

PHOTOCHEMICAL AUTOOXIDATION OF SULPHITE CATALYZED BY IRON(III) IONS

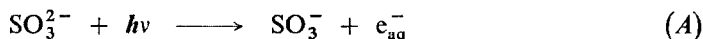
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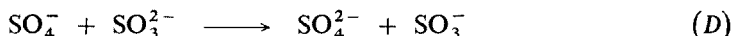
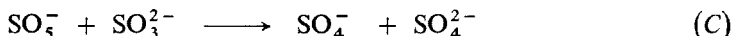
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Photoinitiated autooxidation of sulphite is catalyzed by trace concentrations of some transition metal ions. A distinct catalytic effect has been proved in the case of iron. Quantum yields of the reaction depend on the wavelength of the initiating radiation and concentration of iron(III) ions in the reaction system. Photochemical autooxidation of sulphite can be initiated by radiation of the wavelengths longer than corresponds to absorption of the sulphite itself. The first step of the reaction is interaction of a light quantum with a sulphite complex of a catalyzing cation. In absence of catalyzing metal ions, the photochemical autooxidation of sulphite would not proceed at all.

Although the photochemical autooxidation of sulphite has many times been studied¹⁻⁷, the possibility of this reaction to be catalyzed or trace-catalyzed has never been given any attention. The literature data¹ show that the autooxidation of aqueous sulphite solutions is initiated by absorption of a light quantum by sulphite anion and subsequent formation of SO_3^- radical.



High quantum yields of the reaction are explained¹ by a chain mechanism, *i.e.* by subsequent propagation reactions:



The termination reactions have not been specified unambiguously; the possibilities of radicals to recombine between one another have been merely suggested.

The fact that the rate of the photoinitiated autooxidation of sulphite is affected by presence of trace concentrations of iron has been presented in our preceding

communication⁸. This paper aims at studying, in more detail, the effect of iron concentration at various wavelengths of the initiating radiation (225–463 nm) and at determining quantum yields of photochemical autoxidation of sulphite.

EXPERIMENTAL

Reagents

The reagents were all of A. R. grade purity. Purity of sodium sulphite A. R. (Reanal) was orientationally tested for the amount of copper which is the most efficient catalyst of a thermal reaction. Additions of [Cu] as low as $\sim 10^{-7}$ M have been found to be catalytically highly efficient for solutions with $[\text{SO}_3^{2-}] \leq 10^{-2}$ M so that concentration of copper as impurity is in these solutions considerably lower than 10^{-7} M. Redistilled water only, whose conductivity was periodically checked, was used to prepare all the solutions as well as to wash the reaction system and vessels employed. No special attention was paid to the purity of the other reagents employed, which were present in catalytic concentrations only. Potassium ferrioxalate, used as an actinometer⁹, was prepared from potassium oxalate and iron(III) chloride. The preparation was carried out in the red safe light with use of the illumination filter Foma 640 (Fotochema, Hradec Králové). The obtained $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3 \text{H}_2\text{O}$ was three times recrystallized from hot water.

Apparatus and Methods

The photoinitiated autoxidation of sulphite took place in a teflon flow cell (our own construction) with quartz windows. The cell was from one side connected to a thermostated vessel in which the reaction solution was saturated with oxygen by bubbling it through the reaction mixture; from the other side a flow-cell of spectrophotometer SP 800 B UNICAM (Cambridge) was attached. Stirring and circulation of the reaction solution in the system: thermostated vessel-irradiated reaction flow cell-spectrophotometer flow cell was accomplished by a rotating teflon turbine situated in the thermostated vessel. This arrangement made it possible to follow continually the sulphite concentration which was determined from absorbance of the reaction mixture at 230–245 nm. It is well-known from the literature¹ that the sulphite anion in aqueous solutions obeys the Beer law in a wide concentration range of $5 \cdot 10^{-5}$ – 0.5 M in the region of wavelengths from 200 to 260 nm.

According to the wavelength required, three various sources of initiating radiation were employed:

a) For wavelengths longer than 325 nm, high-pressure mercury lamp HBO 500 (Narva, Berlin) was used. The lamp was placed in a water-cooled aluminium block. When working with this lamp, particular attention was paid to slight constant cooling which, unlike the lamps mentioned below, strongly influenced the light flux. Since a point source of radiation was involved, a silica condenser ($f = 8.5$ cm, $\varnothing = 4$ cm) and aperture 2 cm in diam. could be used to achieve a parallel beam of rays.

b) For wavelengths of 225–325 nm, a medium pressure mercury spectral lamp Philips No 93136 was used.

c) The wavelength of 253.7 nm was obtained from a low-pressure mercury spectral lamp Philips No 93109.

The lamps mentioned in b) and c) provided constant light flux which was partially independent

of the intensity of cooling the lamp casing. Both lamps are likewise surface sources so that a parallel beam of rays was obtained by a system of apertures.

To make the light monochromatic, interference filters were employed. For ultraviolet region (225–325 nm) a series of UVKSIF filters (Carl Zeiss, Jena), for visible region (350–436 nm) a series of IF filters (Carl Zeiss, Jena) were used. When necessary, residual transmittance of the interference filter was suppressed by an additional liquid filter. Individual wavelengths of the initiating radiation were obtained by the following combinations of lamps, interference filters, and liquid filters:

a) Wavelength of 225 nm was isolated from spectrum of medium pressure mercury spectral lamp Philips No 93136 using interference filter UVKSIF 225 nm and a 3 cm thick liquid filter of composition acetone : water = 1 : 20 (vol.).

b) Wavelength of 253.7 nm was obtained by combining the low-pressure mercury lamp Philips and interference filter UVKSIF 254 nm or by employing the medium-pressure mercury spectral lamp Philips No 93136 and interference filter UVKSIF 250 nm. The second combination gave an approximately ten times higher light flux, the strict monochromaticity of radiation, however, being impaired.

c) Wavelengths of 275 nm, 300 nm, and 325 nm were selected from spectrum of the medium-pressure spectral lamp Philips No 93136 with use of an appropriate interference filter UVKSIF and a 3 cm thick liquid filter consisting of 1M sulphite which served to cut out residual radiation of wavelengths shorter than 265 nm.

d) The other wavelengths of 350 nm, 375 nm, 400 nm, and 436 nm were directly selected from spectrum of the high-pressure mercury lamp HBO 500 by means of interference filters IF which are manufactured from glassy material so that the radiation wavelengths from far UV region ($\lambda < 310$ nm) were reliably removed.

Intensity of the initiating radiation (quant. $\cdot s^{-1}$) was measured by means of the potassium ferrioxalate actinometer⁹. The $6 \cdot 10^{-3} M$ solution of the latter compound in $0.1N-H_2SO_4$ was employed. The actinometer solution was placed in the reaction system and let to circulate between the irradiated cell and thermostated vessel during the irradiation period (in the same way as in the study of the kinetics of photochemical autooxidation). The actinometric mixture was within the whole time of irradiation protected by a nitrogen atmosphere freed from oxygen traces by chromium(II) ions and zinc amalgam. The times of irradiation varied, according to light intensity, from 2 min to 4 hours. Quantity of the Fe^{2+} produced was determined by *o*-phenanthroline. Each value of the intensity of initiating radiation was measured at least three times for three different irradiation times, and linear increase of the amount of produced Fe^{2+} as dependent on the irradiation time was checked. Intensity of radiation I (quant. $\cdot s^{-1}$) was then calculated from

$$I = 6.023 \cdot 10^{20} \cdot V_1 \cdot [Fe^{2+}] / t, \quad (1)$$

where V_1 is the volume of the actinometer in ml, $[Fe^{2+}]$ denotes concentration of produced bivalent iron in $mol \cdot l^{-1}$, t is time in s.

As has been mentioned above, the experimental arrangement allowed to obtain a continual record of the time dependence of the sulphite concentration. Since iron catalyzes not only the photochemical, but also the thermal* reaction, only the initial rate of the photochemical reaction

* The term "thermal reaction" is used for the reaction in absence of light and serves only to distinguish it from the light-initiated reaction, the photochemical reaction.

(further denoted as v_{f0}) was mostly determined by subtraction of the rate of the thermal reaction immediately before admission of light to the reaction system from the initial total reaction rate during irradiation.

RESULTS AND DISCUSSION

Examination of the catalytic effect of iron on the rate of the thermal autooxidation of sulphite was the first problem to solve; it was therefore necessary to pay attention at first to the oxidation degree of iron added into the reaction solution. Preliminary experiments led to the finding that immediately after addition of $\text{Fe}_{\text{aq}}^{2+}$ into the reaction solution, a rapid decrease of sulphite takes place (autooxidation), which, however, ceases within several seconds and the reaction further proceeds at a rate which is the same, as if the reaction were started by $\text{Fe}_{\text{aq}}^{3+}$. In accordance with this kinetic fact it was found spectrophotometrically (see Fig. 1) that immediately after mixing solutions of $\text{Fe}_{\text{aq}}^{2+}$ (curve 1) and sulphite, the sulphitoferrous complexes are produced (curve 2) which are immediately oxidized to sulphitoferric complexes (curve 3), irrespective of the excess of sulphite.

It is therefore not possible to study effect of Fe(II) on the photochemical autooxidation of sulphite (even though the above-mentioned facts are substantial for considerations on the possible mechanism of catalysis of a photochemical reaction — see below) and attention was therefore paid to the effect of catalytic concentrations of Fe(III).

The photochemical autooxidation of sulphite exhibits all the properties that are typical for the trace-catalyzed reaction, *i.e.* poor reproducibility of results which can be improved by keeping the level of metal impurities strictly constant both in solution and in the surface of the reaction vessels.

For connections of the thermostated vessel, irradiated reaction cell, and spectrophotometer flow cell, PVC tubings were used. These tubes can at certain concentrations (10^{-5}M) retain a part of added catalyst and in the subsequent experiment again release iron into the reaction solution. An equilibrium is here obviously established between complexing capability of sulphite and the capability of the PVC tube

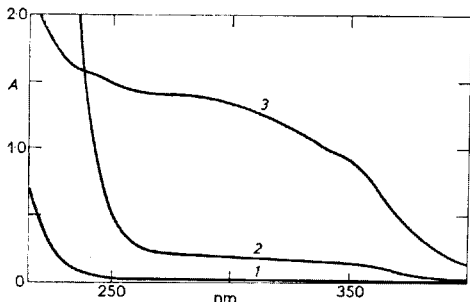


FIG. 1

Absorption Spectra

1 $2.91 \cdot 10^{-4}\text{M-FeSO}_4$; 2 $2.78 \cdot 10^{-4}\text{M-FeSO}_4 + 10^{-2}\text{M-SO}_3^{2-}$ in the N_2 atmosphere; 3 composition as for 2; spectrum measured immediately after the outset of bubbling oxygen through the solution. Cell — 2 cm; $t = 20^\circ\text{C}$.

to act as an ion exchanger. It was therefore necessary to wash the whole reaction system at first with diluted acid then with a complex agents and finally with the sulphite solution. The washing with sulphite solution employed (10^{-2}M) was repeated until the initial rate of the photoinitiated autooxidation did not change. If, for example, redistilled water only, instead of the sulphite solution, was used for washing, the rate of photochemical autooxidation of sulphite in the subsequent experiment was much lower (thanks to removal of catalyzing metal ions from the reaction sulphite solution), irrespective of the number and time of washings with redistilled water.

In the first series of the experiments, catalytic effect of iron at various wavelengths of the initiating radiation was studied. By combination of the lamps, interference and liquid filters (see Experimental), the following wavelengths of the initiating radiation were selected: 225 nm; 254 nm; 275 nm; 300 nm; 325 nm; 350 nm; 375 nm; 400 nm; 436 nm. In Table I, results obtained for individual wavelengths of the initiating radiation are summarized.

It follows from the data given in Table I that the rate of photochemical autooxidation of sulphite rises with the increasing concentration of iron at all the wavelengths of initiating radiation. The range of wavelengths was at the same time chosen so that it might cover both the region of light absorption merely by sulphitoferric

TABLE I

Initial Rates of Photochemical Autooxidation ($v_f \cdot 10^7$, $\text{mol l}^{-1} \text{s}^{-1}$) of Sulphite, Initiated by Light of Various Wavelengths at Varying Concentration of Iron
 $[\text{SO}_3^{2-}]_0 = 1 \cdot 10^{-2}\text{M}$, $[\text{O}_2] = \text{sat}$, $t = 20^\circ\text{C}$.

λ^a nm	Intensity ^b	Concentration of added iron, mol l^{-1}					
		0	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$8 \cdot 10^{-5}$
initial rate of photochemical reaction, $v_{f0} \cdot 10^7$							
225	2.01	6.48	8.81	10.7	16.7	17.6	19.9
254	0.20	1.39	1.85	2.32	3.47	3.01	—
275	6.21	26.8	50.70	75.10	91.70	—	—
300	7.01	3.46	13.20	13.20	24.30	27.80	—
325	2.87	2.34	3.25	9.26	9.26	—	—
350	41.50	3.89	13.90	24.10	38.40	54.20	78.50
375	41.50	1.95	2.78	4.17	9.73	13.30	18.10
400	19.80	0.834	1.39	1.11	3.06	6.67	9.45
436	66.70	immeasurably		3.82	4.17	—	6.95

slow

^a Wavelength of initiating radiation, ^b of initiating radiation $I \cdot 10^{-14} \text{hv} \cdot \text{s}^{-1}$.

complexes ($\lambda \geq 300$ nm), and the region, where the absorption mainly by sulphite alone (225 nm) takes place.

A particular problem of the photochemical autooxidation of sulphite are the quantum yields. Generally, a quantum yield is defined as a number of molecules, which react during absorption of one quantum of the initiating radiation. A real quantum yield of the photochemical reaction, however, must relate merely to radiation

TABLE II

Extinction Coefficients ($\text{mol}^{-1} \text{ l cm}^{-1}$) of Sulphite Water Solutions for Wavelengths of 225–300 nm and Quantity of Absorbed Light (Cell 6 cm) for Wavelengths of Initiating Radiation $t = 20^\circ\text{C}$, $[\text{SO}_3^{2-}]_0 = 1 \cdot 10^{-2} \text{ M}$.

nm	ϵ	Absorbed light, %	nm	ϵ	Absorbed light, %
225	$7.9 \cdot 10^2$	100.00	270	0.45	—
230	$4.9 \cdot 10^2$	—	275	0.13	1.78
240	$1.4 \cdot 10^2$	—	280	$5.0 \cdot 10^{-2}$	—
250	37.4	—	290	$4.9 \cdot 10^{-3}$	—
254	19.5	92.76	300	$5 \cdot 10^{-4}$	0.01
260	2.0	—			

TABLE III

Quantum Yields

λ^a nm	Concentration of added iron, mol l^{-1}				
	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$8 \cdot 10^{-5}$
quantum yields, $\Phi \cdot 10^{-2}$, of molecules/ $h\nu$					
436	—	0.22	0.15	—	0.15
400	0.29	0.15	0.25	0.42	0.49
375	0.20	0.19	0.27	0.31	0.36
350	0.80	0.82	0.87	1.04	1.37
325	2.2	4.0	2.7	—	—
300	3.2	2.0	2.7	2.8	—
275	11.9	11.8	10.8	—	—
254	5.8	7.1	10.5	9.12	—
225	2.6	3.2	5.0	5.3	6.0

^a Wavelength of initiating radiation.

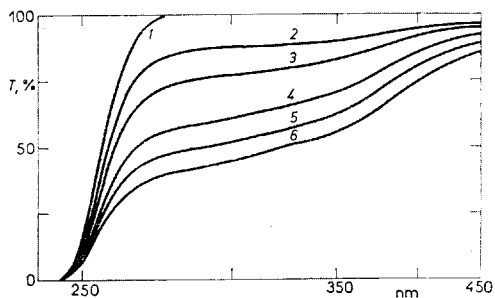
absorbed by the component which initiates the reaction. In our case, *i.e.* in the photochemical autooxidation of sulphite, catalyzed by iron, the initiating radiation is absorbed both by sulphite and by sulphitoferric complexes. If the initiation by light proceeded in the way described in the literature [reaction (A)], *i.e.* by interaction of the light quantum with the sulphite anion, the light should have no effect on the rate of photochemical autooxidation of sulphite in the region, where sulphite does not practically absorb (*i.e.* at $\lambda \geq 300$ nm). Values of the molar extinction coefficients of sulphite and the amount of light absorbed by the reaction solution of sulphite in the reaction cell are given in Table II.

It follows from a comparison of the data in Tables I and II that the reaction cannot be initiated by absorption of light by the sulphite anion, for in that case the quantum yields of the reaction would have to increase extremely with the rising wavelength, this fact being at most improbable. For example, at the wavelength 225 nm the corresponding quantum yield (for $1 \cdot 10^{-2} \text{M-SO}_3^{2-}$) would make $1.94 \cdot 10^2$, whereas at the wavelength 300 nm even $2.97 \cdot 10^5$. The quantum yields for 320–400 nm would have to be even much higher; their accurate values, however, cannot be presented, since in this region, the light absorption even by the most concentrated sulphite solutions is immeasurably small. The only one component of the reaction mixture, which in the region of wavelengths $\lambda > 300$ nm absorbs, are the sulphite complexes of catalyzing ions, in our case (if Fe (III) is added) the sulphitoferric complexes. The photochemical autooxidation of sulphite is thus not initiated by absorption of light by a free sulphite anion, but by its complex with the catalyzing cation. The absorption spectra of the reaction mixtures at concentrations employed are presented in Fig. 2.

In Table III, the quantum yields of the photochemical autooxidation are summarized, expressed by the number of oxidized sulphite molecules per one quantum absorbed by the reaction mixture. Quantum yield Φ was therefore calculated from

$$\Phi = v_{f0} \cdot A \cdot V / (I(1 - 10^{-E})), \quad (2)$$

FIG. 2
Absorption Spectra
Dependence of Transmittance of Reaction Solutions on the Fe(III) Concentration. $[\text{SO}_3^{2-}] = 1 \cdot 10^{-2} \text{M}$; $[\text{Fe(III)}]$: 1 0; 2 $1 \cdot 10^{-5} \text{M}$; 3 $2 \cdot 10^{-5} \text{M}$; 4 $4 \cdot 10^{-5} \text{M}$; 5 $6 \cdot 10^{-5} \text{M}$; 6 $8 \cdot 10^{-5} \text{M}$. Cell 2 cm; $t = 20^\circ \text{C}$.



where v_{f0} ($\text{mol l}^{-1} \text{s}^{-1}$) is the initial rate of photoinitiated autooxidation of the sulphite; $A = 6.023 \cdot 10^{23}$ (the Avogadro number), I ($\text{quant.} \cdot \text{s}^{-1}$) number of quanta of the initiating radiation, incident to irradiated cell, E = extinction of the reaction solution at the wavelength of initiating radiation, and $V(l)$ is volume of the reaction mixture.

As has been presented, for $\lambda \geq 300$ nm the light is practically absorbed only by the sulphitoferric complexes so that in this region of wavelengths of the initiating radiation, the given quantum yield corresponds to the number of sulphite molecules which have reacted as a result of the interaction of one molecule of the sulphitoferric complex with a light quantum. The situation can be, in fact, more complicated. In the reaction solution, of course, a series of sulphitoferric complexes exist, of which only some could be photochemically active. Numerical values of the quantum yields, however, are even more problematic for wavelengths of 225 nm and 254 nm, when absorption both by the free sulphite anion and by the anion bound in the sulphitoferric complex, is applied to a greater extent.

As can be seen in Table III, calculated quantum yields Φ increase with the decreasing wavelength up to 275 nm. For shorter wavelengths (254 and 225 nm) a decrease takes place; this may be caused by absorption of light by free sulphite anion, which is, as has been shown above, inactive to the photochemical reaction. The quantum yields likewise slightly increase with rising concentration of Fe(III) in the reaction mixture, but the dependence is not unambiguous; for some wavelengths, the quantum yields were owing to the varying concentration of Fe(III) virtually constant.

Reaction Mechanism

As has already been presented, the first step is the interaction of the light quantum with the sulphitoferric complex. Excitation of this complex then generally yields three possibilities for further course of the reaction:

I. Intramolecular redox process, in which Fe(II) is produced. As shown above, Fe(II) is a highly active catalyst of the thermal autooxidation of sulphite. Effect of light would then in this case consist in generation of the catalyst of the thermal reaction.

II. The produced excited state of the sulphitoferric complex is extraordinarily catalytically active and enables the appropriate number of sulphite and oxygen molecules (see the quantum yield) to react. Owing to the relatively high quantum yields, this possibility does not seem to be probable.

III. Analogously to case *I*, internal redox process takes place, where Fe(II) is produced and SO_3^- radical, which would initiate the reaction, subsequently dissociated off. But the fact that Fe(II) has a distinct catalytic effect on the thermal re-

action stands against this possibility. If the excited sulphitoferric complex decomposed to Fe(II) and free sulphite SO_3^- radical, iron in the oxidation state +2 should be inhibitor of the thermal reaction; it would, namely, act as a scavenger.



Of the three possibilities given, the first one seems to be the most probable. Photochemical behaviour of Fe(III) complexes with the reducing ligand is well-known from the literature¹⁰. A typical example is the ferric oxalate actinometer¹¹. Formation of the thermal catalyst, *i.e.* of Fe(II), by photoreaction allows then to explain high quantum yields, without the chain free radical mechanism being necessary to consider. (The authors, however, do not mean elimination of the participation of the radical particles in the coordination sphere of the catalyzing ion.) We have also experimentally found accordance (as to the order of magnitude) between the number¹² of oxidized sulphite molecules belonging to one added Fe(II) before its deactivation takes place by oxidation to Fe(III), and the quantum of the catalyzed photochemical reaction, catalyzed by iron.

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