H}^+] \text{ (table 1).}$$

3.3 Solvent effect

The rate of oxidation of TGA was determined in solvents containing different proportions of acetic acid and water. The rate decreases with an increase in the proportion of acetic acid in the solvent (table 4).

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 3.92 ± 0.11 . This indicated that Mn(VII) is reduced to Mn(IV). To confirm that Mn(IV) is indeed formed as a result of oxidation of thioacids 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 $\pm 10\%$. It was also observed that BBCP has virtually no absorption at 418 nm. This agrees with the observations of earlier workers (Freeman and Kappos 1985; Lee and Perez-Benito 1988).

4. Discussion

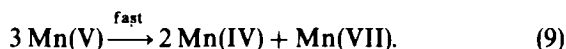
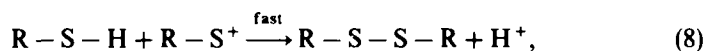
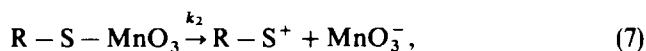
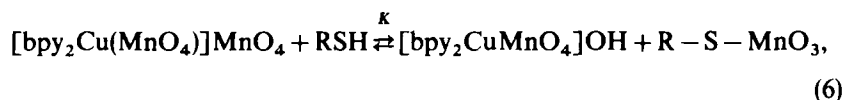
Not much is known about the structure of BBCP. In particular, the nature of bonding of the permanganate anions with the $[\text{bpy}_2\text{Cu(II)}]^{+2}$ cation is not certain. However, in the corresponding halide complexes, it has been shown that one halide ion is joined to the central metal atom by a covalent bond and another by an electrovalent bond (Barclay *et al* 1963). Therefore, BBCP can also be represented as $[\text{bpy}_2\text{Cu MnO}_4]\text{MnO}_4$.

The observed solvent effect (table 4) indicates that the transition state is more polar than the reactant state. A plot of $\log k_{\text{obs}}$ against the inverse of dielectric constant is nonlinear. The solvent effect was analysed using the Grunwald–Winstein (Cowen *et al* 1950; Falnberg and Winstein 1956) equation

$$\log k_{\text{obs}} = \log k_0 + mY. \quad (5)$$

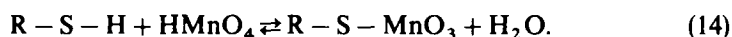
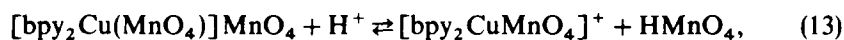
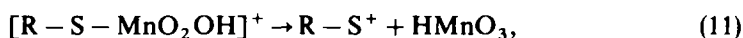
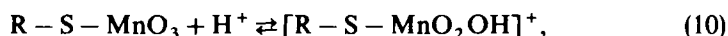
The plot of $\log k_{\text{obs}}$ versus Y is linear ($r = 0.9988$) with $\log k_0 = -1.35 \pm 0.10$ and $m = 0.87 \pm 0.06$. The value of m indicates an S_N1 -type transition state.

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 for the observed data.



The observed value of m supports the formation of two oppositely charged ions in the rate-determining step.

The observed acid-catalysis can be due to either a protonation of the thioester prior to its decomposition or a protolysis of BBCP prior to the formation of the thioester



A similar mechanism has been proposed for the oxidation of thioacids by permanganate ions (Asopa *et al* 1990).

Acknowledgement

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