

**EFFECT OF THE GAS PHASE COMPOSITION
AND OF THE METHOD OF THE PREPARATION OF THE SOLID
ON THE REACTION KINETICS OF SODIUM SULPHITE OXIDATION***

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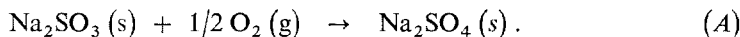
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The effect has been investigated of the partial pressure of oxygen (from 37 to 293 Torr) and of water vapour (from 10^{-4} to 17.5 Torr) on the course of oxidation of the solid sodium sulphite in the range of temperatures from 270 to 334°C. The sodium sulphite has been prepared by reacting an active sodium carbonate with the gaseous sulphur dioxide. The energy of activation has been evaluated and the dependences of the parameters of the Avrami's type kinetic equation have been determined. Comparative reactivity measurement have been carried out with samples of the sodium sulphite prepared by different methods. The process of a simultaneous formation and oxidation of the sodium sulphite has been investigated.

In the previous paper¹ an experimental technique which enables to measure continuously the oxidation rate of solids and the use of this technique in a study of the oxidation of sodium sulphite — reaction (A) — with the humid air have been described.



It has been shown¹ that the rate of oxidation of the sodium sulphite, occurring in a differential fixed bed reactor, may be expressed as a function of the feed rate, F_0 , of the mole fraction of oxygen, y_0 , of the number of moles of the solid in the bed, n_s , and of the mole fraction of oxygen at the reactor outlet, y . The reaction rate, r , is given by the relation

$$r \equiv dx/d\tau = (2F_0/n_s) (y_0 - y) / [(1 - y_0) + (y_0 - y)], \quad (\text{I})$$

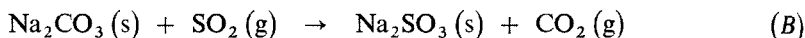
where x is the degree of conversion of the solid and τ is the time. In this notation, the dependence of the degree of conversion on time is given by the following expression

$$x_\tau = (2F_0/n_s) \int_0^\tau \{(y_0 - y) / [(1 - y_0) + (y_0 - y)]\} d\tau; \quad (\text{2})$$

* Part II in the series Kinetics of the Oxidation of the Solid Sodium Sulphite by Oxygen; Part I: This Journal 40, 827 (1975).

the integral on the right hand side of the equation (2) is evaluated by numerical integration; the input data are the time dependence of the continuously measured quantity ($y_0 - y$).

The present work aims at an investigation of the effect of the gas phase composition and of the genesis of the solid on the kinetics of the reaction (A). In addition, the simultaneous action of the sulphur dioxide and of the oxygen on an active sodium carbonate has been investigated, when the formation of the sodium sulphite



and the subsequent reaction (A) take place. The hindering effect of the presence of oxygen in the gas phase on the kinetics of the reaction (B) at temperatures exceeding

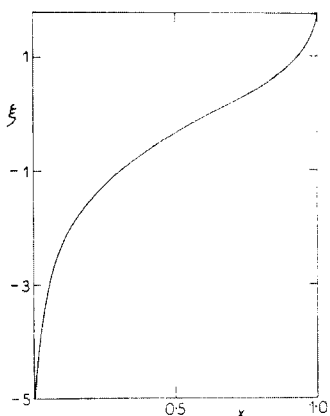


FIG. 1

Dependence of ξ on Degree of Conversion x According to Equation (5)

$$\lim_{x \rightarrow 0} \xi = -\infty, \quad \lim_{x \rightarrow 1} \xi = \infty,$$

$$x = 0.9999 \quad \xi = 2.25.$$

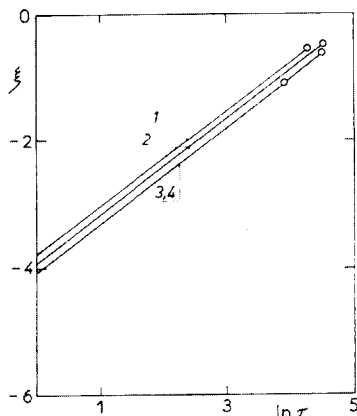


FIG. 2

Time Dependence of Degree of Conversion According to Equation (4) for Different Concentrations of Water Vapour in Gas Phase

Time τ in minutes, \circ values determined by analysis of the solid at the end of the experiment. 1 $p_{\text{H}_2\text{O}} \approx 10^{-4}$, $t = 307.5^\circ\text{C}$, $n = 0.746$, $k = 10.25 \cdot 10^{-5}$; 2 $p_{\text{H}_2\text{O}} = 17.535$, $t = 305.4^\circ\text{C}$, $n = 0.762$, $k = 9.63 \cdot 10^{-5}$; 3 $p_{\text{H}_2\text{O}} = 5.777$, $t = 304.1^\circ\text{C}$, $n = 0.770$, $k = 8.09 \cdot 10^{-5}$; 4 $p_{\text{H}_2\text{O}} \approx 10^{-4}$, $t = 303.6^\circ\text{C}$, $n = 0.743$, $k = 8.43 \cdot 10^{-5}$.

Values of correlation coefficients of the straight lines: 1 0.9983, 2 0.9997, 3 0.9992, 4 0.9995.

160°C has been ascribed² to the oxidation of the sodium sulphite being formed, however, without any proof of quantitative nature.

EXPERIMENTAL

Chemicals

The sodium sulphite has been prepared by reacting an active sodium carbonate with the gaseous sulphur dioxide in the way described previously¹. The measurements have been carried out with a sample of the particle size up to 0.1 mm. In an alternative test, a commercial sample of Na₂SO₃ A. G. (Lachema) containing 99% of the sodium sulphite and 0.06% of the sodium carbonate has been used. As reported, this sample has been prepared by crystallization at temperatures exceeding 33.4°C.

Gaseous mixtures of oxygen and nitrogen have been prepared in a mixing pressure tank². The content of water vapour in the gas has been adjusted during measurements either by keeping the water saturator at a constant temperature or by inserting a column with a drying agent (ascarite and the molecular sieve Calsite 5A). The remaining substances and gases have been prepared or purified in the way described previously¹.

Analytical Methods

The solids and the gas have been analyzed in the same way as described in the previous paper¹. In measurements with different contents of oxygen in the gas, the sensitivity of the electrochemical oxygen analyzer has been varied in such a way that the composition of 0.05 y₀ corresponded approximately to 50 mm of the record. Thus, with a feed composition of 5 mole percents of oxygen the measurements were carried out with the maximum sensitivity when the analyzer signal has been recorded with a sensitivity of 200 mm to 1% of oxygen in the gas. The apparatus, procedure of measurement, and evaluation of results have been described in the previous paper¹.

RESULTS

The reaction course has been described by the kinetic equation¹

$$x = 1 - \exp [-(k\tau)]^n \quad (3)$$

which fits even the experimental data obtained in this study.

The dependence of the degree of conversion on time is given in the linearized form as

$$\zeta = n \ln k + n \ln \tau, \quad (4)$$

where ζ is a function of x defined by the relation

$$\zeta = \ln [-\ln (1 - x)]. \quad (5)$$

The transformation given by the equation (5) is illustrated in the Fig. 1.

For the dependence of the reaction rate r on the degree of conversion and on the time, the following expressions are valid:

$$r = kn(1 - x) [-\ln(1 - x)]^{(n-1)/n} \quad (6)$$

and

$$r = k^n n \exp [-(k\tau)]^n \tau^{n-1}. \quad (7)$$

Effect of the Presence of Water Vapour in the Gas on the Reaction Course

Kinetics of the reaction has been studied in the range of partial pressures of water vapour from approximately 10^{-4} Torr (gas dried with molecular sieve) up to 17.53 Torr at temperatures near to 305°C and at a partial pressure of oxygen of 157 Torr (air).

The time course of the reaction at various humidities of air is illustrated in the Fig. 2. In the Table I, the values of rate constants, referred by means of the Arrhenius equation to the temperature of 305.0°C (the energy of activation $E = 24.2$)¹ are given.

It is evident that the course of the reaction (A) does not depend on the partial pressure of water vapour in the gas. The mean value of the rate constant at 305.0°C is $(9.01 \pm 0.40) \cdot 10^{-5}$ with a maximum deviation of 7 relative percents. The average value of the exponent n amounts to 0.755 ± 0.011 ; this is in a good agreement with the value determined previously¹ in the oxidation with humid ($p_{\text{H}_2\text{O}} = 17.535$) air: $n = 0.756$.

Effect of the Partial Pressure of Oxygen

The effect of the partial pressure of oxygen on the course of oxidation has been investigated at a constant temperature of $305.0 \pm 0.1^\circ\text{C}$ and at a constant partial pressure of the water vapour of 17.535 Torr in a range of oxygen partial pressures

TABLE I
Value of Rate Constant k at Different Partial Pressures of Water Vapour
 $t = 305.0^\circ\text{C}$

$p_{\text{H}_2\text{O}}$, Torr	$k \cdot 10^5$, s^{-1}
10^{-4}	9.34
10^{-4}	8.86
5.77	8.35
17.535	9.47

from 36.7 to 293 Torr (*i.e.* from 4.9 to 38.9 volume percents of oxygen in the gas). The results of ten experiments have been taken into account in addition to the measurement with the air.

The dependences of the reaction rate on the degree of conversion for typical cases are illustrated in the Fig. 3. The time dependence of the conversion degree in corresponding experiments is plotted in the Fig. 4, where the found values of kinetic parameters are given, too. It is evident that with the partial pressure of oxygen not only the value of the rate constant but also the values of the exponent n are varying.

From the results of these measurements and from the values obtained in the measurement with the air¹ ($n = 0.756 \pm 0.013$), the dependence of the exponent n on the partial pressure of oxygen has been evaluated as

$$n = 0.874 - 0.7467 \cdot 10^{-3} p_{\text{O}_2}. \quad (8)$$

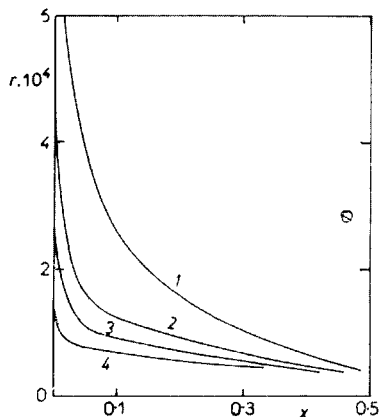


FIG. 3

Dependence of Reaction Rate r on Degree of Conversion x

$t = 305.0 \pm 0.1^\circ\text{C}$; partial pressure of oxygen, Torr: 1 293.1, 2 151.7, 3 68.7, 4 36.7.

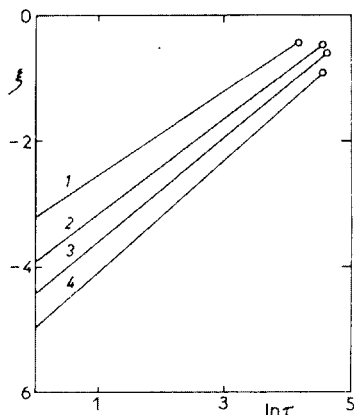


FIG. 4

Time Dependence of Degree of Conversion According to Equation (4) at Different Partial Pressures of Oxygen

Time τ is given in minutes; \circ values determined by analysis of the solid phase at the end of the experiment $t = 305.0 \pm 0.1^\circ\text{C}$. 1 $p_{\text{O}_2} = 293.1$ Torr, $n = 0.6618$, $k = 13.16 \cdot 10^{-5}$; 2 $p_{\text{O}_2} = 151.7$ Torr, $n = 0.762$, $k = 9.63 \cdot 10^{-5}$; 3 $p_{\text{O}_2} = 68.7$ Torr, $n = 0.8272$, $k = 7.26 \cdot 10^{-5}$; 4 $p_{\text{O}_2} = 36.7$ Torr, $n = 0.8870$, $k = 6.10 \cdot 10^{-5}$.

Values of correlation coefficient of straight lines: 1 0.9997, 2 0.9997, 3 0.9998, 4 0.9995.

The dependence of the effective rate constant k can be expressed in the form

$$k = K p_{O_2} / (1 + K_{O_2} p_{O_2}), \quad (9)$$

where the constants K and K_{O_2} are functions of temperature only. At a temperature of 305.0°C the following values have been found by the method of averages

$$K = 2.575 \cdot 10^{-6} \text{ Torr}^{-1} \text{ s}^{-1}$$

and

$$K_{O_2} = 2.0345 \cdot 10^{-2} \text{ Torr}^{-1}.$$

The dependence (9) and the values of rate constants determined from experimental data are illustrated in the Fig. 5.

Activation Energy of the Reaction (A)

The effect of temperature on the reaction course has been measured at a lower level of the partial pressure of oxygen than in the measurements with the air reported previously¹. The measurements have been carried out in the temperature range from 270 to 344°C at a partial pressure of oxygen of 38.5 ± 2 Torr, and at a constant humidity ($p_{\text{H}_2\text{O}} = 17.535$). The results of seven experimental series have been evaluated.

The kinetic equation (3) or (6) and (7) reproduces the reaction course in all the regimes studied and meets the assumption that the kinetic equation may be written in the form of

$$r = k(T, p_{O_2}) f(x). \quad (10)$$

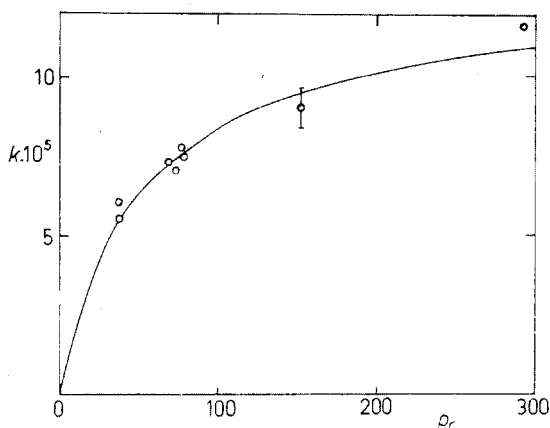


FIG. 5
Dependence of Rate Constant k
on Partial Pressure of Oxygen
 $t = 305.0 \text{ C}$; the curve represents the dependence (9).

Consequently, the activation energy may be determined from the dependence of $\log r$ on $1/T$ at a constant degree of conversion, x^1 . The dependences obtained are illustrated in the Fig. 6. The corresponding energies of activation amount to

$$E = 23.41 \quad \text{at} \quad x = 0.1$$

$$E = 24.41 \quad \text{at} \quad x = 0.2.$$

These values are in a good agreement with the values obtained at $p_{O_2} = 157$ Torr. The average value of activation energy of the reaction (A) evaluated from the measurements at both partial pressures of oxygen amounts to

$$E = 24.02 \pm 0.72 \text{ kcal mol}^{-1}.$$

Reactivity of the Solid Sodium Sulphite in Dependence on the Method of Preparation

The reactivity of the sample of the sodium sulphite prepared from an active sodium carbonate has been compared with that of the commercial sample. The latter was

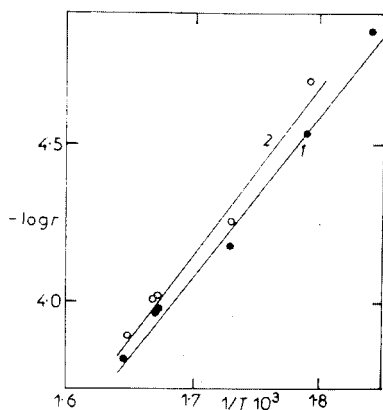


FIG. 6

Dependence of Reaction Rate on Temperature at Constant Partial Pressure of Oxygen and Constant Degree of Conversion x

$p_{O_2} = 36.7$ Torr; 1 $x = 0.1$, $\log r = 5116.5/T - 4.6217$, correlation coefficient = 0.9859; 2 $x = 0.2$, $\log r = 5333.4/T - 4.920$, correlation coefficient = 0.9806.

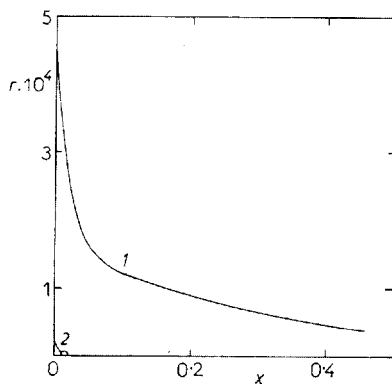


FIG. 7

Dependence of Reaction Rate on Degree of Conversion x

$t = 305.0^\circ\text{C}$, humid air; 1 substance prepared from the active sodium carbonate, 2 commercial sample.

reported to have been prepared by crystallization from solution and it has reacted with the oxygen at a rate which was at least one order of magnitude lower. The dependences of the reaction rate on the degree of conversion are illustrated in the Fig. 7. In the case of the commercial sample, the oxidation of 1.55% has been obtained within 48 minutes, and the corresponding reaction rate was lower than $6 \cdot 10^{-6}$. With the second sample, the oxidation of 31.5% has been obtained within the same time interval.

Simultaneous Formation and Oxidation of the Sodium Sulphite

The process in which the reaction (B) and the consecutive reaction (A) take place simultaneously has been investigated in the following way: the sulphur dioxide (approximately 1 volume percent) and air have acted on the active sodium carbonate and this gas mixture was led through the bed of the sodium carbonate until a twofold of the stoichiometric amount of the sulphur dioxide has passed (approximately 60 min). Thereafter the solid has been analyzed. The results of measurements carried out at 100–300°C are illustrated in the Fig. 8.

The oxidation of the sodium sulphite being formed takes place at a much higher velocity than in the cases studied previously, *i.e.* when the reaction (B) does not take place simultaneously. The oxidation plays a significant role already in the range of temperatures from 140 to 180°C, and at higher temperatures the rate-controlling

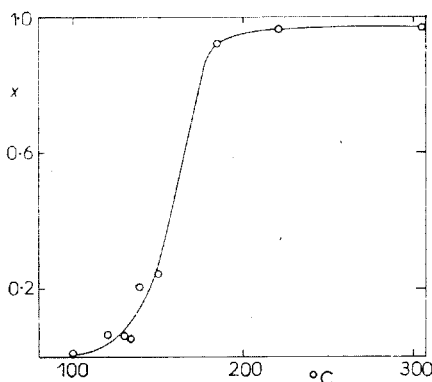


FIG. 8

Degree of Oxidation of Sodium Sulphite During Simultaneous Action of Sulphur Dioxide and Oxygen on Sodium Carbonate

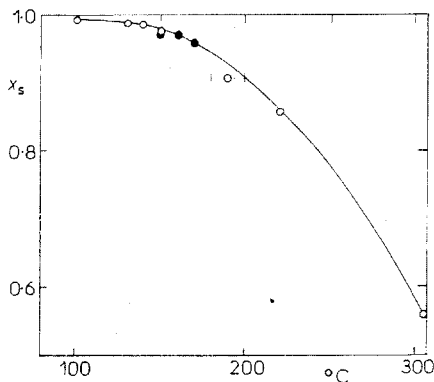


FIG. 9

Dependence of Degree of Conversion of Sodium Carbonate x_s on Temperature

○ Measurements carried out in this study, $p_{\text{SO}_2} = 7$ Torr, $W = 2$, ● data², $p_{\text{SO}_2} = 1$ Torr, $W = 1.3$.

step of the process is the formation of the sodium sulphite, the sodium sulphate being practically the only reaction product. With increasing degree of oxidation of the sulphite being formed, the attainable degree of conversion of the sodium carbonate to sodium sulphite or sulphate decreases. Let us define the quantity x_s by the relation

$$x_s \equiv (n_{\text{Na}_2\text{SO}_3} + n_{\text{Na}_2\text{SO}_4})/n_{\text{Na}_2\text{O}} \quad (11)$$

as a degree of conversion of the carbonate to sulphur compounds. The dependence of x_s on the temperature is illustrated in Fig. 9. The quantity W denotes the multiple of the stoichiometric amount of the sulphur dioxide passed through the bed²:

$$W = F_0 Y_{\text{SO}_2} \tau / n_{\text{Na}_2\text{O}} \cdot \quad (12)$$

DISCUSSION

The most striking feature of the reaction studied is the dependence of the reaction course on the genesis of the solid. This phenomenon seems rather usual with the solids and frequently it stems from structural reasons.

The structure of the sodium sulphite has been investigated recently by Larsson³ with samples prepared by crystallization from solution. The same author investigated the structure of the sodium carbonate prepared in a dry way from the active sodium carbonate, and he has found⁴ that both the dimensions of the unit cell and the structural type are identical, *i.e.* the space group $P\bar{3}$, $a = 5.45$, $c = 6.17$. Therefore, the differences in the reactivity of the samples cannot be explained by differences on the level of structural units.

It is probable that a significant role in the reactivity is played by the arrangement of microcrystallites in the skeleton of the solid. According to Larsson⁴, the sodium sulphite, formed from the sodium carbonate which has been prepared from monocrystals of the sodium hydrogen carbonate, consists of the aggregate of small, randomly arranged crystals. This fact corresponds to the kinetic behaviour of the active sodium carbonate with respect to the sulphur dioxide as it has been interpreted

TABLE II
Surface Area of Solids

Substance	NaHCO ₃	Na ₂ CO ₃	Na ₂ SO ₃	Na ₂ SO ₄
Specific surface area, m ² /g	0.015	2.83	2.47	2.40
Surface area, m ² /mol Na ₂ O	1.3	300	311	341

by means of a growth model of statistical nature⁵. The surface area of substances in which the consecutive reactions (B) and (A) take place does not practically change during the conversions. The data on the surface areas of these substances obtained by the desorption method are given in the Table II. The sodium hydrogen carbonate represents the parent substance for the preparation of the active sodium carbonate. The oxidation of the sulphite, however, takes place in an entirely different way than its formation, even though both reactions evidently take place on a similar crystal matrix. The oxidation takes place more slowly, with a higher energy of activation, it is not affected by the presence of the water vapour, and the reaction rate is a monotonously decreasing function of the conversion of the solid in contrast to the sulphite formation⁶. It is necessary to note that the two-parameters equation (3) with the exponent $n < 1$ is of an empirical nature. The consistence of all the experimental data with the form of the equation and the dependences of its parameters on the state variables indicate that the equation expresses a certain physical reality even though a different one from the original Avrami's model. For the present, this problem remains open.

The investigation of the simultaneously occurring reactions (B) and (A) has confirmed the original supposition², namely that the cause of the decrease of the reaction rate of reaction (B) in the presence of oxygen at temperatures higher than 160°C consists in the oxidation of the sodium sulphite being formed. The blocking of a part of the phase boundary between the sulphite and the carbonate results both in a decrease of the reaction rate and in the decrease of the attainable degree of conversion of the sodium carbonate.

We are indebted to Dr L. O. Larsson, Stockholm University, for performing the X-ray structure analysis of samples of the sodium sulphite. Dr J. Šubrt has taken part in this study during his study leave at The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences.

LIST OF SYMBOLS

E	activation energy (kcal . mol ⁻¹)
F_0	gas feed rate (mol . s ⁻¹)
K	constant defined by equation (9) (Torr ⁻¹ . s ⁻¹)
K_{O_2}	constant defined by equation (9) (Torr ⁻¹)
k	rate constant defined by equation (3) (s ⁻¹)
n	kinetic parameter defined by equation (3)
n_s	amount of sodium sulphite in bed (mol)
n_i	amount of substance i (mol)
p_i	partial pressure of the i -th component (Torr)
r	reaction rate defined by equation (1) (s ⁻¹)
t	temperature (°C)
T	absolute temperature (K)
W	quantity defined by equation (12)

x	degree of conversion of sodium sulphite
x_s	degree of conversion of sodium carbonate defined by equation (11)
x_τ	value of x in time τ
y	mole fraction of oxygen in gas after passing the bed
y_0	mole fraction of oxygen in feed
y_i	mole fraction of substance i
τ	time (s)
ξ	quantity defined by equation (4)

REFERENCES

1. Mareček J., Bareš J., Erdös E.: This Journal 40, 827 (1975).
2. Mareček J., Mocek K., Erdös E.: This Journal 35, 154 (1970).
3. Larsson L. O.: Univ. Stockholm Chem. Commun. 1971, No V.
4. Larsson L. O.: Private communication.
5. Erdös E.: This Journal 36, 485 (1971).
6. Erdös E., Bareš J., Mareček J., Mocek K. in the book: *Festkörperchemie* (V. V. Boldyrev, K. Meyer, Eds), p. 478. Deutscher Verlag für Grundstoffindustrie, Leipzig 1973.

Translated by the author (E. E.).