

## REACTIONS IN FUSED SALTS. VII.\*

OXIDATION OF SULPHITE IONS WITH OXYGEN  
IN A MELT OF EUTECTIC MIXTURE OF LITHIUM  
AND POTASSIUM CHLORIDES

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The reaction of sulphite ions with gaseous oxygen in melts of lithium and potassium chlorides has been studied in the temperature range 414–504°C. It was found that the rate of change of the concentration of sulphite can be described by the empirical equation  $r = -d[\text{SO}_3^{2-}]/dt = k'p_{\text{O}_2}$ , where  $k'$  depends on temperature (activation energy 15 kcal/mol), on oxygen flow rate and on the initial concentration of sulphite ions in the melt. On the basis of analysis of experimental results a hypothesis is proposed on the possible reaction mechanism.

The first study of oxidation of sulphite ions with oxygen was carried out by Bäckström<sup>1</sup> and was later interpreted by Franck and Haber<sup>2</sup> who assumed the formation of free radicals by electron transfer. In the presence of cupric ions the radical  $\text{SO}_3^{\cdot-}$  is formed first which is in equilibrium with  $\text{HSO}_3^{\cdot}$ . In the presence of oxygen a chain reaction takes place, while in its absence dimerization of the radical  $\text{HSO}_3^{\cdot}$  occurs, yielding dithionic acid. Formation of the radical  $\text{HSO}_3^{\cdot}$  as intermediate was also assumed by Baumgartner and Eber<sup>3</sup>. Abel<sup>4</sup> suggested a general scheme of anionic autoxidation according to which radicals  $\text{O}_2^{\cdot-}$  and  $\text{OH}^{\cdot}$  formed in the reaction of water with oxygen initiate the reaction proper. Recently, Schroeter<sup>5,6</sup> has also dealt with the reaction of sulphite ions assuming, too, the radical mechanism as suggested by Abel. Some authors<sup>7,8</sup> applied the process of oxidation of sulphite ions with oxygen to investigate the diffusion phenomena in the absorption of gas in to solution and demonstrated the relation between the rate of absorption of oxygen into the solution of sulphite ions and the rate of chemical reaction.

## EXPERIMENTAL

## Apparatus and Chemicals

Experimental arrangement was similar to that described in paper<sup>9</sup>. Eutectic mixture of LiCl–KCl was prepared from chemicals (Merck) which were freed from organic admixtures by addition of potassium perchlorate (0.5 g per 100 g of the eutecticum) at c. 500°C under simultaneous bubbling with nitrogen for one hour. In some experiments chemicals designated "Suprapur" were used without any further treatment. Sodium sulphite (Merck) was used without further

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purification. Some other compounds which were used, all of them in small amounts, as admixtures ( $\text{Na}_2\text{S}_2\text{O}_5$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{O}_2$ ) were products of Lachema and were not further treated. The gases used (oxygen, nitrogen) were dried by bubbling through concentrated sulphuric acid and passing over potassium hydroxide.

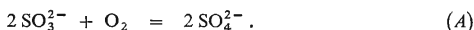
### Procedure

The fused eutecticum, previously bubbled through with nitrogen, was treated with appropriate amount of sodium sulphite and after dissolution and after having taken the zero-th sample oxygen was started to bubble through the melt. Samples of the melt were taken in suitable time intervals and were analyzed iodometrically for sulphite ions.

In order to establish the stoichiometry of the reaction several of the experiments were carried out in a closed system. The whole system was first evacuated and then filled with oxygen (partial pressure equal to unity) and the volume absorbed was measured. After the experiment had been finished the content of sulphite and sulphate ions in the melt was determined (by precipitation as barium sulphate). The experiments were carried out in the concentration range 0.13–0.77 mol/kg sodium sulphite, at partial pressures of oxygen 0.2–1 atm and at oxygen flow rates 50–400 ml/min. Total weight of the melt was 30 g throughout. Concentration of sulphite ions is expressed in molalities ( $\text{mol kg}^{-1}$ ).

### RESULTS AND DISCUSSION

Reaction of sulphite ions with oxygen proceeds up to a total disappearance of these ions from the solutions. Analyses after finishing the reaction and the results of measurements in a closed system showed that 1 mol of oxygen is consumed per two moles of sulphite ions under the formation of 2 mol of sulphate ions. The overall reaction can be written in the form



From the kinetic data it was found that the rate of sulphite ions oxidation with oxygen is of the 1st order with respect to the partial pressure of oxygen, is independent of the concentration of sulphate ions and in the course of the experiment is also independent of the concentration of sulphite ions in the melt (Fig. 1). The rate of decrease of the concentration of sulphite can thus be formally described by the following empirical equation

$$r = -d[\text{SO}_3^{2-}]/dt = k' p_{\text{O}_2}. \quad (1)$$

However, the rate constant  $k'$  depends not only on temperature, but also on both the flow rate of gas and on the initial concentration of sulphite in the melt ( $[\text{SO}_3^{2-}]_0$ ). Activation energy, calculated from the temperature dependence of  $k'$ , is 15 kcal/mol.

With respect to the rate of decrease of the concentration of sulphite on the flow rate of oxygen, the possibility must be taken into account that the rate of reaction

of sulphite ion with oxygen is affected by the rate of oxygen transfer through the gas-melt interface. The transfer rate is directly proportional to the total interface area. According to experimental data the dependence of the reaction rate on the flow rate of oxygen is a straight line which does not intersect the coordinates origin.

According to Yagi and Inoue<sup>8</sup> who measured the rate of reaction of dissolved oxygen with sulphite ions in aqueous solution by means of polarography, the reaction is first order with respect to the concentration of dissolved oxygen. In further experiments they led the gaseous oxygen into the solution of sulphite ions and determined the rate of oxygen absorption. By comparison of both parts of the work using penetration and film theory they demonstrated the relation between the absorption rate of oxygen into the solution of sulphite ions and the rate of chemical reaction. They classified the absorption of oxygen by the solution of sulphite ions as physical absorption, accompanied by a 2nd order chemical reaction, in the liquid film at the interface.

In the case of the reaction of sulphite ions in the melt with oxygen we assume that first of all oxygen is dissolved in the melt



and subsequently it reacts irreversibly with the sulphite ion dissolved in the liquid phase (or in the liquid film)

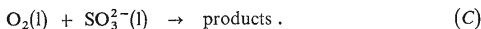
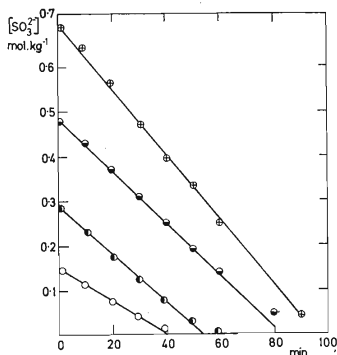
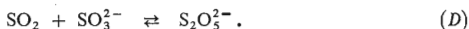


FIG. 1  
Time Dependences of the Decrease of Sulphite Ions Concentration during Their Reaction with Oxygen

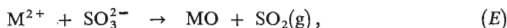
Flow rate of oxygen 200 ml/min,  $[\text{SO}_3^{2-}]_0$  (mol kg<sup>-1</sup>): ○ 0.144, ● 0.276, ● 0.478, ⊕ 0.690. Full lines denote calculated values.



A very difficult problem is the interpretation of the effect of initial concentration of sulphite on the rate constant  $k'$ . In the course of the experiment the rate of decrease of the concentration of sulphite ions is independent of the concentration of sulphite ions, however, a higher initial concentration of sulphite in the melt causes an increase in the reaction rate, Therefore it is necessary to find the difference between the sulphite concentration which changes during the reaction with oxygen and the initial sulphite concentration. It has been demonstrated experimentally that addition of sulphide, polysulphide, thiosulphate and of other decomposition products of sulphite does not affect the rate of decrease of the concentration of sulphite. The possibility of the effect of products of protolytic reactions of sulphite was also investigated. Addition of sulphur dioxide to oxygen causes a rather distinct increase in the rate of oxydation of sulphite ion in the melt. Therefore we assumed that the active ion could be the disulphite formed in the reaction



However, addition of disulphite to the melt did not affect the reaction rate. Also the addition of oxide or peroxide ions had no considerable effect on the reaction rate. The effect of superoxide<sup>10</sup> in the presence of oxygen remained also unproved, since neither saturation of oxygen with water vapour nor carrying out the reaction in a platinum crucible resulted in any change in the rate of oxidation of sulphite ions. The last possibility to be considered was the catalytic effect of some trace admixtures (*e.g.* cations of heavy metals) which are either present in the chemicals used or can appear in the melt as the result of corrosion of the reaction vessel. A greater content of these cations is improbable since it has been found that they react with sulphite ions in the melt according to equation



where  $\text{M}^{2+}$  denotes *e.g.* a bivalent ion of a heavy metal. The evolution of sulphur dioxide from the melt is thus a good indication of even small amounts of heavy metals. Moreover, this conclusion was verified by using "Suprapur" chemicals which did not affect the rate of sulphite oxidation by oxygen. Actually, it is not possible, when working with fused salts, to exclude the presence of trace amounts of impurities which can be catalytically active only up to their threshold concentration<sup>11</sup>.

However, even this assumption did not correspond completely to the experimental data. To explain the effect of  $[\text{SO}_3^{2-}]_0$  on the rate constant of the reaction, the source of trace catalyst should be the sulphite used. This would mean that after the reaction is finished, a further addition of sulphite should have a double effect since a greater amount of catalyst would accumulate in the melt. This assumption was not verified.

However, the concentration of the catalyst might possibly decrease *e.g.* by reaction (E). For this reason, experiments were carried out in which the melt was bubbled with nitrogen for a long time and only then the reaction with oxygen was continued. The reaction

TABLE I

Values of Empirical Constant  $k'$  (Eq. (I)) under Various Conditions

$p_{\text{CO}_2}$  1 atm, flow rate 200 ml/min.

$t$ °C	$k' \cdot 10^3$ mol kg <sup>-1</sup> · min <sup>-1</sup> atm <sup>-1</sup>	$[\text{SO}_3^{2-}]_0$ mol kg <sup>-1</sup>	$t$ °C	$k' \cdot 10^3$ mol kg <sup>-1</sup> · min <sup>-1</sup> atm <sup>-1</sup>	$[\text{SO}_3^{2-}]_0$ mol kg <sup>-1</sup>
448	4.5	0.276	504	10.6	0.463
448	4.5	0.274	504	14.5	0.735
452	4.5	0.283	450	3.06	0.295 <sup>b</sup>
451	4.4	0.266 <sup>a</sup>	452	2.6	0.277 <sup>b</sup>
449	3.6	0.134	452	2.4	0.280 <sup>c</sup>
450	3.6	0.144	450	2.1	0.288 <sup>c</sup>
449	6.5	0.470	450	6.85	0.280 <sup>d</sup>
450	5.3	0.478	448	4.8	0.270 <sup>e</sup>
448	7.4	0.690	448	4.9	0.270 <sup>f</sup>
450	6.7	0.755	448	5.6	0.271 <sup>g</sup>
415	2.8	0.273	476	5.5	0.281 <sup>h</sup>
416	2.4	0.286	476	5.75	0.288 <sup>i</sup>
415	1.9	0.139	476	5.8	0.283 <sup>j</sup>
415	2.7	0.482	476	5.9	0.310 <sup>k</sup>
416	3.3	0.755	476	15.7	0.328 <sup>l</sup>
476	5.2	0.142	450	3.0	0.278 <sup>m</sup>
476	6.6	0.278	450	3.6	0.283 <sup>m</sup>
474	6.9	0.264	452	4.3	0.278 <sup>n</sup>
476	7.3	0.452	452	4.4	0.287 <sup>o</sup>
476	9.2	0.740	452	4.3	0.260 <sup>p</sup>
504	7.0	0.139	452	4.1	0.277 <sup>r</sup>
504	9.0	0.274	452	5.3	0.352 <sup>r</sup>
498	10.0	0.255			

<sup>a</sup> +0.3 mol/kg SO<sub>4</sub><sup>2-</sup> from the beginning of the experiment; <sup>b</sup> flow rate 100 ml/min; <sup>c</sup> flow rate 50 ml/min; <sup>d</sup> flow rate 390 ml/min; <sup>e</sup>  $p_{\text{O}_2}$  0.5 atm; <sup>f</sup>  $p_{\text{O}_2}$  0.75 atm; <sup>g</sup>  $p_{\text{O}_2}$  0.25 atm; <sup>h</sup> oxygen bubbled through water (50°C); <sup>i</sup> +0.2 mol/kg O<sup>2-</sup> (as sodium peroxide); <sup>j</sup> +0.05 mol/kg O<sup>2-</sup> (as sodium peroxide); <sup>k</sup> in a platinum crucible; <sup>l</sup> 20 ml of SO<sub>2</sub> added by means of a syringe into the melt in the first and the fifth minute; <sup>m</sup> bubbled with nitrogen overnight and then treated with oxygen; <sup>n</sup> +7 mg of sodium pyrosulphite at the beginning of the experiment; <sup>o</sup> +10 mg sodium thiosulphate at the beginning of the experiment. <sup>p</sup> in LiCl-KCl, grade Suprapur; <sup>r</sup> reacted for 60 min up to  $[\text{SO}_3^{2-}] = 0$ , then again treated with sodium sulphite and again reacted for 60 min.

was found to go on after the interruption at the same rate. On the basis of these experiments the only remaining possibility is the desactivation of catalytic admixtures directly in the reaction with oxygen.

Recently, a paper appeared<sup>12</sup> in which an interesting chain mechanism of this reaction was proposed, based on electronic spectra of the unstable intermediates for photochemically initiated autoxidation of sulphite. It is worth mentioning that the authors consider only radicals of the  $\text{SO}_n^-$  type, *i.e.* compounds containing no hydrogen. Possibly, these reactions may proceed even in melts since photochemical initiation can be substituted by electron transfer.

Evidently, to verify this hypothesis new informations in the field of sulphite chemistry in melts are necessary.

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