

AUTOXIDATION OF SULFITE CATALYSED BY 3d TRANSITION METALS AND INHIBITED BY 2-PROPANOL; MECHANISM OF INHIBITED AND INDUCED REACTIONS

Stanislav LUŇÁK, Ahmed M. EL-WAKIL and Josef VEPŘEK-ŠIŠKA

*Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6*

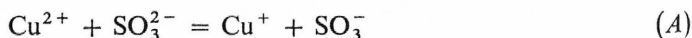
Received August 16th, 1977

The rate of the autoxidation of sulfite catalysed by copper ions and inhibited by 2-propanol and that of the induced oxidation of the inhibitor, respectively, follow the relations

$$-d[\text{SO}_3^{2-}]/dt = \text{const.} \cdot c_{\text{Cu}} \cdot [\text{SO}_3^{2-}]/c_{\text{inh}}, \quad \text{and} \quad -d[\text{inh}]/dt = \text{const.} \cdot c_{\text{Cu}}.$$

By comparing the catalytic influence of several metal ions on the initial reaction rate at equal conditions, the following series was obtained: Fe(II) ~ Co(II) > Mn(II) ~ Cu(I, II) ≫ ≫ Fe(III) ~ Co(III) ≫ Ni(II). No evidence supporting the assumption that the reaction proceeds by a radical chain mechanism was found. The autoxidation of sulfite probably proceeds via a reactive mixed complex $[\text{Cu}(\text{SO}_3)_2\text{O}_2]^{3-}$; a reactive mixed complex $[\text{Cu}(\text{SO}_3)(\text{inh})\text{O}_2]^-$ is the intermediate of the oxidation of the inhibitor.

The autoxidation of sulfite was the first reaction of molecular oxygen explained by the hypothesis of a radical chain mechanism¹⁻⁵. The process is assumed to be initiated by the radical SO_3^- formed, in the case of a thermal reaction, by a one-electron transfer from the sulfite anion⁴ (reaction (A)) or, in the case of a photoinitiated reaction, by the absorption of a light quantum (reaction (B)). This assumption sees the inhibiting influence of alcohols in their interaction with the radical intermediates^{3,6} and in subsequent shortening of the radical chain.



It has recently been shown⁷ that reaction (A) does not represent a partial process of thermal autoxidation of sulfite. As was observed when studying its photochemical reaction⁸⁻¹⁰ the photoinitiated reaction is catalysed by transition metal ions in trace concentrations; in their total absence, it would virtually not proceed at all similarly to the thermal reaction. Considering the foregoing results we came to the conclusion that no mechanism of the autoxidation of sulfite involving partial processes (A) and

(B) is compatible with the latest findings, and that a new mechanism should be formulated.

In connection with efforts to formulate the reaction mechanism we studied the kinetics of the thermal and photochemical autoxidations of sulfite in the presence of inhibitors of various types. The present study aims at obtaining kinetic data on the autoxidation of sulfite inhibited by 2-propanol and on the kinetic course of the induced oxidation* of 2-propanol.

EXPERIMENTAL

Chemicals

All chemicals used were of A.R. grade. The purity of sodium sulfite (Reanal) was tested for Cu at regular intervals. 2-Propanol was purified by distillation in an inert atmosphere, and its purity was checked by gas chromatography and spectrophotometry. The purity of water was periodically controlled by conductivity measurements. Another important criterion of the purity of water was the rate of the oxidation of sulfite when neither catalyst nor inhibitor was added.

Equipment and Procedure

The reaction mixture filled up one third of the total volume of a thermostatted vessel. The gas space was connected to a gas burette with the aid of which a constant moderate overpressure of oxygen (c. 10 kPa) was maintained in the reaction vessel. The reaction vessel was intensively shaken (5 cycles/s). Samples for determining the concentration of sulfite and acetone were taken at regular intervals. As compared to the duration of the experiment, the time of the sampling (ca 5 s) was negligible.

Analytical Methods

The concentration of sulfite was determined iodometrically. 2-Propanol and acetone which was formed during the reaction did not interfere with the determination.

Acetone formed by induced oxidation of 2-propanol was determined by gas chromatography (Chrom 3, Laboratorní přístroje, Prague) with ionisation detection. The length of the chromatographic column was 2400 mm, the inner diameter was 6 mm. The column was filled with Chromosorb G Polyethylene Glycol 1500 20%. The injected quantity was 0.1 ml; the temperature of the injection chamber was 140°C and that of the column 110°C; the carrier gas was nitrogen. The concentration of acetone in the analysed mixture was determined from the ratio of the areas under the peaks of 2-propanol and acetone. In the range of the concentrations of acetone $8 \cdot 10^{-4} \text{ M}$ to $8 \cdot 10^{-3} \text{ M}$, the ratio was a linear function of the concentration of acetone. The change in the concentration of 2-propanol in the course of the reaction was negligible and had no influence on the value of the two peak areas. Sodium sulfite present in the analysed samples did not interfere with the determination of acetone.

* The term "induced oxidation" denotes that type of a cooxidation reaction where the oxidation of one substrate is contingent upon the oxidation of another substrate. Sometimes both the terms are considered as synonyms.

The results obtained were evaluated and the modelling of the kinetic dependences was made on a Hewlett-Packard calculator 9830A. All dependences were treated by the least squares method with a simultaneous evaluation of the scatter and the mean relative deviation.

RESULTS AND DISCUSSION

Kinetics of Autoxidation of Sulfite

In the presence of an inhibitor, in this case 2-propanol, the autoxidation of sulfite proceeds *via* two parallel reactions with a widely different velocity each. The rate of the autoxidation of sulfite is by two (and more) orders of magnitude higher than that of the induced reaction, *i.e.* the oxidation of the inhibitor. This fact, which makes a simultaneous kinetic study of the primary and the induced reactions a rather complicated affair, probably answers for the lack of kinetic studies of the induced reaction of molecular oxygen.

Data on the course of the autoxidation of sulfite given by various authors are at variance⁵ even for solutions of equal composition. Their low reproducibility is due to the fact that the reaction is a trace catalysed one. If, however, the concentration of the catalyst and that of the inhibitor are kept constant, reproducible results are obtained.

According to literary data⁵, the autoxidation of sulfite is a first order reaction with respect to the concentration of sulfite and a zero order reaction with respect to the concentration of oxygen. Deviations from the first order appear at concentration values which, however, vary with the author¹¹⁻¹³.

In our experiments, 0.6M- Na_2SO_3 was employed similarly as in the study by Bäckström¹; according to the literature, marked deviations from the first order should appear under these conditions. As is, however, seen in Fig. 1 in which $\log [\text{SO}_3^{2-}]_0 / [\text{SO}_3^{2-}]$ vs time is plotted, the reaction obeys a first order equation up to considerably high conversion degrees. Only at more elevated concentrations of the catalysing ions, *i.e.* for $c_{\text{Cu}} = 5 \cdot 10^{-3}\text{M}$, deviations from the first order to higher rates occur. It appears that the deviations from the first order reported in the literature⁵ are caused by other effects than the concentration of sulfite. As the concentration of sulfite increases, increases also the rate of the reaction and consequently also the possibility that the reaction is diffusion controlled.

Influence of 2-Propanol on the Kinetics of the Primary Reaction, i.e. on the Autoxidation of Sulfite*

According to Bäckström^{1,2} the dependence of the rate of the autoxidation of sulfite on the concentration of the inhibitor follows the equation

* The term "primary reaction" denotes a process whose course is decisive for the oxidation of another species; in the absence of the former reaction the induced oxidation by molecular oxygen would not proceed at all.

$$v = k_1 / (k \cdot C + k_2), \quad (1)$$

where k_1 , k_2 , k are constants and C is the concentration of the inhibitor. The value of k depends on the nature of the inhibitor, and is the measure of its inhibiting effect. For more elevated concentrations of the inhibitor $k \cdot C \gg k_2$, and equation (1) takes the form of (2)

$$v = k^* / C. \quad (2)$$

In Bäckström's papers^{1,2} the reaction rate is not accurately defined; the mean velocity was calculated by a simple division of the decrease in the sulfite concentration by time. The validity of relation (2) in the present paper was verified in two series of experiments at two different concentrations of the catalysing copper ions: $1 \cdot 10^{-5}$ and $5 \cdot 10^{-6}$ M. Through the experimentally found values of the rate constant, the rearranged "Bäckström equation" (1) was lead by the least squares method.

$$k = 1 / (k' + k''[(\text{CH}_3)_2\text{CHOH}]). \quad (3)$$

In Fig. 2, the values of the found reaction constants $k(\text{s}^{-1})$ of the autoxidation of sulfite are plotted at a constant concentration $c_{\text{Cu}} = 1 \cdot 10^{-5}$ M and a variable concentration of 2-propanol 0.1–1.5 M.

For constants k' and k'' the following values were found:

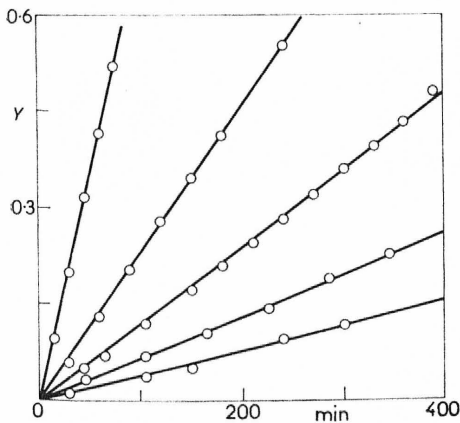


FIG. 1

Autoxidation of Sulfite, Validity of First Order Kinetic Law at Various Concentrations of 2-Propanol

$Y = \log ([\text{SO}_3^{2-}]_0 / [\text{SO}_3^{2-}])$ vs time.
 $[\text{SO}_3^{2-}]_0 = 0.6\text{M}$; $c_{\text{Cu}} = 1 \cdot 10^{-5}\text{M}$; $c_{\text{ox}} = \text{sat}$; $t = 20^\circ\text{C}$; [2-propanol]: from left to right 1.5M, 0.94M, 0.52M, 0.31M, 0.10M.

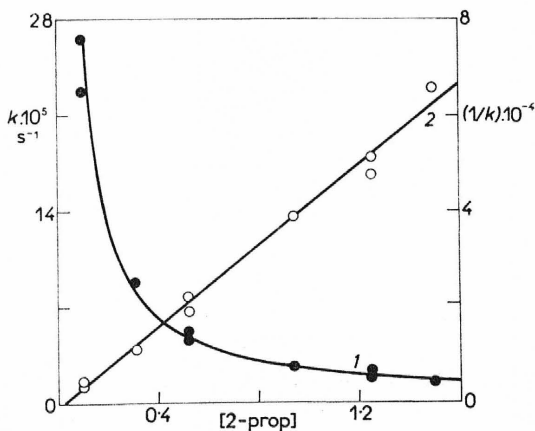


FIG. 2

Dependence of Velocity of the Autoxidation of Sulfite on Concentration of 2-Propanol
 $[\text{SO}_3^{2-}]_0 = 0.6\text{M}$; $c_{\text{Cu}} = 1 \cdot 10^{-5}\text{M}$; $c_{\text{ox}} = \text{sat}$; $t = 20^\circ\text{C}$; 1 values of rate constants $k(\text{s}^{-1})$ vs concentration of 2-propanol
 $2 \cdot 1/k$ vs concentration of 2-propanol.

$$k' = (-0.9058 \pm 2.869) \cdot 10^3 \text{ s}$$

$$k'' = (4.1998 \pm 0.325) \cdot 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{s}.$$

The dependence lead through the above points is given in Fig. 2. It follows from the reported values of k' and k'' and from the calculated errors that the value of k' is statistically not important and consequently the original relation (1) reduces to equation (2). For illustration, the linearised relation $1/k = k' + k'' \cdot [(\text{CH}_3)_2\text{CHOH}]$ was plotted in Fig. 2, and a straight line was lead through the values $1/k$.

In another series of experiments, the dependence of the rate constants $k(\text{s}^{-1})$ of the autoxidation of sulfite was related to the varying concentration of 2-propanol (0.1–1.5M) at a minute constant concentration of copper $c_{\text{Cu}} = 5.2 \cdot 10^{-6}\text{M}$. Through the experimental values of the constant $k(\text{s}^{-1})$, relation (3) was again lead. Constants k' and k'' acquire values $k' = (0.0065 \pm 1.633) \cdot 10^4 \text{ s}$, $k'' = (7.2892 \pm 1.815) \cdot 10^4 \cdot \text{mol}^{-1} \cdot \text{l} \cdot \text{s}$. Correspondingly to the foregoing dependence, the value of the constant k' is statistically unimportant and the experimental values conform to equation (2).

For both the above concentrations of copper the dependence of the rate constants of the autoxidation of sulfite on the concentration of 2-propanol was satisfactorily expressed by the simplified "Bäckström equation" (2).

Influence of Metal Ions on the Autoxidation of Sulfite at Constant Concentration of 2-Propanol

In the present paper, the influence of a variable concentration of copper was primarily studied. In addition, the influence of further 3d transition metals *i.e.* manganese, iron, cobalt, and nickel was compared.

The equipment used enabled measurements of reactions of a considerable velocity, the influence of the diffusion of oxygen on the overall rate of the autoxidation being eliminated. In spite of that, even when using the highest possible concentration of 2-propanol 1.5M (concentrations above this value induced deposition of sulfite from the reaction solution) it was possible to change the concentration c_{Cu} only in the range $c_{\text{Cu}} = 5 \cdot 10^{-6} - 1 \cdot 10^{-4}\text{M}$. At concentrations $c_{\text{Cu}} > 1 \cdot 10^{-4}\text{M}$, diffusion of oxygen may have influenced the kinetics of the reaction. The kinetics of the autoxidation of sulfite was therefore measured at a constant concentration of 2-propanol 1.5M and a variable concentration of copper ($5 \cdot 10^{-6} - 1 \cdot 10^{-4}\text{M}$). The dependence on the concentration of the catalyst is highly important for the formulation of the reaction mechanism and literary data on the reaction order with respect to the catalyst concentration vary a great deal⁵; for this reason, the rate constant was determined by several independent measurements for each copper concentration. Of all the experimental values obtained, the extreme two values (*i.e.* the highest and the lowest one obtained at one and the same concentration) were excluded, and a polynomial

of the first and second order were lead through. It appeared that the dependence is best satisfied by a polynomial of the first order passing through the origin with the slope $(1.296 \pm 0.098) \text{ s}^{-1} \cdot \text{mol}^{-1} \cdot \text{l}$. The rate of the autoxidation of sulfite catalysed by copper ions and inhibited by 2-propanol may thus be expressed by equation (4):

$$-d[\text{SO}_3^{2-}]/dt = \text{const} \cdot c_{\text{Cu}} \cdot [\text{SO}_3^{2-}]/c_{\text{inh}} \quad (4)$$

In a further series of experiments, the influence of a varying concentration of manganese on the rate of the autoxidation of sulfite at a constant concentration of 2-propanol was followed. In a reaction catalysed by manganese, deviations from the first reaction order (with respect to the concentration of sulfite) occur at a higher conversion degree, tending to lower velocities, *i.e.* just in the opposite sense than those in copper catalysed reactions. In a following series of experiments, the values of the rate constants $k(\text{s}^{-1})$ at a constant concentration of 2-propanol (1.5M) and a varying concentration of manganese were determined. If a straight line is lead through the values of the rate constants $k(\text{s}^{-1})$ obtained, a value of $(4.071 \pm 0.43) \text{ mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}$ and $(0.316 \pm 2.21) \text{ s}^{-1}$ are obtained for the slope and the intercept, respectively. From the magnitude of scatter follows that the intercept is negligible (statistically not important), and consequently the rate constant $k(\text{s}^{-1})$ of the autoxidation of sulfite increases, similarly as in copper catalysed reactions, directly with the increase in the concentration of manganese in the reaction solution. In the present reaction system (unbuffered solution of sulfite, $[\text{SO}_3^{2-}]_0 = 0.6\text{M}$, $\text{pH} = 8.5$), manganese(II) ions were catalytically superior to those of copper.

Iron(II) and cobalt(II) ions added to the reaction solution as catalysts were identical in behaviour. Immediately after their addition to the reaction solution a primary reaction (autoxidation of sulfite) proceeds at a very high rate which, in our classical experimental set-up, was beyond measurement. But soon the catalytic activity of the ions is lost and the reaction virtually stops. The depletion of sulfite immediately after the addition of the catalysts was found to increase with an increase in the concentration of the added catalyst. The loss of the catalytic activity of Fe(II) and Co(II) may most probably be ascribed to their oxidation to Fe(III) and Co(III) which, as was shown by spectrophotometry¹⁰, sets in at any chosen surplus of sulfite immediately upon the contact of the solution of sulfite complexes of Fe(II) or Co(II) with oxygen.

As compared to other cations studied, the ions of Ni(II) have only a weak influence. By comparing the catalytic activities of Ni(II) and Mn(II) it follows that concentrations of Ni(II) higher than those of Mn(II) by a factor of 10^3 are required to attain the same reaction rate at otherwise equal conditions. It is therefore most probable that Ni(II) alone has no catalytic effect on the autoxidation of sulfite at all, and that the increase of the rate following the addition of increasing quantities of nickel is due to copper and manganese present as impurities in the nickel salts.

The autoxidation of sulfite was catalysed by such metal ions which exist in two oxidation steps differing by unity: Mn(II, III), Fe(II, III), Co(II, III), and Cu(I, II). In those cases where the dependence on the concentration of the catalyst (*i.e.* for copper and manganese) could be followed, the rate of the reaction increased linearly with the concentration of the catalyst.

Kinetics of Induced Autoxidation of 2-Propanol

Literary data on the kinetics of induced reactions¹⁴ are scarce and the problem of the kinetics of the induced autoxidation of 2-propanol and the influence of the catalyst concentration on its velocity have not been studied at all.

In the present paper, the influence of a variable concentration of the catalyst and the influence of a variable concentration of 2-propanol on the kinetics of the induced oxidation of 2-propanol are studied.

In the first series of experiments, the influence of a variable concentration of 2-propanol (0.1–1.26M) at a constant concentration of copper $c_{\text{Cu}} = 1 \cdot 10^{-5}\text{M}$ was studied. It follows from Fig. 3 that acetone is formed at a constant rate irrespective of the employed concentration of 2-propanol (0.1–1.26M) and the degree of conversion of sulfite (followed up to 90% conversion *i.e.* 0.6–0.06M).

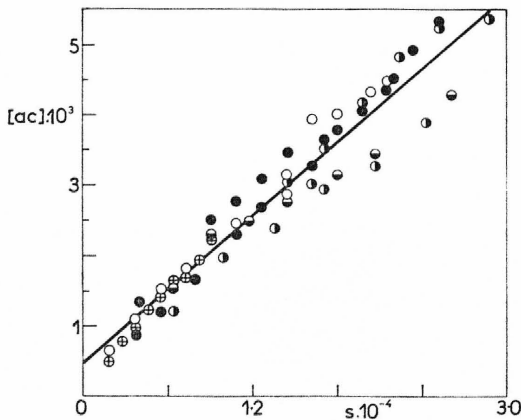


FIG. 3

Induced Oxidation of 2-Propanol; Concentrations of the Resulting Acetone *vs* Time at Various Concentrations of 2-Propanol

$[\text{SO}_3^{2-}]_0 = 0.6\text{M}$; $c_{\text{Cu}} = 1 \cdot 10^{-5}\text{M}$; $c_{\text{ox}} = \text{sat}$; $t = 20^\circ\text{C}$; [2-propanol]: $\oplus = 0.1\text{M}$; $\circ = 0.31\text{M}$; $\bullet = 0.52\text{M}$; $\ominus = 0.94\text{M}$; $\omin� = 1.26\text{M}$.

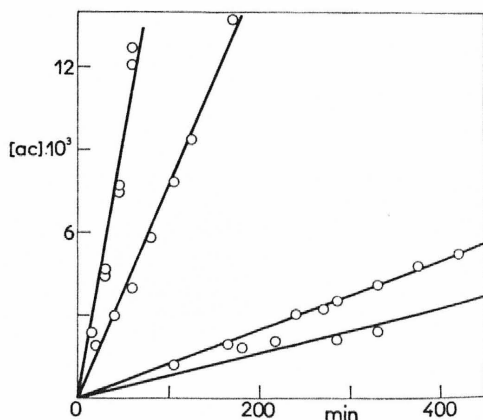


FIG. 4

Induced Oxidation of 2-Propanol; Concentrations of the Resulting Acetone *vs* Time at Various Concentrations of Copper

$[\text{SO}_3^{2-}]_0 = 0.6\text{M}$; [2-propanol] = 0.94M; $c_{\text{ox}} = \text{sat}$; $t = 20^\circ\text{C}$; c_{Cu} : from left to right $5.2 \cdot 10^{-6}\text{M}$; $1 \cdot 10^{-5}\text{M}$; $5.2 \cdot 10^{-5}\text{M}$; $1 \cdot 10^{-4}\text{M}$.

Through all the experimental values of the concentration of acetone, a straight line was lead by the least squares method (Fig. 3). The mean relative deviation amounted to only 9.31%. This experimental series confirmed the finding by Bäckström that the rate of the induced reaction does not depend on the concentration of 2-propanol and, in addition, demonstrated that in the concentration range under study it is even independent of the concentration of sulfite.

In another series of experiments, the influence of a variable concentration of copper at a constant concentration of 2-propanol (0.94M) on the rate of the induced reaction was studied. In Fig. 4 the concentrations of the resulting acetone are plotted *vs* time for various concentration values of copper ($5.2 \cdot 10^{-6} - 1 \cdot 10^{-4}$ M). Similarly as in the foregoing dependence on the concentration of 2-propanol, at a constant concentration of copper as well, acetone was formed at a constant rate irrespective of the degree of conversion of sulfite; the individual reaction courses could thus be approximated by straight lines. The slopes of the straight lines characterising the velocities of the formation of acetone are given in Table 1. Table 1 demonstrates that the velocity of the formation of acetone *i.e.* the rate of the induced reaction, increases linearly with the increase in the concentration of copper added into the reaction solution. The concentration of the catalyst is thus the only factor which determines the rate of the induced reaction at the given conditions ($[O_2] = \text{sat}$). The dependence obtained shows that if the concentration of the catalyst tends to zero both the rate of the primary reaction and that of the induced reaction *i.e.* the autoxidation of 2-propanol approach zero as well.

The rate of the induced oxidation of 2-propanol may therefore be expressed by equation (5)

$$-d[2\text{-propanol}]/dt = d[\text{acetone}]/dt = \text{const.}' \cdot c_{\text{Cu}} \quad (5)$$

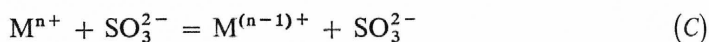
TABLE I

Dependence of the Rate of Induced Autoxidation of 2-Propanol on the Concentration of Copper
 $[SO_3^{2-}]_0 = 0.63\text{M}$, $[2\text{-propanol}]_0 = 0.94\text{M}$, $c_{0x} = \text{sat}$, $t = 20^\circ\text{C}$, $v_{ac} = -d[2\text{-propanol}]/dt = d[\text{acetone}]/dt$

$c_{\text{Cu}} \cdot 10^6$ mol . l ⁻¹	$v_{ac} \cdot 10^7$ mol . l . s ⁻¹	$(v_{ac}/c_{\text{Cu}}) \cdot 10^2$
5.2	1.360 ± 0.34	2.62
10.4	2.086 ± 0.04	2.01
52.0	12.815 ± 0.71	2.46
104.0	31.050 ± 3.38	2.98

Reaction Mechanism

The classical radical chain mechanism^{3,4,6} was formulated on the basis of photochemical studies of the reaction; the assumption of a chain reaction made it possible to explain high quantum yields. Based on the studies of the influence of inhibitors on photochemical and thermal reactions, the radical chain mechanism was also used to explain the mechanism of thermal reactions^{3,4}. As has however been shown⁸⁻¹⁰, reaction (B) cannot be a partial process of the photoinitiated autoxidation and the high quantum yields may be explained by another conception than the hypothesis of the free radical chain mechanism. There are, therefore, no reasons here for explaining the course of the thermal autoxidation of sulfite by the hypothesis of the radical chain mechanism. In addition, this explanation suffers from a serious deficiency: the reaction being catalysed by metal ions in the lower (and not the higher) oxidation step, the reaction

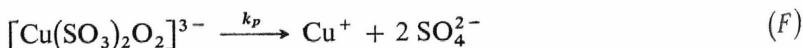
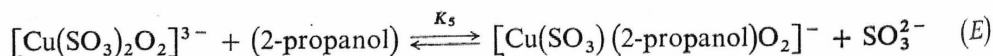
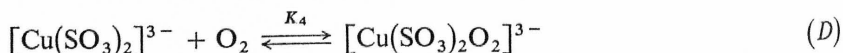


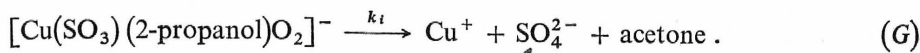
cannot be the initiating step of the radical chain reaction.

The mechanism of the autoxidation of sulfite must, in the first place, come out of well known facts on the state and the potential reactions of the catalysing metal ions in the reaction system. These facts, however, were not taken into account⁵ in spite of the fact that as early as 1903 Titoff¹³ reported that the autoxidation of sulfite was a trace metal catalysed reaction, and that in a complete absence of transition metal ions it would not proceed at all.

The catalysing metal ions and sulfite ions form considerably stable complexes and, therefore, are present in the reaction system almost exclusively in this form⁷. Tabulated values of equilibrium constants¹⁵ of sulfitocuprous complexes are $K_1 = 10^{7.85}$, $K_2 = 7.08$, $K_3 = 4.57$. It is most probable that the sulfitocuprous complexes form mixed complexes with other components present in the system, such as $[Cu(SO_3)_2O_2]^{3-}$, $[Cu(SO_3)_2(2\text{-propanol})]^{3-}$, $[Cu(SO_3)(2\text{-propanol})O_2]$. As was shown by Siegel¹⁶, the stability of mixed complexes is often considerably higher than that of the corresponding binary complexes.

Some of these complexes are probably redox active and react under the formation of sulfate or sulfate and acetone





According to this hypothesis, the mixed complex $[\text{Cu}(\text{SO}_3)_2\text{O}_2]^{3-}$ is the intermediate of the primary reaction, *i.e.* the autoxidation of sulfite, and the mixed complex $[\text{Cu}(\text{SO}_3)(2\text{-propanol})\text{O}_2]^-$ is the intermediate of the induced reaction, *i.e.* the autoxidation of 2-propanol. The rate of the autoxidation of sulfite and that of the induced oxidation of 2-propanol is then given by equations (6) and (7).

$$v = k_p \cdot [\text{Cu}(\text{SO}_3)_2\text{O}]^{3-} \quad (6)$$

$$v' = k_i \cdot [\text{Cu}(\text{SO}_3)(2\text{-propanol})\text{O}_2]^- . \quad (7)$$

Expressing the concentrations of the reactive mixed complexes by analytical concentrations of the reacting components and taking into account the appropriate equilibrium constants, we obtain (under the condition that copper is present in a catalytic concentration only, *i.e.* $c_{\text{Cu}} \ll c_{\text{sulf}}$) for the rate of the primary and the induced reactions the following relations (8) and (9):

$$v = k_p \cdot K_1 \cdot K_2 \cdot K_4 \cdot c_{\text{ox}} \cdot c_{\text{sulf}}^2 \cdot c_{\text{Cu}}/A \quad (8)$$

$$v' = k_i \cdot K_1 \cdot K_2 \cdot K_4 \cdot K_5 \cdot c_{\text{ox}} \cdot c_{\text{sulf}} \cdot c_{\text{inh}} \cdot c_{\text{Cu}}/A , \quad (9)$$

where

$$A = 1 + K_1 \cdot c_{\text{sulf}} + K_1 \cdot K_2 \cdot c_{\text{sulf}}^2 + K_1 \cdot K_2 \cdot K_3 \cdot c_{\text{sulf}}^3 + K_1 \cdot K_2 \cdot K_4 \cdot c_{\text{ox}} \cdot c_{\text{sulf}}^2 + K_1 \cdot K_2 \cdot K_4 \cdot K_5 \cdot c_{\text{ox}} \cdot c_{\text{sulf}} \cdot c_{\text{inh}} ,$$

c_{Cu} , c_{sulf} and c_{ox} are overall, *i.e.* analytical concentrations of copper, sulfite, and oxygen, K_1 , K_2 and K_3 are stability constants¹⁵ of sulfitecuprous complexes, K_4 and K_5 are equilibrium constants of reactions (D) and (E). Inserting tabulated values of constants K_1 , K_2 and K_3 into (8) and (9) and assuming that $K_4 > 10^5$ and $K_5 > 10^2$ expressions (8) and (9) are reduced to equations (4) and (5), *i.e.* they are identical to relations obtained for the rate of the induced reaction by experiment.

The assumption that the intermediates of the reactions of molecular oxygen are mixed complexes is frequently accepted in the case of enzymatic reactions, and in several systems it was experimentally confirmed¹⁷. The suggested mechanism of the autoxidation of sulfite postulates that the reaction intermediates are mixed complexes $[\text{Cu}(\text{SO}_3)_2\text{O}_2]^{3-}$ and $[\text{Cu}(\text{SO}_3)(2\text{-propanol})\text{O}_2]^-$, and that their stability constants are $K_4 > 10^5$ and $K_5 > 10^2$. If the assumed values of the stability constants K_4 and K_5 are reasonable the suggested mechanism is correct. In contrast to the radi-

cal chain mechanism^{1-4,6}, the suggested associative mechanism of the autoxidation of sulfite is not at variance with any one known experimental fact and permits an explanation of all the features of the thermal reaction.

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Translated by M. Svatá.