

922. Induction Effects in the Oxidation of Bisulphite Ion at pH 4.

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The rate of oxygen absorption by bisulphite solutions at pH 4 in the presence of Cu^{2+} and Mn^{2+} has been studied with emphasis on the phenomena occurring when the oxygen supply is temporarily withdrawn. The absorption of oxygen after interruption follows a different course from that of an uninterrupted reaction and is most satisfactorily explained by a slow reaction of the metal catalyst with the sulphite solution.

AQUEOUS solutions of potassium metabisulphite (pyrosulphite) ($0.10\text{M-K}_2\text{S}_2\text{O}_5$) in potassium hydrogen phthalate buffer (0.2M) were mechanically shaken with oxygen at 25° , and the volume of oxygen absorbed determined as a function of time. Oxidation proceeds to HSO_4^- , with 1—2% at most of $\text{S}_2\text{O}_6^{2-}$. As with the extensively investigated oxidation of SO_3^{2-} at pH 8—11 the system is highly sensitive to traces of catalysts such as Cu^{2+} and to inhibitors, but at pH 4 the rate is comparatively low. No extended effort was made to work with pure solutions; instead, catalysts have been deliberately added.

EXPERIMENTAL

Materials.—"AnalaR" potassium metabisulphite and potassium hydrogen phthalate were twice recrystallised; the water used was prepared as for conductivity purposes and finally distilled from a silica still. Other chemicals were "AnalaR." The oxygen, normally stored over distilled water, was either prepared by the action of heat on "AnalaR" potassium permanganate and circulation over moist potassium hydroxide pellets to remove carbon dioxide, with dust filters to remove dust or manganese compounds, or obtained from a cylinder and passed slowly over platinised asbestos at 800° to oxidise possible traces of organic compounds. No difference could be detected between the samples.

Apparatus.—The absorption apparatus was a flask of 110 ml. capacity fitted with two B16 standard conical joints, one serving as a stopper through which reagents were introduced, and the other leading *via* a flexible glass tube to a 50 ml. constant-pressure absorption burette with mercury as the confining liquid. Both joints remained essentially gas-tight for an indefinite period when lubricated with a few drops of water and firmly assembled. The absorption flask was shaken by a reciprocating action through about 1 in. at a maximum rate of 400 times per min. in a thermostat at 25° . The burette was kept at the same temperature by a water jacket through which circulated water from the thermostat. The oxygen and water supplies were stored in all-Pyrex apparatus to eliminate possible inhibitors from rubber connections.

A three-way tap between the burette and the absorption flask enabled the flask to be purged with oxygen, the burette to be refilled in a few seconds, or cylinder nitrogen, cylinder carbon dioxide, and vacuum connections to be used.

Method.—The reaction flask was cleaned briefly with "chromic acid," steamed for an hour, and thoroughly rinsed with distilled water before each run. The necessary buffer solution was added, and the flask positioned in the shaker and left for 30 min. to come to temperature equilibrium. Then the required amount of solid metabisulphite was dropped into the buffer, the flexible lead attached, and the air displaced with oxygen. Finally the oxygen-filled burette was connected to the flask. The experiment was started by switching on the shaker and continued by taking readings of the volume absorbed at suitable time intervals. Virtually no oxidation takes place before shaking begins because little metabisulphite dissolves unassisted and the rate of reaction with unshaken solutions is very low. Tests with alkaline pyrogallol showed that the uptake of oxygen was five times that of the highest obtained with sulphite so that we were confident that oxygen diffusion into the solution was never a limiting factor. Reagents were introduced when required through the standard joint-stopper arm during a momentary cessation of the shaking.

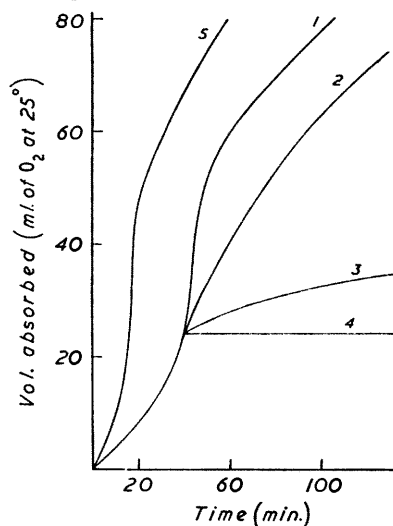
Results.—The results are shown in Figs. 1—5. In each experiment it was usual to take

volume readings at intervals of 1 min. for the first hour and then at longer intervals. The experimental points did not deviate from the smooth lines shown by more than 0.5 ml.

Curve 1, Fig. 1, shows the absorption-time curve for 75 ml. of a solution of 0.10M-potassium metabisulphite and 0.2M-potassium hydrogen phthalate without any deliberately added catalyst or inhibitor. This form of curve was followed closely (± 3 min., ± 2 ml.) on repetition with samples from one batch of metabisulphite and phthalate, and with a somewhat greater scatter with varying sources of material.

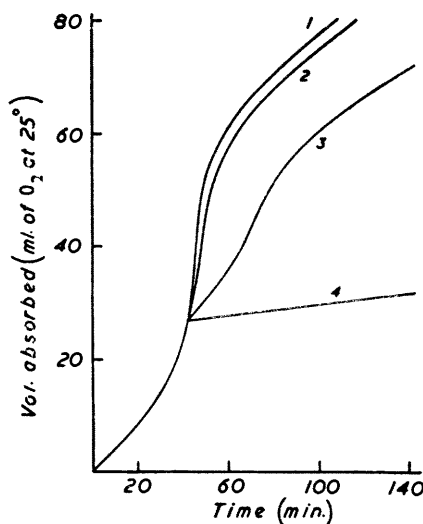
The uptake of oxygen in curve 1 amounted to only about one-third of the theoretical for $\text{HSO}_3^- \rightarrow \text{HSO}_4^-$. Analysis, by iodine titration, showed that the sulphite removed corresponded accurately to the oxygen uptake, and it was difficult to demonstrate convincingly that any dithionate was formed. As HSO_4^- is a much stronger acid than HSO_3^- , the solution, despite the buffer action, has a tendency to become more acid and to deposit phthalic acid.

FIG. 1. Oxygen absorption by bisulphite at pH 4, showing effect of injection of potassium ferricyanide solution.



1, Untreated; 2, 10^{-7}M -; 3, 10^{-6}M -; 4, 10^{-2}M - $\text{K}_4\text{Fe}(\text{CN})_6$; 5, 10^{-6}M - Cu^{2+} .

FIG. 2. Oxygen absorption by bisulphite solution at pH 4, showing effect of withdrawal of oxygen for various periods.



1, No delay; 2, 10 minutes' delay; 3, 78 minutes' delay; 4, 18 hours' delay.

Attention was then focused on the sensitivity of the reaction to catalysis and inhibition. Curves 2, 3, and 4 show the effect of the injection into the solution of small amounts of relatively concentrated potassium ferrocyanide solution. An amount sufficient to bring the overall concentration to 10^{-7}M has a perceptible retarding action. Fluoride and phosphate show little activity. Conversely, the initial addition of copper salts (see curve 5, Fig. 1) decreases the induction period and increases the maximum observed rate. No doubt very low concentrations of catalysts were initially present in the buffer reaction medium; analysis of the solid sulphite and phthalate by complete oxidation followed by spot tests indicated concentrations of 10^{-7}M at most. Chromic ion, a possible contaminant from the "chromic acid" cleansing of the glassware, is non-catalytic.

In an attempt to obtain more information, the reaction was stopped at a definite early stage by withdrawal of the oxygen supply and then re-started after a delay. For delays of a few minutes the aqueous medium was deprived of oxygen simply by stopping the shaking so that the oxygen uptake through the liquid surface became negligible; for longer periods the oxygen was displaced by nitrogen or carbon dioxide.

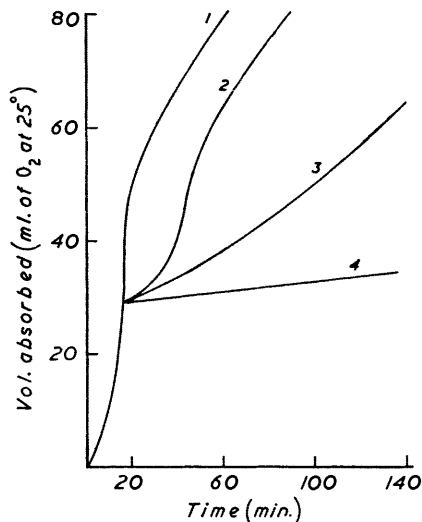
Fig. 2, curve 1, shows the course of the adsorption normally obtained without added catalyst. Curves 2, 3, and 4 show the form of the subsequent reaction when a solution initially following curve 1 is stopped after 27 ml. of adsorption and deprived of oxygen for 10 min., 78 min., and

18 hr. respectively. For convenience in display, the duration of the delay is omitted from the time curves. The curves for absorption after the delay show neither the form given initially by the system nor the form expected had there been no delay.

Two explanations seem possible. During the delay, either some inhibitor has found its way into the reaction medium or some catalyst present and functioning at the stop-point has been lost. The glass walls of the vessel, the grease on the three-way tap between flask and burette, the gas present in the flask during the delay, and the mercury in the burette appear the only possible sources of contamination. Various experiments have been carried out to eliminate these factors. Paraffin-lined vessels, silver-plated vessels, all-silica reaction vessels, phosphoric acid and Silicone greases as lubricant, delays with the flask evacuated, and water in the burette instead of mercury, were all tried but in each case a very similar delay effect was observed. Inhibition seems eliminated as the cause.

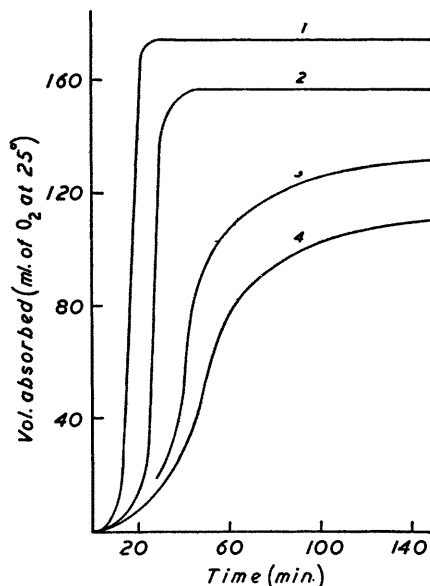
Loss of catalyst by adsorption on the surface of the Pyrex vessels was shown to be of no importance by carrying out runs with the addition of many grams of well-washed finely ground Pyrex glass. Similarly, the delay experiments gave the same results when the aqueous medium

FIG. 3. Oxygen absorption by bisulphite solution at pH 4 with added Cu^{2+} (10^{-6}M), and showing the effect of various delays.



1, No delay; 2, 24 hours' delay; 3, 72 hours' delay; 4, 240 hours' delay.

FIG. 4. Oxygen absorption by bisulphite solution at pH 4 with Mn^{2+} at various concentrations as catalyst.



1, 10^{-2}M ; 2, $0.5 \times 10^{-2}\text{M}$; 3, 10^{-3}M ; 4, 10^{-4}M .

contained finely powdered silica or barium sulphate. We conclude that the variation in reaction rate is due to the loss of an initially present catalyst from the solution by some process such as slow complex-formation with the sulphite-buffer system or dispersion as a colloidal phase.

Further results are presented in Fig. 3, where the same delay technique has been applied to a reaction mixture originally made 10^{-6}M in Cu^{2+} . A 10-day delay here greatly reduces the effectiveness of the copper catalysis. Similar results were obtained at 10^{-5}M-Cu^{2+} and 10^{-4}M-Cu^{2+} .

The phenomenon is not peculiar to cupric catalysis of the reaction. Fig. 4 shows the oxidation of HSO_3^- by oxygen in presence of Mn^{2+} . The family of curves differs from the corresponding series for Cu^{2+} in that oxidation is carried much nearer completion in comparable times. This may be considered as due to the catalytic mechanism's being much less adversely affected by increasing acidity in the Mn^{2+} than in the Cu^{2+} case. Fig. 5 shows a series of delay experiments carried out with Mn^{2+} at 10^{-4}M . Further results showed that even at 10^{-2}M-Mn^{2+}

the catalytic effect could be counterbalanced by a sufficiently long delay. The extremely active catalytic nature of Mn^{2+} towards the system oxygen-saturated sulphur dioxide-water was pointed out by Bassett and Parker.¹ Hoather and Goodeve² performed similar experiments in which the oxygen uptake for Mn^{2+} catalysis proceeded rapidly at a constant rate until near completion, thus paralleling our results in Fig. 4.

Acetic acid-sodium acetate and citric acid-disodium hydrogen phosphate buffers showed similar general behaviour for the absorption after a delay, though the details were different.

The phenomena observed are consistent with the viewpoint that HSO_3^- in aqueous solution at pH 4 reacts slowly with Cu^{2+} and Mn^{2+} in such a way as to reduce their ability to catalyse the oxidation of the HSO_3^- . Experiments have been performed to cause reaction of Cu^{2+} and Mn^{2+} with HSO_3^- under various conditions. Several solid products have been obtained from

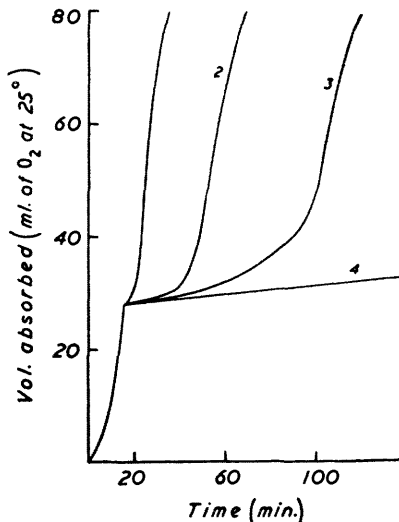


FIG. 5. Oxygen absorption by bisulphite solution at pH 4 catalysed by 10^{-4}M-Mn^{2+} , showing effect of various delays.

1, 1 Hour's delay; 2, $13\frac{1}{2}$ hours' delay; 3, 70 hours' delay; 4, 240 hours' delay.

Cu^{2+} and will be described shortly, but no such solids have been produced from Mn^{2+} . During the delay experiments with Cu^{2+} and sulphite some separation of a copper-containing solid phase occurs; with the lowest copper concentrations this precipitation is best demonstrated by its red Tyndall beam. The slow re-dissolution of this copper material during the subsequent oxidation accounts for the observation that with Cu^{2+} catalysis the second maximum rate, especially after long delays, does not equal the expected value, whereas with Mn^{2+} the second maximum rate is much the same for all delays and similar to the expected maximum for a non-delayed run.

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¹ Bassett and Parker, *J.*, 1951, 1540.

² Hoather and Goodeve, *Trans. Faraday Soc.*, 1934, 30, 1149.