Mechanism of Reduction of Sulphur Dioxide by Formic Acid *

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Dedicated to Professor *Holger Erdtman* on his 60th birthday

The oxidation of formic acid with sulphur dioxide was found to follow a second order kinetic. The rate has a maximum at pH 2—3. A mechanism for the reaction has been suggested.

A detrimental by-reaction during the sulphite pulp cooking is the reduction of sulphur dioxide to thiosulphate by monosaccharides and other components of the waste liquor. A simple substance which is present in the liquor and can perform this reduction is formic acid [2] which reacts according to the equation:

$$2\,HCOOH + 2\,SO_2 = 2CO_2 + S_2O_3^{2-} + 2\,H^+ + H_2O.$$
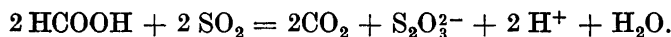
Kinzelberger [3] has reported in a patent dealing with the manufacture of sodium dithionite, that this salt is formed when sodium pyrosulphite is treated with a solution of formic acid and sodium formate in dilute alcohol. When repeating his experiments we obtained no dithionite. When a shorter reaction time was used a small amount of dithionite was found. It is therefore probable that dithionite is the primary reduction product of the formic acid-bisulphite reaction and that it, when formed, rapidly reacts with water yielding bisulphite and thiosulphate. The existence of this reaction path is supported also by the wellknown fact that dithionite is formed from bisulphite or sulphite by many other types of reduction (*e.g.* with sodium amalgam or zinc).

We have examined the kinetics of the bisulphite-formic acid reaction. It was carried out at 135°C in an acetate buffer of pH 5. The reaction was followed by determining the thiosulphate and bisulphite concentrations. The results obtained showed that the reaction was of the second order, the rate being proportional to the concentrations of both bisulphite and formate ions (see experimental part).

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* Part 3 in the series Reactions of thiosulphate during sulphite cooking. Part 2, see Ref. [1].

Table 1. The concentrations of thiosulphate formed when sulphur dioxide-sodium sulphite solutions of varying pH were heated with formic acid.

pH at 20°C	Thiosulphate, mM				
	100°C			70°C	
	1 h	2 h	5 h	2 h	5 h
1.3	0.6	0.8	1.3	0.1	0.2
1.7	3.3	3.8	3.9	0.2	0.3
2.1	—	—	—	0.6	1.0
3.0	3.0	3.7	3.9	—	1.3
4.3	—	—	—	0.1	0.1
6.8	0.0	0.0	0.0	—	—
8.2	0.0	0.0	0.0	—	—

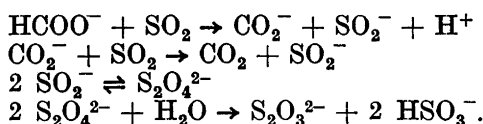Stockman [2] found that the oxidation proceeds more rapidly when the pH is increased and this has recently been confirmed by Slávik [4]. As the pH in their investigations was not increased above about 2 we have determined how the oxidation rate varies over a greater acidity range.

Formic acid was heated in Na_2SO_3—SO_2-solutions, the pH of which ranged from 1.5 to 8 but had the same "total" concentration of sulphur dioxide (that is the concentration sum: $[SO_2] + [HSO_3^-] + [SO_3^{2-}]$). The concentration of formic acid was low (10 mM) compared to that of the other reactant (the "total" concentration of sulphur dioxide was 390 mM). In this way the thiosulphate formed (at most 5 mM) was stabilised by the sulphur dioxide and its degradation could be neglected even in the most acidic of the solutions used.

The reaction was found to proceed fastest in those solutions which at room temperature had pH 2—3 (see Table 1). We have tried to compare the pH dependence with simple functions of the concentrations. Such comparisons can not be carried out exactly because the activity coefficients are not known. It is evident however, from Fig. 1, that the products $[HCOOH][HSO_3^-]$ and $[HCOO^-][SO_2]$ (calculated at 70°C) have maxima at pH 3.0. When the temperature of such a SO_2—HSO_3^- solution is decreased to 20° its pH is changed to about 2.5.

The rate maximum thus falls in the same pH range as the concentration products above have their maxima. The reaction may therefore involve an oxidation of $HCOO^-$ by SO_2 (or H_2SO_3, which is, however, present in only small amounts) [7] or a reaction between $HCOOH$ and HSO_3^-. Of these two alternatives the first is more probable as sulphur dioxide may accept an electron more easily than the negatively charged bisulphite ion, and similarly the formate ion may donate an electron more readily than formic acid.

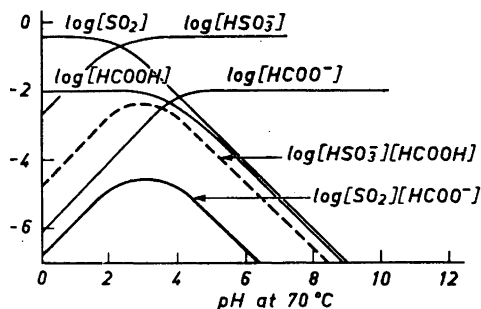From these findings the following reaction path for the reaction is suggested.

$$HCOO^- + SO_2 \rightarrow CO_2^- + SO_2^- + H^+$$
$$CO_2^- + SO_2 \rightarrow CO_2 + SO_2^-$$
$$2\ SO_2^- \rightleftharpoons S_2O_4^{2-}$$
$$2\ S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2\ HSO_3^-.$$

Fig. 1. The concentrations of SO_2, HSO_3^-, $HCOOH$, $HCOO^-$ and the products $[SO_2]\cdot$ $[HCOO^-]$ and $[HSO_3^-]\cdot[HCOOH]$ *versus* the pH. The total concentration of sulphur dioxide is 0.39 M and that of formic acid 0.01 M.
All values were calculated for 70°C using for pK_a of SO_2 at 70°C the value 2.3 [5] and for $HCOOH$, 3.8 [6]. The activity coefficients were neglected.
For a $SO_2 - HSO_3^-$ solution pH is decreased about 0.5 when the temperature is decreased from 70°C to 20°C as the pK_a for SO_2 is 1.8 at 20°C.

The first step is assumed to be slow compared to the others and should therefore be the rate controlling one.

The intermediate from the formate ion is here written as the radical ion CO_2^-. Another alternative would be the radical $HCOO$, which is assumed to be formed in the Kolbe electrolytic oxidation of formate [8]. The radical ion SO_2^- suggested to be the primary reduction product of sulphur dioxide is probably in equilibrium with the dithionite ion [9]. Its electronic structure and stability have been discussed in Ref.[10].

EXPERIMENTAL

Bisulphite reduction according to Kinzelberger [3]. Sodium formate (6.8 g) and formic acid (5.2 g) were dissolved in water-ethanol (16:84 w/w, 195 ml). Sodium pyrosulphite (16 g) was added to the solution, which was then heated at 70°C for 3 1/2 h with stirring. The undissolved material was collected and dried in vacuum. In aqueous solution it gave a white precipitate with silver nitrate solution (dithionite gives a black precipitate) and did not decolourise an alkaline resazurin solution (as do dithionite solutions) [11]. Dithionite was therefore not present. An iodometric titration in the presence of formaldehyde showed that the material contained 13 % of sodium thiosulphate. The IR spectrum of the material (peaks at 3.6, 4.3, 6.3, 7.3, 8.5, 9.4, 10.2, 12.9 μ, KBr plate) is composed of the superimposed spectra of sodium bisulphite and sodium formate.

If the reaction mixture was heated for only 1 1/2—2 h the above tests for dithionite were positive. The amount of sodium dithionite formed must however be low, at most a few percent.

Kinetic examination of the formate-bisulphite reaction. Aliquots (50 ml) of a solution containing sodium bisulphite (x mM), sodium formate (y mM) and sodium acetate-acetic acid (0.666 M and 0.277 M, respectively, pH 5) were heated for varying times in steel autoclaves at 135 $\pm$ 1°C.

The bisulphite and formate concentrations were in the three kinetic series I: $x = 85.3$ and $y = 100$ mM. II: $x = 258$ and $y = 100$ mM. III: $x = 80.0$ and $y = 200$ mM.

The concentrations of thiosulphate and of bisulphite in the solutions obtained after heating were determined by iodine titrations with and without addition of formalde-

Table 2. Kinetic experiments, series I.

Time min	$[S_2O_3^{2-}]$ mM	$[HSO_3^-]$ mM	$[HCOO^-]$ mM	$k_2 \times 10^4$ mmole^{-1} min^{-1}
0	—	85.3	100.0	
15	3.5	71.3	93.0	
30	10.3	52.9	79.4	1.8
60	17.9	35.0	64.2	1.5
90	22.9	24.7	54.2	1.9
120	25.7	22.0	48.6	1.6
150	28.1	17.6	43.8	1.8
180	29.3	14.2	41.4	1.1

$\bar{k}_2 = (1.6 \pm 0.25) \times 10^{-4}$ mmole^{-1} min^{-1}

Table 3. Kinetic experiments, series II.

Time min	$[S_2O_3^{2-}]$ mM	$[HSO_3^-]$ mM	$(HCOO^-)$ mM	$k_2 \times 10^4$ mmole^{-1} min^{-1}
0	—	258	100.0	
15	6.7	232	86.6	
30	22.1	201	55.8	1.3
45	31.5	185	37.0	1.4
60	38.3	172	23.4	1.7
75	41.9	164	16.2	1.5
90	42.2	160	11.6	1.4

$\bar{k}_2 = (1.5 \pm 0.2) \times 10^{-4}$ mmole^{-1} min^{-1}

Table 4. Kinetic experiments, series III.

Time min	$[S_2O_3^{2-}]$ mM	$[HSO_3^-]$ mM	$[HCOO^-]$ mM	$k_2 \times 10^4$ mmole-^{1} min-^{1}
0	—	80	200	
15	5.2	64	190	
30	12.5	49	175	1.5
45	18.8	33	162	1.2
60	23.8	24	152	1.6
75	27.0	18	146	1.3
90	29.3	13	141	1.5
105	30.6	8	138	1.2

$\bar{k}_2 = (1.4 + 0.2) \times 10^{-4}$ mmole^{-1} min^{-1}

hyde. The solutions obtained gave negative test for dithionite. The results are collected in Tables 2—4. The formate concentrations were calculated by subtraction of twice the thiosulphate concentration from the formate concentration in the starting solutions.

During the first 15 min bisulphite was consumed rather quickly without any corresponding formation of thiosulphate. This was probably due to a rapid oxidation of bisulphite by the oxygen in the autoclave. The rate constant, k_2, was therefore not calculated for the first 15 min of the reaction time. For all the other determinations within a series the sum: $2[HSO_3^-] + [S_2O_3^{2-}]$ was constant ($\pm$ 3 mM) which showed that bisulphite was not consumed in other ways than by thiosulphate formation. The reaction was followed until that reactant, which was present in the smaller amount, had been consumed to about 85 %.

The k_2 values for the three series were, within experimental error, identical ($10^4 \times k_2$ was for I 1.6 $\pm$ 0.25, for II 1.5 $\pm$ 0.2 and for III 1.4 $\pm$ 0.2). The reaction was thus of the second order.

The pH dependence of the reaction. Two aqueous solutions, one of which contained formic acid (5 mM) and sulphur dioxide (0.39 M) and the other the same amount of formic acid but with sodium sulphite (0.39 M) in stead of sulphur dioxide, were mixed in different ratios. Aliquots (50 ml) of the solutions obtained were heated at 100°C and at 70°C for varying times. The amount of thiosulphate formed was determined by iodine titration in the presence of formaldehyde. The results are collected in Table 1.

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