

Kinetics and mechanism of the oxidation of formic acid by *bis*-(2,2'-bipyridyl) copper(II) permanganate

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Abstract. The oxidation of formic acid by *bis*-(2,2'-bipyridyl)copper(II) permanganate (BBCP) is first order with respect to BBCP. The order with respect to formic acid is less than one in the absence of perchloric acid whereas in the presence of perchloric acid, it is more than one but less than two. Thus in both the cases Michaelis–Menten type kinetics were observed with respect to formic acid. The overall formation constants for the formic acid–BBCP complexes and their rates of decomposition have been evaluated. Thermodynamic parameters for complex formation and the activation parameters for their decomposition have also been calculated. The hydrogen-ion dependence has the form $k_{\text{obs}} = a + b[\text{H}^+] + c[\text{H}^+]^2$. The oxidation of deuterioformic acid showed the presence of a primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 4$). An increase in the amount of acetic acid in the solvent mixture, acetic acid and water, increases the rate. The addition of 2,2'-bipyridine and acrylonitrile has no effect on the rate. Suitable mechanisms have been proposed.

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

1. Introduction

Oxidation of organic compounds by aqueous potassium permanganate, a widely used oxidising 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 (Firouzabadi *et al* 1984). One such reagent is *bis*-(2,2'-bipyridyl)copper(II) permanganate (BBCP). We have been interested in the kinetic and mechanistic studies of its oxidation reactions and have reported the oxidation of thioacids and aliphatic aldehydes by BBCP (Kothari 1991; Kothari *et al* 1992). In continuation of our previous work, we now report the kinetics and mechanism of oxidation of formic acid (FA) by BBCP in aqueous acetic acid solution.

2. Experimental

2.1 Materials

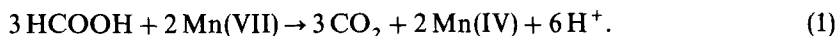
Formic acid (AR, BDH) and deuterioformic acid (Sigma, USA) were commercial products and were used as such. Formic acid solutions were standardised by alkalimetry. BBCP

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was prepared by reported method (Firouzabadi *et al* 1984). Acetic acid was refluxed with CrO_3 and acetic anhydride for 6 h and then distilled (Orton and Bradfield 1924, 1927) Perchloric acid (Merck) was used as a source of hydrogen ions.

2.2 Stoichiometry

Excess of BBCP ($\times 5$ or greater) was allowed to react with formic acid at various acidities, in 1:1 (v/v) acetic acid–water mixture, and the amount of residual BBCP after the completion of reaction was measured spectrophotometrically. Iodometric determination of completely reduced reaction mixtures showed that the oxidation state of the reduced manganese species is 4.12 ± 0.23 . The overall reaction may be written as



2.3 Kinetic measurements

Reactions were studied under pseudo-first-order conditions by maintaining a large excess of formic acid ($\times 15$ or more) over BBCP. The solvent was 1:1 (v/v) acetic acid–water mixture, unless mentioned otherwise. The reactions were carried out at a constant temperature (± 0.1 K) and were followed up to 80% reaction by monitoring the decrease in [BBCP] at 529 nm. The pseudo-first-order rate constants, k_{obs} , were computed from the linear ($r > 0.990$) least-squares plot of $\log[\text{BBCP}]$ vs time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. Preliminary experiments showed that the reaction is not sensitive to changes in ionic strength. Hence no attempt was made to keep the ionic strength constant.

3. Results and discussion

3.1 Rate laws

Oxidation of formic acid by BBCP is found to be first order with respect to BBCP both regarding time (as evidenced by good fits of $\log[\text{BBCP}]$ against time plots) and concentration (as shown by the time order rate coefficient being independent of initial [BBCP]) (table 1). The order of the reaction with respect to formic acid, in the absence of acid, is less than one (table 2). A plot between $1/[\text{HCOOH}]$ against $1/k_{\text{obs}}$ is linear ($r = 0.9995$) with an intercept on the rate ordinate. Thus the reaction exhibits

Table 1. Dependence of the reaction rate on oxidant concentration.

[FA] = 0.26 mol dm^{-3} ; $[\text{H}^+] = 1.22 \text{ mol dm}^{-3}$; $T = 293 \text{ K}$

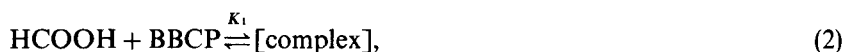
$10^4[\text{BBCP}](\text{mol dm}^{-3})$	0.50	1.00	2.00	3.00	5.00
$10^2 k_{\text{obs}}(\text{s}^{-1})$	4.38	4.27	4.22	4.50	4.41

Table 2. Dependence of the reaction rate on substrate in the absence of perchloric acid.

[BBCP] = $2.5 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 293 \text{ K}$.

[FA](mol dm^{-3})	0.26	0.51	1.29	1.55	2.57	3.86	5.14
$10^2 k_{\text{obs}}(\text{s}^{-1})$	1.16	1.45	1.73	1.76	1.84	1.88	1.91

Michaelis–Menten type kinetics with respect to formic acid. This indicates the following overall mechanism, [(2) and (3)] and rate law, [(4)].



$$-d[\text{BBCP}]/dt = \frac{k_1 K_1 [\text{HCOOH}][\text{BBCP}]}{1 + K_1 [\text{HCOOH}]}. \quad (4)$$

In the presence of acid, the order with respect to substrate is more than one but less than two (table 3). A plot of $1/k_{\text{obs}}$ against $1/[\text{HCOOH}]^2$ is linear ($r = 0.9910$) with an intercept on rate ordinate. Thus under these conditions also, the reaction exhibits a Michaelis–Menten type kinetics but the oxidant to reductant ratio, in the intermediate complex, is 1:2. For the acid-catalysed reaction, the following overall mechanism may, therefore, be proposed.



$$-d[\text{BBCP}]/dt = \frac{k_2 K_2 [\text{BBCP}][\text{HCOOH}]^2}{(1 + K_2 [\text{HCOOH}]^2)}. \quad (7)$$

The variation in substrate concentration was studied at different temperatures in the absence and the presence of acid. The values of overall formation constants and rate of decomposition of formic acid–BBCP complexes were determined from the double reciprocal plots under both the conditions. The thermodynamic and activation parameters

Table 3. Dependence of reaction rate on substrate in the presence of perchloric acid.

$$[\text{BBCP}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}, [\text{H}^+] = 1.22 \text{ mol dm}^{-3}, T = 293 \text{ K}$$

[FA](mol dm ⁻³)	0.26	0.51	1.02	1.53	2.04	3.06	4.08
$10^2 k_{\text{obs}}$ (s ⁻¹)	4.56	11.3	27.7	34.1	68.0	84.1	166.0

Table 4. Formation constants and thermodynamic parameters of FA–BBCP complex in the absence and in the presence of perchloric acid.

[H ⁺] (mol dm ⁻³)	K (dm ³ mol ⁻¹) at			ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	283 K	293 K	303 K			
0.00	7.48 ± 0.23	5.51 ± 0.18	3.67 ± 0.13	-27.2 ± 1.0	-79 ± 3.5	-3.7 ± 0.8
1.22	1.61 ± 0.09	1.24 ± 0.05	0.95 ± 0.04	-18.8 ± 0.3	-63 ± 1.0	-0.2 ± 0.02

Table 5. Rate of decomposition and activation parameters of FA–BBCP complex in the absence and in the presence of perchloric acid.

[H ⁺] (mol dm ⁻³)	10 ² k ₂ (s ⁻¹)			ΔH* (kJ mol ⁻¹)	ΔS* (J mol ⁻¹ K ⁻¹)	ΔG* (kJ mol ⁻¹)
	283 K	293 K	303 K			
0.00	0.95 ± 0.05	1.97 ± 0.11	4.00 ± 0.19	48.7 ± 0.2	- 112 ± 1	81.9 ± 0.2
1.22	0.41 ± 0.05	0.62 ± 0.06	0.93 ± 0.06	26.7 ± 0.2	- 158 ± 1	73.7 ± 0.2

Table 6. Dependence of reaction rate on acidity.

[BBCP] = 2.5 × 10⁻⁴ mol dm⁻³; [FA] = 0.26 mol dm⁻³; T = 293 K

[H ⁺] (mol dm ⁻³)	0.12	0.37	0.61	0.98	1.22	1.46	1.83	2.20
10 ² k _{obs} (s ⁻¹)	1.43	1.81	2.88	3.51	4.56	12.9	30.3	55.5

were calculated from the values of the equilibrium constants and the rate constants of the decomposition at different temperatures respectively (tables 4 and 5).

3.2 Effect of hydrogen ions

The effect of variation of concentration of hydrogen ion showed that the reaction rate increases with an increase in the concentration of hydrogen ion (table 6). A plot of rate versus [H⁺] is a curve concave to the rate axis and makes an intercept on the rate axis. This indicates that there is more than one protonated species and all the species are reactive and that the protonation constants are small (Gupta and Gupta 1984). The dependence on the hydrogen ion has the form $k_{\text{obs}} = a + b[\text{H}^+] + c[\text{H}^+]^2$. Similar dependence in acidity is observed in the oxidation of hydrogen peroxide by iodate ion (Liebhafsky 1931; Peard and Wells 1951). It implies that there are two catalytic protons which are added in pre-equilibria.

3.3 Solvent effect

The rates of oxidation of formic acid were determined in solvents containing different proportions of acetic acid in acetic acid–water mixture. It was found that the rate increased slightly with an increase in the amount of acetic acid in the solvent mixture (table 7). This may be attributed to the change in the acidity of the medium with a change in the amount of acetic acid. Wiberg and Evans (1958) have determined the Hammett's acidity function, H_0 , for low concentrations of perchloric acid in a series of acetic acid–water mixtures. They observed that the acidity increases as the concentration of water decreases. The reaction under investigation is an acid-catalysed one and with an increase in the acidity of the solution, the rate is expected to increase.

3.4 Kinetic isotope effect

To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, the oxidation of DCOOH was studied both in the presence and absence of

Table 7. Effect of solvent composition on the oxidation of formic acid by BBCP. $[\text{BBCP}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{FA}] = 0.26 \text{ mol dm}^{-3}$; $[\text{H}^+] = 1.22 \text{ mol dm}^{-3}$; $T = 293 \text{ K}$

% AcOH (v/v)	20	30	40	50	60	70
$10^2 k_{\text{obs}}/\text{s}^{-1}$	2.49	3.26	3.95	4.56	9.23	13.95

Table 8. Kinetic isotope effect in the oxidation of formic acid by BBCP.

$[\text{BBCP}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{FA}] = 0.26 \text{ mol dm}^{-3}$; $T = 293 \text{ K}$

$[\text{H}^+]$ (mol dm^{-3})	$10^2 k_{\text{obs}} (\text{s}^{-1})$		$k_{\text{H}}/k_{\text{D}}$
	HCOOH	DCOOH	
1.22	4.56	1.18	3.86
0.00	1.16	0.29	4.00

Table 9. Effect of bipyridine on the oxidation of formic acid by BBCP.

$[\text{BBCP}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{FA}] = 0.26 \text{ mol dm}^{-3}$; $[\text{H}^+] = 1.22 \text{ mol dm}^{-3}$; $T = 293 \text{ K}$

$10^2 [\text{bpy}] (\text{mol dm}^{-3})$	0.00	0.005	0.01	0.02	0.03
$10^2 k_{\text{obs}} (\text{s}^{-1})$	4.50	4.45	4.58	4.62	4.40

perchloric acid. The results showed the presence of a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 4$) (table 8).

3.5 Effect of bipyridine

Addition of bipyridine does not affect the rate (table 9). This rules out the possibility of a pre-equilibrium involving bipyridine as one of the products.

3.6 Induced polymerisation of acrylonitrile

The oxidation of formic acid, under a nitrogen atmosphere, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile has no effect on the oxidation rate. Thus a one-electron oxidation, giving rise to free radicals, is unlikely.

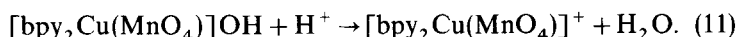
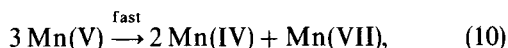
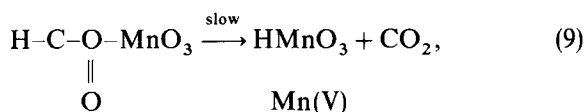
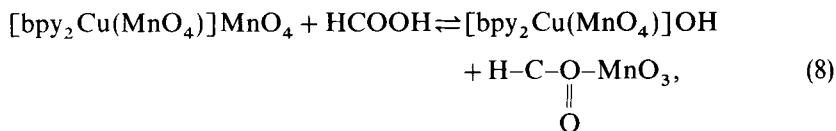
3.7 Mechanism

Not much is known about the structure of BBCP. In particular, the nature of bonding of the permanganate anions with the $[\text{bpy}_2\text{Cu(II)}]$ 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). Based on this analogy, BBCP may also be represented as $[\text{bpy}_2\text{Cu(MnO}_4)]\text{MnO}_4$.

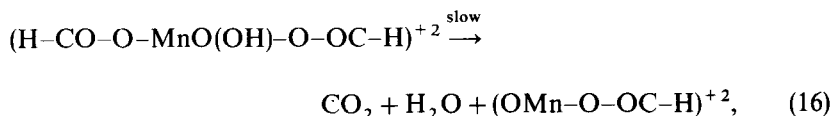
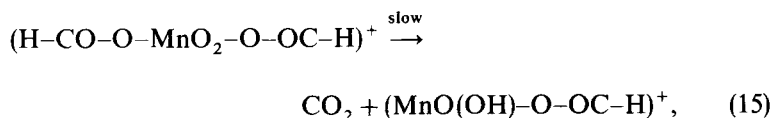
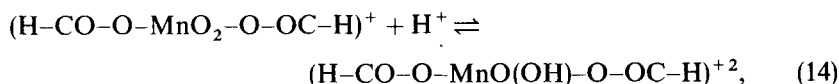
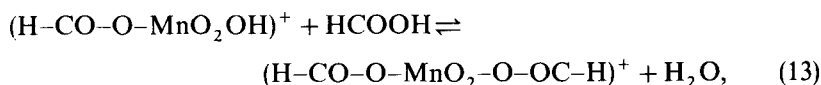
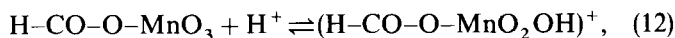
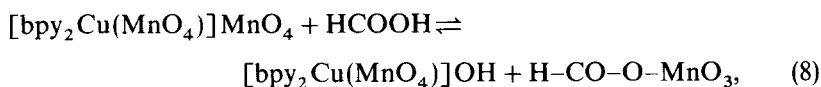
In view of the discussions in the foregoing paragraphs, it is suggested that, in the acid-independent path, the rate-determining step involves a complex of FA and BBCP

whereas in the acid-dependent path, protonated and doubly protonated forms of a complex of two molecules of FA and one molecule of BBCP are involved. The presence of a substantial primary kinetic isotope effect confirms that the C–H bond is cleaved in the rate-determining step. Thus, based on all the experimental facts presented above, the following mechanisms are proposed for the acid-independent and the acid-dependent paths.

Acid-independent path:



Acid-dependent path



followed by reactions (10) and (11).

Acknowledgement

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