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Figure 1

Figure 1: Figure 1

Abstract

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KINETICS AND MECHANISM OF THE OXIDATION OF ALCOHOLS AND ALDEHYDES BY ACTIVE CHLORINE

In studies on the kinetics of oxidation by active chlorine, the cases examined so far have been those in which the direct oxidation reaction of an alcohol or aldehyde group could be complicated by side reactions of neighboring functions, including enolization. This applies to acetaldehyde (1), glycolaldehyde and glucose (2), lactic and other hydroxy acids (3).

Fig. 1. **A**–Oxidation of *m*-sulfobenzyl alcohol.
1–$A = 0.2\ M$, $C_0 = 0.00697\ M$, pH 7.02; 2–$A = 0.1\ M$, $C_0 = 0.00697\ M$, pH 7.05.
B–Oxidation of *m*-sulfobenzaldehyde.
1–$A = 0.1\ M$, $C_0 = 0.00516\ M$, pH 10.75;
2–$A = 0.05\ M$, $C_0 = 0.00505\ M$, pH 10.80.

In the present investigation, *m*-sulfobenzyl alcohol and *m*-sulfobenzaldehyde (in the form of sodium salts) were taken as compounds that make it possible to observe, in pure form, the reaction of oxidation of an alcohol or aldehyde group by active chlorine in aqueous solutions.

Oxidation of *m*-sulfobenzyl alcohol

It was first established that, with a large excess of the sulfo alcohol, the slight consumption of active chlorine in the secondary reaction of oxidation of the aldehyde formed may be disregarded.

At a constant pH value and with a large excess of *m*-sulfobenzyl alcohol, the decrease in the titer of active chlorine (C) in the presence of a buffer salt follows a monomolecular kinetic equation, as demonstrated by the logarithmic anamorphosis (Fig. 1A). On the other hand, the rate

Fig. 2. Dependence of the oxidation rate of m-sulfobenzyl alcohol (1) and m-sulfobenzaldehyde (2) on pH

Figure 2: Fig. 2. Dependence of the oxidation rate of m-sulfobenzyl alcohol (1) and m-sulfobenzaldehyde (2) on pH

the reaction proves to be almost exactly proportional to the concentration of the sulfoalcohol and, in general, at constant pH is expressed by the equation:

$$-\frac{dC}{dt} = k_2 AC \tag{1}$$

where A is the alcohol concentration, and C is the concentration of active chlorine.

The dependence of the reaction rate on pH can be followed from Fig. 2, where the values $\tau/2$, i.e., the times for the active-chlorine concentration to fall by half, are plotted against the pH values. $\tau/2$ was calculated from the values of k_2 by the formula: $\tau/2 = 0.693/k_2$.

The maxima and minima on this curve are connected primarily with the composition of active-chlorine solutions. The rate maximum at pH 0–2 upon addition of hydrochloric acid corresponds to the state of active chlorine in the form of Cl_2. Using the hydrolysis constant of active chlorine, it can be established that even in 0.1 M hydrochloric acid very little free HOCl remains, and a further increase in the HCl concentration changes the Cl_2 concentration hardly at all. As a result, the value of $\tau/2$ remains constant at pH < 1. Thus, there is no doubt that in the strongly acidic region the active oxidizing agent for m-sulfobenzyl alcohol is molecular chlorine.

Fig. 2. Dependence of the oxidation rate of m-sulfobenzyl alcohol (1) and m-sulfobenzaldehyde (2) on pH.

In the region pH > 2.5, the reaction rate rapidly decreases with increasing pH and passes through a minimum at pH about 4. The minimum point corresponds approximately to the state of active chlorine in the form of free HOCl. The relatively low activity of this agent is also known for other reactions of active chlorine ($^{2-4}$).

With a further increase in pH, the oxidation rate of m-sulfobenzyl alcohol increases, reaches a new maximum at pH about 7.5, and then again falls, becoming very small at pH > 10. Meanwhile, in active-chlorine solutions the HOCl concentration decreases continuously with increasing pH above 5 owing to the conversion of HOCl into OCl^- (^{5}), in accordance with the formula

$$[\mathrm{HOCl}] = \frac{[\mathrm{H}^+]C}{[\mathrm{H}^+] + K_{a.c}},$$

where $K_{a.c}$ is the electrolytic dissociation constant of HOCl, equal to $4.1 \cdot 10^{-8}$ (^{2}).

The hypochlorite ion is evidently incapable of oxidizing the sulfoalcohol, since oxidation does not occur in a strongly alkaline medium. Consequently, at intermediate pH values the direct or intermediate oxidizing agent is hypochlorous acid. Together with this conclusion it must be accepted that hydroxyl ion and the anions of buffer salts exert a catalytic effect on the reaction of HOCl with the sulfoalcohol.

If the rate constants are referred to the concentration of free hypochlorous acid and related to the activity of the OH-ion, a_{OH^-}, and to the concentration of the buffer-salt anion [An], then in the pH interval from 4 to 10 the reaction rate can be expressed by the equation:

$$-\frac{dC}{dt} = k_4^0 A[\mathrm{HOCl}] + k_4^{\mathrm{An}} A[\mathrm{HOCl}] \cdot [\mathrm{An}] + k_4^{\mathrm{OH}} A[\mathrm{HOCl}]\, a_{\mathrm{OH}^-}^{0.75}, \qquad (2)$$

where $k_4^0 = 2.2 \cdot 10^{-3}$; $k_4^{\mathrm{An}} = 0.0234$ for acetate ion, 0.245 for hydrophosphate-ion, about 0 for the carbonate ion; $k_4^{\mathrm{OH}} = 1.3 \cdot 10^3$. All are in moles per liter per minute.

The data of our experiments are given in an excerpt in Table 1, where the experimental values of k_2 are shown in comparison with k_2 calculated by means of the constants k_4 of equation (2). It can be seen that the experimental and calculated constants agree satisfactorily over a considerable pH interval.

The most probable mechanism of the reaction, in our view, is the mechanism proposed earlier for oxidation reactions of oxo compounds (^{3}). We suppose that alcohol oxidation proceeds through the stage of formation of a hypochlorous acid ester:

$$\mathrm{Ar{-}CH_2OH + HOCl \rightleftarrows Ar{-}CH_2OCl + H_2O} \qquad \text{(I)}$$

$$\mathrm{Ar{-}CH_2OCl + OH^- \rightarrow Ar{\cdot}CHO + H_2O + Cl^-} \qquad \text{(IIa)}$$

$$\mathrm{Ar{-}CH_2OCl + An^- \rightarrow Ar\ CHO + HAn + Cl^-} \qquad \text{(IIb)}$$

The rates of both reactions are comparable. At low pH, ester formation proceeds rapidly and the reaction rate is limited by the rate of decomposition, which increases with increasing base concentration. At high pH, the oxidation rate is determined by the stage of alkyl hypochlorite formation. Superposition of the rates of stages I and II causes the appearance of a rate maximum at pH about 7.5.

Table 1

pH	10^3C, mol/l	A, mol/l	10^2[An], mol/l	10^3k_2, exp.	10^8k_3	10^3k_2, calc.
***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**	***m*-Sulfobenzyl alcohol, 30°**
4.05	4.17	0.2	Ac 5	3.5	3.5	3.4
4.70	4.14	0.2	Ac 15	6.0	6.0	5.9
5.52	4.10	0.2	Ac 22.5	8.0	8.0	8.3
6.55	3.84	0.1	Ph 3	13.0	14.9	13.0
7.02	6.97	0.2	Ph 6	18.3	26.2	20.3
7.05	6.97	0.1	Ph 6	20.0	30.2	20.4
7.51	3.09	0.1	Ph 8	23.0	53.6	21.6
7.51	1.50	0.1	Ph 8	23.0	53.6	21.6
8.91	4.64	0.1	C 1	9.5	$3.3 \cdot 10^2$	9.4
9.85	4.25	0.088	C 10	5.9	$17 \cdot 10^2$	5.6
12.85	4.11	0.2	–	1.1	$3.2 \cdot 10^5$	1.0
***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**	***m*-Sulfobenzaldehyde, 30°**
4.04	4.87	0.1	Ac 5	9.1	9.1	9.7
4.88	5.03	0.1	Ac 16	17	17	15.9
5.2	4.81	0.1	Ac 20	16	16	18
6.55	6.31	0.1	Ph 4	24.6	28.4	25
7.0	5.30	0.1	Ph 6	33	46.5	33.5
7.45	5.20	0.1	Ph 4	30	64.8	30
8.9	5.50	0.1	C 1	37	$1.2 \cdot 10^3$	35
9.9	4.80	0.05	C 5	37	$12 \cdot 10^3$	35
10.75	5.16	0.1	C 9	36	$83 \cdot 10^3$	35
10.8	5.05	0.05	C 9	36	$94 \cdot 10^3$	36
12.85	5.60	0.05	–	34	$1 \cdot 10^7$	34

Note. [An] is the concentration of the buffer salt; Ac is the acetate ion, Ph the hydrogen phosphate ion, C carbonate; k_2 is the constant of the equation $-dC/dt = k_2AC$; k_3 is the same constant recalculated to the concentration of HOCl.

This hypothesis is qualitative in character, since mathematical treatment of the results is difficult. However, in support of it one may cite the analogy with the oxidation of alcohols by other oxidizing agents, for example chromic acid or persulfates, where intermediate esters of the corresponding acids are also formed ([6],[7]).

Oxidation of m-sulfobenzaldehyde. The oxidation rate of m-sulfobenzaldehyde at constant pH and an excess of aldehyde is expressed by a monomolecular equation (see Fig. 1B).

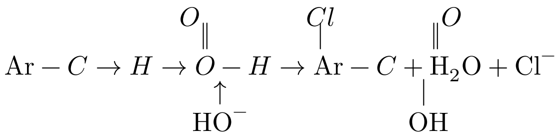
The dependence of the oxidation rate on pH in the presence of a buffer mixture is shown in Fig. 2 (curve 2). It can be seen that in the acidic region at pH from 0 to 5 the curve repeats the course of the curve for m-sulfobenzyl alcohol. In the strongly acidic region oxidation proceeds through molecular chlorine, while free hypochlorous acid is a weak oxidizing agent. After pH about 4 the reaction rate first increases, but, in contrast to the oxidation of the alcohol, does not pass through a maximum, but reaches a constant value, which does not change in the pH interval from 8 to 13. As in the case of m-sulfobenzyl alcohol, anions of the salts of the buffer mixture catalyze the reaction.

The general kinetic equation of the reaction may be given in the form:

$$-\frac{dC}{dt} = k_4^0 A[\mathrm{HOCl}] + k_4^{\mathrm{An}} A[\mathrm{HOCl}][\mathrm{An}] + k_4^{\mathrm{OH}} A[\mathrm{HOCl}] a_{\mathrm{OH}^-}. \tag{3}$$

Here $k_4^0 = 7 \cdot 10^{-3}$; $k_4^{\mathrm{An}} = 0.053$ for the acetate ion, 0.25 for the phthalate ion, 0.43 for the hydrophosphate ion; $k_4^{\mathrm{OH}} = 7.6 \cdot 10^4$. The units are moles per liter per minute (see Table 1).

Equation (3) and the curve of the dependence of the rate on pH are explained by the assumption that the reaction proceeds according to the scheme:



$$\mathrm{Ar} - C \rightarrow H \rightarrow \underset{\underset{\mathrm{HO}^-}{\uparrow}}{\overset{O}{\overset{\|}{O}}} - H \rightarrow \mathrm{Ar} - \overset{Cl}{\overset{|}{C}} + \underset{\underset{\mathrm{OH}}{|}}{\overset{O}{\overset{\|}{\mathrm{H_2O}}}} + \mathrm{Cl}^-$$

The OH ion may be replaced by a water molecule or by the anion of weak acids. The reaction through the hydroxyl ion is analogous to the Cannizzaro reaction, with the sole difference that the hydrogen acceptor is a molecule of hypochlorous acid.

In the oxidation by active chlorine of the para- and ortho-sulfobenzaldehydes, the same kinetic relationships are retained as for the meta isomer. Under identical experimental conditions, the para isomer is oxidized 1.2 times faster, and the ortho isomer 5-7 times more slowly, than meta-sulfobenzaldehyde.

Experimental Data

m-Sulfobenzyl alcohol was obtained by reduction of sodium m-benzaldehydesulfonate with hydrogen over a platinum catalyst ([8]). m-Benzaldehydesulfonate was obtained by sulfonation of benzaldehyde with oleum ([9]). The sodium salts of the sulfonic acids obtained were purified by repeated recrystallizations from water and alcohol.

Mixtures with active chlorine were prepared in a blackened flask, into which solutions of the components, heated in a thermostat to $30 \pm 0.05°$, were poured by pipettes. Samples were taken with the aid of a constant-level pipette (^{2}). Active chlorine was determined iodometrically; the pH of the mixture, potentiometrically with a glass electrode to an accuracy of 0.05. The reaction in hydrochloric-acid medium was carried out in a special apparatus making it possible to avoid volatilization of chlorine. No correction for the self-decomposition of hypochlorite was introduced because of its small magnitude (^{2}).

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