

EFFECTS OF TRACE METALS ON THE PHOTSENSITIZED AUTOXIDATION OF SULPHITE

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Summary

The methylene-blue-sensitized photooxidation of sulphite by molecular oxygen is catalysed by trace metals. In the absolute absence of catalysing metal ions the reaction would not proceed at all. With increasing concentrations of Mn(II) and Fe(III) the reaction velocity and consequently the overall quantum yields increase.

1. Introduction

It has recently been found [1 - 4] that photoinitiated autoxidation of sulphite is catalysed by metal ions present in trace concentrations in the background of the reaction system. A definite photocatalytic effect was found with Fe(III) and Mn(II) ions. Both the rate and the quantum yields of the photoinitiated reaction decreased with decreasing concentration of these ions. The experimental results suggested that in a total absence of transition metal ions no measurable reaction rate of photoinitiated autoxidation of sulphite would be found.

Until now no attention has been paid to trace metals present in the background of photochemical systems. In the case of sulphite the photoinitiated reaction is affected by trace metals and the disregard of this fact was the cause of distorted conclusions concerning its reaction mechanism. The present paper is therefore aimed at examining the extent to which metal ions in trace concentrations influence the photosensitized reaction. Methylene blue (MB), whose effect on photooxidation of sulphite has already been described [2, 5, 6], was employed for sensitizing the reaction.

2. Experimental

All chemicals employed were of AR grade. Special attention was paid to the purity of the water, however. Redistilled water was used and its

purity was controlled at regular intervals. The rate of thermal and photochemical reactions proceeding without addition of catalysing ions and sensitizer was adopted as the criterion of the purity of the water and of the entire reaction system.

The photoinitiated reaction was carried out in a Teflon flow-through cell provided with quartz sight holes. The irradiated cell was connected on one side by polyethylene tubing to a thermostatted vessel where the reaction was saturated with oxygen, and on the other side to the flow-through cell of a spectrophotometer (Unicam SP 800 B, Cambridge). A rotating Teflon turbine ensured agitation and circulation of the liquid. This set-up, which has been described previously [3], permitted continuous monitoring of sulphite concentration by determining the absorbance of the reaction mixture at $\lambda = 230$ nm. The addition of MB in the concentrations used (10^{-8} - 10^{-6} M) had no effect on the spectrophotometric determination of sulphite.

The 577 nm line of a high pressure mercury arc (HBO 500 W, Narva, Berlin) combined with an interference filter (IF 575, Carl Zeiss, Jena) was used to initiate the reaction. The intensity of the initiating radiation (quanta s^{-1}) was measured by means of the chemical actinometer $K[Cr(NH_3)_2(NCS)_4]$ described by Wegner and Adamson [7].

The experimental results were evaluated on a Hewlett-Packard 9830 A calculator. Functional dependences were plotted by the method of least squares polynomial regression; at the same time the scatter of the data and the mean relative deviation were calculated.

3. Results and discussion

In the first series of experiments the photocatalytic influence of manganese on the autoxidation of sulphite at three different concentrations of MB (6×10^{-8} M, 1×10^{-7} M and 2×10^{-7} M) was studied. In all the experiments the initial concentration of sulphite was 1×10^{-3} M and the concentration of manganese was varied in the range 1×10^{-7} - 1.2×10^{-6} M. Figure 1 shows the influence of various concentrations of manganese ions on the photooxidation of sulphite at a MB concentration of 2×10^{-7} M. It is seen in Fig. 1 that in the initial stage of the sensitized reaction the dependence of the decrease of the sulphite concentration on time is almost linear. Deviations from the linear relation are found only in values obtained immediately after starting the reaction. A comparison of the slopes of the lines in Fig. 1 shows that an increasing concentration of manganese ions produces an increase in the rate of the photosensitized reaction.

In Fig. 2 the rate of sensitized oxidation is plotted against the concentration of manganese for various concentrations of MB. It is evident that the rate of sensitized photooxidation of sulphite increases linearly with increasing concentration of manganese ions. As additions of manganese do not change the quantity of light absorbed by the reaction mixture the increase of the reaction velocity with the manganese concentration must be

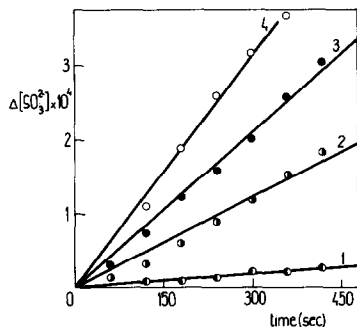


Fig. 1. Dependence of $\Delta[\text{SO}_3^{2-}] (= [\text{SO}_3^{2-}]_0 - [\text{SO}_3^{2-}])$ on time for various concentrations of added Mn(II): $[\text{SO}_3^{2-}]_0 = 1 \times 10^{-3}$ M; $[\text{MB}] = 2 \times 10^{-7}$ M; $[\text{O}_2] = \text{saturation}$ at 20°C . $[\text{Mn(II)}]$: curve 1, 0; curve 2, 3×10^{-7} M; curve 3, 9×10^{-7} M; curve 4, 1.2×10^{-6} M.

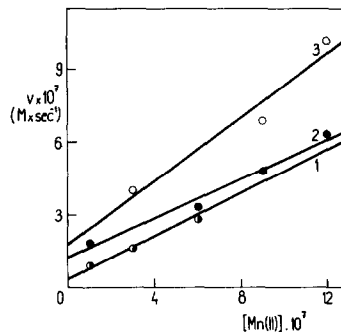


Fig. 2. Dependence of the reaction on the concentration of added Mn(II) at various MB concentrations. $[\text{SO}_3^{2-}]_0 = 1 \times 10^{-3}$ M; $[\text{O}_2] = \text{saturation}$ at 20°C . $[\text{MB}]$: curve 1, 6×10^{-8} M; curve 2, 1×10^{-7} M; curve 3, 2×10^{-7} M.

caused by the increase of the overall quantum yields. Unlike manganese, MB additions change the absorbance of the reaction solution. The small rise of the reaction velocity with MB concentration is therefore not due to the increase of the quantum yields but to the higher light absorption (see Table 1).

In another series of experiments the influence of a variable concentration of iron was investigated. The initial concentration of sulphite was again 1×10^{-3} M, the concentrations of MB were 6×10^{-8} M, 1×10^{-7} M and 2×10^{-7} M and the concentration of iron was varied in the range 1×10^{-7} - 1.2×10^{-5} M. Contrary to the results for manganese, in the case of iron no statistically important influence of Fe(III) on the rate of the photosensitized photooxidation was found below concentrations as high as 1×10^{-6} M. Above this limit the rate of sensitized photooxidation increased with increasing iron concentration. The scatter in the values of the reaction rates was, however, very marked and it was therefore not possible to ascertain the shape of the functional dependence. The reason for so great a scatter was the tendency of the trivalent iron to hydrolyse and to form undefined deposits of catalytically active iron hydroxides on the reaction vessel walls.

It follows from Figs. 1 and 2 that a sensitized reaction does proceed even at zero addition of catalysing ions. Zero addition is not identical with zero concentration, however. Even in ultra-pure reaction systems the concentration of manganese ions may be in the range 10^{-10} - 10^{-8} M; indeed, trace concentrations of iron are much higher. The question of whether or not the value of the reaction rate in systems where no catalysing ions are added is determined by the background now arises; in another words, would a sensitized photooxidation of sulphite proceed in a total absence of catalyzing ions? To answer this question a series of experiments to investigate

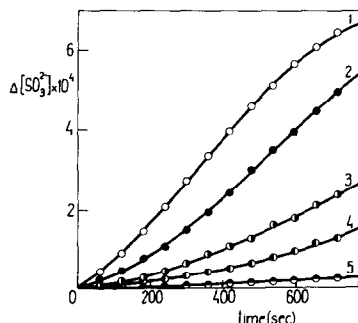


Fig. 3. Dependence of $\Delta[\text{SO}_3^{2-}] (= [\text{SO}_3^{2-}]_0 - [\text{SO}_3^{2-}])$, on time for various concentrations of TRIEN. $[\text{SO}_3^{2-}]_0 = 1 \times 10^{-3} \text{ M}$; $[\text{MB}] = 1 \times 10^{-6} \text{ M}$; $[\text{O}_2] = \text{saturation at } 20^\circ \text{C}$. $[\text{TRIE N}]$: curve 1, 0; curve 2, $6 \times 10^{-7} \text{ M}$; curve 3, $1 \times 10^{-6} \text{ M}$; curve 4, $3 \times 10^{-6} \text{ M}$; curve 5, $6 \times 10^{-6} \text{ M}$.

the influence of complexing agents on the reaction rate was undertaken. The complexing agents (triethylenetetramine (TRIE N) and ethylenediaminetetraacetic acid (EDTA)) employed reduced the reaction rate and in larger concentrations even stopped the reaction. Figure 3 shows the dependence of the rate of the reaction proceeding without the addition of a catalyst (*i.e.* at a metal concentration given by the background) on the concentration of TRIEN. It is evident that the addition of the complexing agent not only reduced the rate of the photosensitized reaction but also changed the reaction kinetics.

All the experimental results point uniquely to the fact that without catalysing ions sensitized photooxidation would not proceed at all. In agreement with this conclusion a striking dependence of the reaction rate on the cleanliness of the reaction vessel was observed. When a thoroughly clean reaction vessel which had never contained a solution of catalysing cations was used extremely low reaction rates were observed. These low reaction rates are difficult to obtain once the reaction vessel has come into contact with catalysing cations. The original low reaction rates were obtained again only after washing the reaction vessel with a solution of a chelating agent and rinsing carefully with double-distilled water.

Table 1 gives the quantum yields of photosensitized reactions at various concentrations of manganese ions. Since the manganese concentrations used do not affect the absorption spectrum of the reaction mixture [4], it can be concluded that it is the concentration of manganese in the reaction system which determines the magnitude of the quantum yields. In the case of iron the situation is more complex; the absorption of sulphito-ferric complexes lies partly in the visible region of the spectrum.

4. Reaction mechanism

The mechanism of the photosensitized reaction of molecular oxygen is explained by the classical chain mechanism [8], by the formation of a reac-

TABLE 1

Quantum yields at various concentrations of Mn(II) and MB

[Mn(II)] $\times 10^7$	[MB]		
	6×10^{-8}	1×10^{-7}	2×10^{-7}
1.0	147.7	232.5	
3.0	359.4		254.1
6.0	569.1	415.6	
9.0	967.2	598.7	436.3
12.0		794.1	645.8

tion adduct of the sensitizer with oxygen [9] or by the formation of a singlet oxygen [10]. However, all these considerations are at variance with the experimental facts described earlier. The reactive adduct mechanism and the singlet oxygen mechanism do not permit an explanation of the quantum yields found which, as seen in Table 1, are very much greater than unity. None of the mechanisms quoted can explain the catalytic influence of metal ions.

Good agreement exists, however, between the experimental data and the mechanism of photochemical generation of the unstable catalyst of a thermal reaction which has been suggested for the unsensitized photochemical autoxidation of sulphite [3, 11]. As can be seen from Table 1 the overall quantum yields decrease with increasing concentration of MB. In our opinion this effect is caused by the influence of MB on the catalysing metal ions. With increasing MB concentration the number of free coordination places available to sulphite ions decreases. As we showed recently [3, 11] the coordination of sulphite to metal ions conditioned the photoinitiated (non-sensitized) autoxidation of sulphite. It seems that the same condition must be satisfied in the case of the photosensitized reaction. The intermediate product of the sensitized reaction would in this case be one of the mixed complexes of manganese (or iron) with MB, sulphite and perhaps oxygen.

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