

MATHEMATICAL TREATMENT OF THE MODEL OF DECOMPOSITION OF DITHIONITE IN AQUEOUS SOLUTIONS

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On the basis of experimental results obtained in studying the course of spontaneous decomposition of dithionite in acidic aqueous solutions, models of the decomposition mechanisms were formulated of increasing complexity. Their mathematical treatment made it possible to estimate the significance of partial reactions and revealed that the adopted model is roughly consistent with the observed relationships. A full agreement, however, could not be attained, since, for mathematical reasons, the reactions leading to polymerization of sulphur could not be included. Also the contribution of microheterogeneous reactions was neglected which are probably significantly effective, especially near the end of the decomposition process.

Our preceding communication¹ has brought an ample experimental material on the decomposition of dilute aqueous solutions of dithionite under the conditions that the initial phase of slow decomposition and accumulation of intermediates, which accelerate the decomposition (induction period), can be well distinguished from the phase of fast decomposition. The reaction conditions (temperature and pH) were chosen so that the decomposition might easily be followed polarographically, either as the time dependence of polarographic waves at a given electrode potential or by means of repeated polarographic curves in the chosen potential interval. The lack of time prevented us to extend our experiments to the investigation of the effect of temperature and of pH in order to precise our concepts of the reacting ionic forms and also to differentiate the possible mechanisms according to activation energies. The fact that the reactions, initiating the decomposition and the formation of active intermediates, are by several orders of magnitude slower than the reactions proceeding in the phase of fast decomposition, is advantageous in that it allows a simpler interpretation of this fast phase. On the other hand, however, only few conclusions can be drawn on the mechanism in the induction phase, since already at 1% decomposition the kinetics is dominantly governed by fast reactions of the main decomposition phase. The prevailing part of the induction period consists of gradual accumulation of active intermediates. For this reason the attempts to interpret the processes of the initial phase in terms of the time course of the decomposition curve at the very beginning of the decomposition, as it is *e.g.* in the works of Lem and Wayman^{2,3}, must be considered with great criticism. Another great disadvantage in this case is the experimental instability of the induction period, caused by the non-reproducible trace decomposition of dithionite which has been introduced into the reaction cell.

The main decomposition products of dithionite, *i.e.* sulphite, hydrogen sulphide, thiosulphate and sulphur, form themselves a very active and kinetically complex system, known as the Wackenröder solution⁴. Many of the reactions of this system which are kinetically reactions of high

orders (formation of polysulphides and polythionates) could be eliminated by working with solutions of dithionite concentration not higher than 10^{-2} M, in most cases with concentrations $2.5 \cdot 10^{-3}$ M. Nevertheless, there remains an ample choice of various reactions whose relative significance must be estimated by evaluation of experimental results.

From the experimental results it is evident that the main reaction partners of dithionite in its decompositions are hydrogen sulphide and active sulphur. The fact that at low concentrations of dithionite the main decomposition products are sulphite and hydrogen sulphide, in addition to minor amounts of thiosulphate and colloidal sulphur, shows that the reaction of dithionite with active sulphur proceeds at a much greater rate than with hydrogen sulphide. Thus, the concentration of active sulphur can be taken as negligibly small nearly over the whole decomposition process, with the exception of its final phase. Only near the end of the decomposition the accumulation of polarographically active sulphur occurs which is manifested by the formation of a small anodic-cathodic wave, corresponding to the reversible redox reaction of hydrogen sulphide with sulphur.

The formation of colloidal sulphur during decomposition makes the mathematical treatment of the problem rather difficult, even when only homogeneous reactions are taken into account. In general, heterogeneous reactions must be accepted, too, in view of the surface activity of colloidal particles. Their importance increases with the degree of decomposition. Since, however, the concentration of active sulphur is assumed to be negligibly small, the reaction routes leading to polymerization of sulphur can be omitted, as long as the residual concentration of dithionite is high enough to make the ratio of free dithionite to that adsorbed on colloidal sulphur of the order of magnitude higher than unity. The model treated further ignores the formation of colloidal sulphur, taking into account only the homogeneous reaction system. However, comparison of the calculated model curves with those found experimentally indicates that near the end of the decomposition also the heterogeneous mechanism becomes effective.

MODEL SCHEME OF THE DECOMPOSITION OF DITHIONITE

Notations

The following abbreviations will be used in further calculations to denote relative analytical concentrations, with regard to the initial concentration of dithionite D_0 (mol/l): B sulphite, C hydrogen sulphide, D dithionite, E thiosulphurous acid or, generally, the complex $SO_2 \cdot H_2S$, S sulphur, T thiosulphate.

The real relative concentrations of hydrogen sulphide and sulphite are (C-E) and (B-E), respectively, since the complex $H_2S \cdot SO_2$ (thiosulphurous acid) is included whose formation is taken as reversible with equilibrium shifted strongly towards dissociation.

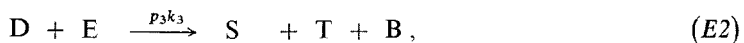
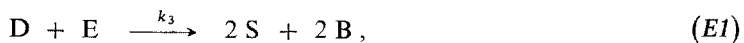
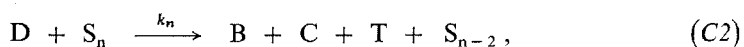
Initiation Reactions

As already mentioned in the introduction, the initiation reactions have in the given case only a negligible effect on the decomposition kinetics already at 1% of decomposed dithionite. Therefore, neither their mechanism nor their kinetics order affect in any way the study of the main phase of decomposition. The kinetic order, however, strongly affects the dependence of the length of the induction period on the initial concentration of dithionite.

Initiation reactions are taken into account in our scheme, mainly in order to make possible the mathematical treatment of the time dependence from the very beginning, because they generate active intermediates. Sulphur was chosen as the most plausible product of primary decomposition, as the formation of hydrogen sulphide requires a higher reorganisation of the oxidation degrees of sulphur. The following formal mechanisms were chosen which appear to be kinetically of the first and second order:



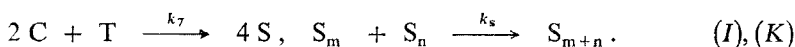
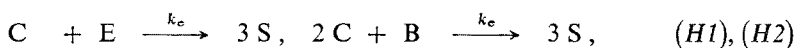
Quantities k_i are here as well as in further kinetic relations related to relative concentrations and therefore they have the dimension s^{-1} throughout. In order to transform these quantities into rate constants k'_i , they have to be divided by the respective power of D_0 .

Mechanisms Leading to the Decomposition of Dithionite

Here, as well as in further schemes the symbols B and C represent, for the sake of simplicity, the true relative concentrations, not the analytical ones. Symbols $p_i k_i$ were employed for parallel reactions (D2) and (E2) so as to avoid the introduction of further subscripts.

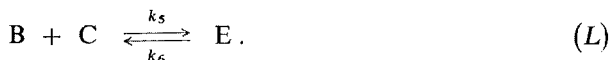
Decomposition reactions (D) and (E) can in this case proceed by two routes and it is formally irrelevant, whether thiosulphate is the primary product of the attack of dithionite by hydrogen sulphide or whether it is formed in a secondary reaction, by combination of S + B before they are spatially separated. Reaction (C1) will be discussed later in more detail. The alternative route (C2) is mentioned only for completeness and is not considered in further mathematical treatment. The subscript n means a low sulphur oligomer, able to react with dithionite at a rate comparable with the rates of the concurrent reaction (C1).

Side Reactions



The last mechanism, describing the polymerization of sulphur, will not be taken into account in mathematical treatment, as noted above. The quantity k_s depends here of course on subscripts m and n.

Reversible Reactions



DISCUSSION OF THE MECHANISMS

Reaction of Dithionite with Active Sulphur

As mentioned above, it has been experimentally proved that the reaction of dithionite with active sulphur is considerably faster than that with hydrogen sulphide. We can reasonably assume that the rate constants for atomic sulphur S will be not too much different from those of freely bound sulphur of the type S.R., *e.g.* S₂, S₃ or even higher oligomers, or S_{2+n}O₃²⁻ *etc.* As long as the corresponding rate constants are considerably higher than the quantities k_2 and k_3 , it is irrelevant whether for example

reaction (*D1*) yields really two sulphur atoms, or S_2 . For it can be written: $D + S_2 \rightarrow 2B + S + C$ and the released sulphur reacts further. Of course there is the possible parallel reaction (*C2*) which is the source of thiosulphate in the reaction products. This reaction is not considered in our model.* Similarly, we can disregard the lowest degrees of polymerization reaction (*K*), as far as it yields only low oligomers. The term active sulphur includes also sulphur biradicals.

Reaction of Dithionite with Thiosulphate

Experiments in which a great amount of thiosulphate was added at the beginning of the decomposition have shown that reaction (*F*) is relatively slow. It only diminishes the induction period and is not effective in the main decomposition phase. The corresponding rate constant could be evaluated to $k'_4 = 1.25 \cdot 10^{-2} M^{-1} s^{-1}$. Since the final concentration of thiosulphate in the decomposition of pure dithionite is about 10% of the initial dithionite concentration, reaction (*F*) does not contribute significantly to the kinetics of decomposition.

Reactions of Hydrogen Sulphide Yielding Sulphur

Experimental results revealed that reactions (*H*) are considerably faster than reaction (*I*), *i.e.*, than the formation of sulphur from thiosulphate and hydrogen sulphide. Therefore reaction (*I*) need not be considered. Investigation of the kinetics of decomposition of both hydrogen sulphide and sulphite showed that the experimental data are in agreement with mechanism (*H1*) via complex $H_2S \cdot SO_2$. The calculated value of the rate constant of this reaction is $k'_6(k'_5/k'_6) \approx 1.14 \cdot 10^5 M^{-2} s^{-1}$.

Polymerization of Sulphur

Polymerization reaction (*K*) is relatively little effective at higher values of *m* and *n*. This increase of agglomerates of inactive sulphur acts only indirectly in that it decreases the concentration of these agglomerates and thus also the probability of removal of active sulphur from this system becomes lower. Consequently, from the standpoint of kinetics of dithionite decomposition, the most important reactions are polymerizations of the type $S + S_n \rightarrow S_{n+1}$. The consideration of reaction (*K*), even in this simplest form, and hence also the presence of a considerable amount of sulphur in reaction products introduces, however, serious mathematical difficulties in solving the corresponding differential equations. Nevertheless, according to experimental results, colloidal sulphur represents for low dithionite concentrations only a small part of the decomposition products and thus reaction (*K*) can in the first approximation be totally omitted and can only be taken into account as modifier of the kinetics

* The reason is not only the mathematical point of view but also the fact that analogous reactions (*D2*) and (*E2*) have turned out to be insignificant.

at the end of the decomposition. In this phase also the contribution of heterogeneous reactions becomes notable, in which particles adsorbed on agglomerates of colloidal sulphur enter the reaction.

The consequence of the assumed fast reactions and hence of a negligible concentration of active sulphur in the solution is that the rates of its formation and removal are comparable and by order of magnitude higher than the absolute value of the resulting time change dS/dt , *i.e.* a quasistationary approximation can be employed to express the concentration of active sulphur. The most generalized form (*i.e.* using all schemes in which S either is formed or is removed) of the proposed model is as follows

$$S(k_1D + k_1B) \approx 0.5k_mD + k_dD^2 + 2k_2(2 + p_2)CD + k_3(2 + p_3)DE + 3k_eCE + 4k_7C^2T. \quad (1)$$

Here, again, symbols B and C denote, for the sake of simplicity, the true relative concentrations. If we consider also the polymerization reaction (K) in its simplest form, the term $(+k_sS_p)$ must be added in the brackets on the left-hand side of relation (1), where S_p is the relative concentration of all non-active, *i.e.* enough large agglomerates of sulphur, $S_p = \sum_i S_{n_i}$. In this form Eq. (1) is approximately valid even after dithionite has been consumed, since the level of active sulphur remains still very low owing to its removal by sulphite and by sulphur agglomerates.

Thiosulphurous Acid

From the published data^{5,6} it follows that the equilibrium (L) is strongly shifted towards dissociation of thiosulphurous acid or, generally, of the complex $H_2S \cdot SO_2$. Moreover, this complex is removed by reactions with dithionite (E) and with hydrogen sulphide (HI). The resulting concentration of E is thus very low and again a quasistationary approximation can be employed which gives

$$k_5(B - E)(C - E) = [k_6 + (1 + p_3)k_3D + k_e(C - E)]E. \quad (2)$$

Here, symbols B and C denote already analytical relative concentrations. For the presumed low concentrations of E it holds approximately

$$E \approx E_1 \left[1 + \frac{k_e + k_5}{k_5BC} E_1^2 \right], \quad (2a)$$

where

$$E_1 = \frac{k_5BC}{k_6 + (1 + p_3)k_3D + k_eC + k_5(B + C)}. \quad (3)$$

In many cases the simplest form of approximation of (3), i.e. $E \approx E_1$, can be used successfully.

SOLUTION OF KINETIC EQUATIONS

Decomposition Products Are Only Sulphide and Hydrogen Sulphide

The simplest solutions, requiring a single quadrature of integral, are obtained when sulphite and hydrogen sulphide are supposed to prevail in the reaction products, i.e. when the formation of thiosulphate and of sulphur does not contribute significantly to the dynamics of dithionite decomposition. This assumption is evidently non-realistic and is in contradiction to experimental results. Surprisingly enough it was found that this simple model can excellently interpret the course of experimental decomposition curves for dithionite alone and, moreover, in their concentration dependence. This model corresponds to the over-all and formal equation



Let us now introduce a new variable, corresponding to the degree of conversion of dithionite

$$x = 1 - D. \quad (5a)$$

Then it will hold in this simple model

$$B = B_0 + 5x/3; \quad C = C_0 + x/3. \quad (5b)$$

Omitting the reactions in which thiosulphate takes part, the reaction scheme leads to the relation

$$-dD/dt = D[k_m + 2k_d D + k_1 S + k_2(C - E) + k_3 E] \quad (6a)$$

and substituting from (1)

$$\begin{aligned} -dD/dt = 3D[0.5k_m + k_d D + k_2 C + (k_3 - k_2) E + 3(C - E)] + \\ + 3(C - E)[k_c E + k_c(B - E)(C - E)]. \end{aligned} \quad (6b)$$

Since all variables appearing in this relation are single-valued functions of x , (6b) has the form

$$dx/dt = f(x) \quad \text{and consequently} \quad t = \int_0^x dx/f(x)$$

and the decomposition curve of dithionite can be determined by a simple quadrature. In general, this quadrature must be performed numerically. Numerical integration is most suitable also in the approximation (2a). Except for the starting phase of decomposition, the use of the Simpson formula with the integration step 0.0125 is fully satisfactory giving the values of t for intervals $\Delta x = 0.025$. In order to set the value of t for $x = 0.025$ it is advantageous to carry out a precise integration with omission of those terms which are not significant at the beginning. So for enough small C_0 the terms with C^2 , and consequently also with E^2 , can be neglected and E can be substituted by expression E_1 , to obtain integrable forms. On the other side, for enough high values of C_0 the initiation mechanisms can be omitted and numerical integration can be performed successfully from the beginning.

Comparison of calculations with experimental decomposition curves of dithionite alone has shown that up to 95% decomposition the reaction kinetics can successfully be simulated by reactions (C), (D1) and (E1), i.e. without the participation of sulphur formed by side reactions, which means omitting the terms in the last square brackets in Eq. (6b). Let us limit ourselves to the approximation $E \approx E_1$, given by relation (3) and introduce the abbreviated dimensionless denotation

$$K_m = 3k_m/2k_2; \quad K_d = 3k_d/k_2; \quad K_i = k_i/k_6 \quad \text{for} \quad k_i = k_2, k_3, k_5, k_c/3 \\ \text{and} \quad k_e/3. \quad (7)$$

Then it is

$$3E_1 = \frac{3K_5BC}{1 + K_3D + K_5(B + C)} = \frac{K_5(B_0 + 5x/3)(3C_0 + x)}{1 + K_3(1 - x) + K_5(B_0 + C_0 + 2x)} \quad (8)$$

and Eq. (6b) can be written in the form

$$\frac{1}{k_2} \frac{dx}{dt} = (1 - x) \left[K_m + K_d + 3C_0 + (1 - K_d)x + \right. \\ \left. + \frac{K_5(K_3 - K_2)}{K_2} \frac{(B_0 + 5x/3)(3C_0 + x)}{1 + K_3 + K_5(B_0 + C_0) - (K_3 - 2K_5)x} \right] = \\ = \frac{(1 - x)(a + bx + cx^2)}{m - nx}, \quad (9)$$

where the constants of the system are included in constants a , b , c , m , and n . Since, in the relevant case, it always holds that $b^2 > 4ac$, the integral solution of (9) can be written, if the abbreviation $M^2 = b^2 - 4ac$ is used, in the form

$$2(a + b + c) k_2 t = (m - n) \ln \left[\frac{a + bx + cx^2}{y(1 - x)^2} \right] + \\ + \frac{m(b + 2c) + n(b + 2a)}{M} \ln \left[\frac{b + M 2cx + b - M}{b - M 2cx + b + M} \right]. \quad (10)$$

Fig. 1 shows the comparison of the decomposition curve calculated from relation (10) with experimental data for $2.5 \cdot 10^{-3} \text{M}$ dithionite in a buffer of pH 4.31, at 20°C . The courses, calculated for different initial additions of hydrogen sulphide and sulphite are shown, too. The model curve had the following parameters: $K_m = 2.5 \cdot 10^{-4}$, $K_d = 0$, $K_3 = 20$, $K_3/K_5 = 6$ and $K_5 < 1$. Its course for $K_5 < 1$ is independent of K_5 . For a constant ratio $K_5/K_2 = k_5/k_2$ the shape of the curve is relatively little affected by the parameter K_3 , mostly near the end of the decomposition: with increasing K_3 the maximum value of the decomposition rate is shifted towards higher values of x and the model curve approaches therefore more closely the experimental data which admit at most a slight decrease in the decomposition rate at the very end of the reaction.

Fig. 1 shows that the time of decomposition depends very sensitively on the initial concentration of hydrogen sulphide. In fact, for very low concentrations ($C_0 \leq 0.01$) only the induction period is shortened, whereas the shape of the main part of the decomposition curve remains unchanged.* This can explain the experimental variability of the induction period. It is caused by the irreproducibly small degree of decomposition of the dosed dithionite. The experimental results allow therefore to estimate only the upper limit of the rate constant of the initiation reaction. The effective order of the initiation reaction must in this case be estimated by comparing the length of the induction period for different initial concentrations of dithionite. Although the mentioned variability, caused by the variations of the degree of contamination of the dosed solution by decomposition products, impaired the evaluation of results, it was possible to exclude unambiguously the mechanisms, leading to kinetic equations of formal order 2 or 1.5 (as suggested by Rinker and coworkers⁷). The results are best fitted by first-order kinetics, *i.e.* by parameter K_m and not K_d .

Converting the used parameters into absolute rate constants k' , referred to molar solutions, we obtain: $k'_2 = 3 \cdot 10 \text{M}^{-1} \text{s}^{-1}$, $k'_5 = 0.931 \text{M}^{-1} \text{s}^{-1}$, $k'_m \leq 1.29 \cdot 10^{-6} \text{s}^{-1}$, $k'_3/k'_6 \geq 8000$.

In the further step, reactions (H) were included, leading to the formation of active sulphur and to the simultaneous disappearance of hydrogen sulphide. In order

* The division into induction and main decomposition phase is only a heuristic approach and therefore no physically supported definition of a boundary between the two periods can be given. For comparison this limit can be defined *e.g.* as 10% decomposition, or it is possible to consider the time shifts of the decomposition curves.

to be able to apply numerical integration from the very beginning, the procedure according to Simpson was replaced by relations

$$I_h = \int_0^h dx/f(x) \approx h \frac{\ln(y_1/y_0)}{y_1 - y_0}, \quad \text{when } y_i = f(x_i). \quad (11)$$

Using the integration step $h = \Delta x = 0.0125$ this procedure was quite equivalent to that of Simpson in the range $0.05 \leq x \leq 0.95$, often even in a wider one. The error of procedure (11) did not, at the beginning, exceed 0.01 min and only in some extreme cases the integration error at the end of the decomposition was up to 0.1 min.

First of all the integration for $k_c = 0$ (omission of reaction (H2)) was performed. The results are presented in Fig. 2. They show a significant improvement of the fit of the calculated curve with the experimental one near the end of the decomposition, in which the value of k_2 does not change practically. On the other hand, the decomposition reaction of dithionite (E1) can be, to an extent, replaced by the side reaction (H1). Since the concentration of E decreases with increasing K_e , there is a limit of saturation for reactions (H1) and (E1) and the shape of the curve remains practically unchanged for $K_e > 100$. This value, $K = 100$ for $D_0 = 2.5 \cdot 10^{-3} M$, complies

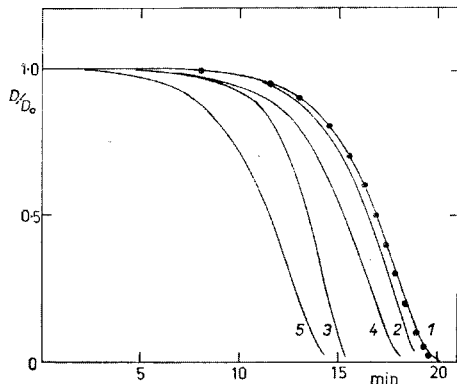


FIG. 1

Decomposition of $2.5 \cdot 10^{-3} M$ Dithionite in a Buffer of pH 4.31 at $20^\circ C$

Model decomposition curves for parameters: $k'_2 = 3 \cdot 10 M^{-1} s^{-1}$, $K_m = 2.5 \cdot 10^{-4}$, $K_2 = 2.5 \cdot 10^{-4}$, $K_3 = 20$, $K_5 = 7.5 \cdot 10^{-5}$. 1 Dithionite alone, 2 $B_0 = 0.1$, 3 $B_0 = 1$, 4 $C_0 = 10^{-4}$, 5 $C_0 = 10^{-3}$. Full points give the experimentally found values.

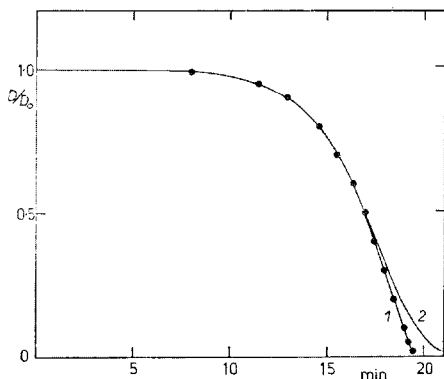


FIG. 2

Decomposition of $2.5 \cdot 10^{-3} M$ Dithionite in a Buffer of pH 4.31, at $20^\circ C$

1 Model, considering the formation of sulphur in the reaction of H_2S with SO_2 , 2 model including the formation of thiosulphate. Full points give the experimentally found values.

with the experimentally found rate constant k'_e . However, the calculations were carried out also for other values of K_e .

In view of the saturation effect in reaction (H1) also the reaction (H2), *i.e.* triple collision $2\text{H}_2\text{S} + \text{HSO}_3^-$ can be effective. Calculations, analogous to the preceding ones ($K_e = 0$; K_e) have shown that a similar effect as for $K_e = 100$ can be attained even for $K_e = 2 \cdot 10^{-5}$ and $K_3 = 20$. In contrast to the preceding reaction, in this case no saturation effect sets on with increasing K_e and the decomposition time becomes gradually shorter. The course of the decomposition curves for $K_3 = 0$; K_e differs from the experimentally found ones, too.

An important feature of the side reactions of the type (H) is that they allow to finish the decomposition of dithionite in a finite time. It should be pointed out, however, that the used calculation scheme fails in the end phase of decomposition, even without taking into account the polymerization of sulphur or possible heterogeneous reactions. The slower is the reaction of dithionite with sulphur as compared with its reaction with hydrogen sulphide, the sooner ceases Eq. (5b) to be valid, the concentration of hydrogen sulphide decreases, because sulphur, released in reactions (H), can no more react at a sufficient rate with dithionite to regenerate hydrogen sulphide. Decomposition rate in the last phase must then necessarily be lower than the calculated value. This is also supported by the fact that the relative concentration of hydrogen sulphide near the end of the decomposition decreases with increasing initial concentration of dithionite.

Thus, the calculations performed so far could not bring any conclusions on the contribution of reactions (E1), (H1) and (H2) to the kinetics of decomposition. A number of various combinations of the corresponding quantities K_3 , K_e and K_e gave practically undistinguishable curves. Moreover, this treatment did not include the formation of thiosulphate and the model dependence on the initial concentration of sulphite was in contradiction to experimental results. Therefore, an attempt was made to solve the system with participation of thiosulphate.

Decomposition Considering the Formation of Thiosulphate

Experimental results indicate that for the decomposition of dithionite alone, the final concentration of thiosulphate is 10% with respect to the dosed dithionite, *i.e.* $T_f \approx 0.1$, independently of its concentration. The yield in T_f increases with increasing concentration of sulphite B_0 and the final concentration of C_f decreases, thereby, as shown in Fig. 3. The scattering of data is great, nevertheless they allow a rough correlation

$$T_f \approx 0.09 + 0.56B_0 \quad (12)$$

Fig. 3 also shows the corresponding relation $C_f = 0.273 - 0.373B_0$, calculated for correlation (12) when the formation of polymer sulphur is neglected. For $B_0 = 0$

the really found value of C_f is only little lower than the calculated one, however, with small additions of sulphite C_f at first decreases far more steeply than it was theoretically expected and only later the slope is the same, as calculated, yet, the absolute value of C_f is significantly lower. This is due to the fact discussed above that near the end of the decomposition, hydrogen sulphide, removed by reaction with sulphite, is not regenerated in sufficient amount in the reaction of sulphur with dithionite. The increasing sulphite concentration causes both the increase of the portion of sulphur, reacting with sulphite and the increase of the portion of reaction (H), so that the final concentration of hydrogen sulphide is lower to considerably lower than that calculated for the assumed very fast reaction (C).

The increase of thiosulphate concentration in the course of decomposition of dithionite alone can be detected with very poor accuracy only. Its concentration seems to remain roughly constant, after initial increase, during the main decomposition phase. Only towards the end of the reaction a considerable increase appears. For a great excess of sulphite ($B_0 = 10$) the accuracy of determination of thiosulphate concentration from polarograms is markedly more favourable. This concentration increases during the whole course of decomposition. Since no sulphur is formed under these conditions, the corresponding concentrations of hydrogen sulphide during decomposition can be calculated from the experimental data. In a typical case, concentration of hydrogen sulphide at first increases, attains the value of $C \approx 0.45$ at $x \approx 0.45$ and afterwards decreases almost to zero concentration. The increase of thiosulphate formation with increasing concentration of sulphite leads to a decrease of the decomposition rate by removing active sulphur. At the same time, however, increasing concentration of the complex $H_2S \cdot SO_2$, as well as the increased formation of sulphur by reaction (H), results in an increase of the decomposition rate. Consequently, small additions of sulphite to the system as well as its additions in the course of decomposition cause a slight acceleration of the decomposition, whereas a great excess of sulphite leads to a marked retardation. In accordance

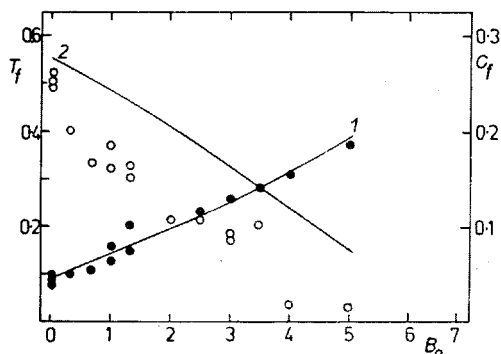


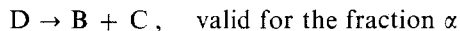
FIG. 3

Effect of the Initial Relative Concentration of Sulphite, B_0 , on the Final Relative Concentrations of Thiosulphate, T_f , and of Hydrogen Sulphide, C_f

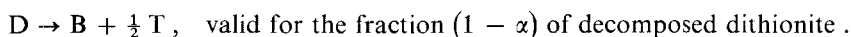
Full points denote experimental values of T_f , empty points the values of C_f . 1 Model course of T_f , 2 model course of C_f in dependence on B_0 .

with this a small acceleration of decomposition was observed in fact for $B_0 < 2$, whereas for $B_0 = 3$ a retardation was found which grew rapidly with increasing B_0 . In view of the instability of the length of the induction period, however, the results are only of qualitative character.

The aim of the model calculations was to ascertain whether some parameters exist that would comply with the mentioned observations. The most advantageous approach in solving the model system, including sulphite, hydrogen sulphide and thiosulphate as intermediates, is to introduce two formal decomposition balances



and



Parameter α is in general a function of the degree of decomposition and thus also of time and allows to express the instantaneous state of the system, regardless whether the considered products are formed and removed with the participation of dithionite or in side reactions.

Let us now denote

$$u = \alpha x = \alpha(D_0 - D)/D_0. \quad (13)$$

Then we can write

$$B = B_0 + x + \frac{2}{3}u; \quad C = C_0 + u/3; \quad T = T_0 + (x - u)/2. \quad (14)$$

The given relative concentrations must be taken as analytical, *i.e.*, they must include also the species which form reversible complexes and compounds. The system of differential equations for kinetic behaviour of the model can be reduced, using Eq. (14), to a differential relation between quantities x and y , in the form

$$du/dx = f(x, u). \quad (15)$$

Its solution gives the parameter u as a function of x and thus, according to (11) also quantities B , C and T appear as functions of x . These values can be then used for numerical quadrature of the kinetic equation $dx/dt = g(x)$, which is the solution of the problem.

Although easily derivable, the form of relation (15) for a general case is rather complex and therefore it is not presented here. In general, this differential equation can be solved only numerically. Only in some cases, neglecting the initiation reaction, Eq. (15) can be transformed into an exactly solvable homogeneous differential equation. However, the resulting expressions are too complicated and they contain both x and u implicate, *i.e.* in the form $f(u, x) = g(u, x)$, so that the corresponding pairs of (x, u) have to be found by trial. For this reason the numerical solution of equation (15) is most advantageous even in these cases.

The first stage of numerical calculations was to find such parameters that the dependence of the final concentration of thiosulphate, T_f , on the initial addition of sulphite would roughly express the experimental relation (12) and, at the same time, the decomposition rate of dithionite with addition of sulphite, would at first increase and then, at $B_0 > 2$, decrease again. Both these requirements can be met only when the participation of reactions (D2) and (E2) is negligible, *i.e.*, provided that thiosulphate is formed practically only in side reaction (G) of sulphur with sulphite and not by the attack of dithionite by sulphide or thiosulphurous acid. Further, reaction (E1) could not be omitted which indicates that the attack by the complex $H_2S \cdot SO_2$ is more productive than that by hydrogen sulphide. However, neither the value of parameter K_3 which is the measure of the significance of reaction (E1), nor the value of K_c , correlated to trimolecular reaction (H2), could be determined. Their variation in a wide range did not affect the fulfillment of both the above requirements. At the same time, it had no detectable effect on the quantity $K_m = k_i/k_1$, giving the ratio of probabilities for the reactions of active sulphur with sulphite and with dithionite. This ratio was in all cases about 0.1. Also the reduced rate constant k_2 of reaction (D1) was practically constant. Its value was for $D_0 = 2.5 \cdot 10^{-3}M$ always near to 0.50 which corresponds to the real rate constant $k'_2 \approx 3.33M^{-1} s^{-1}$. A small increase as compared with the value derived from the simple model is due to the compensation for the formation of thiosulphate, withdrawing active sulphur from the system. The maximum value, k_m , diminished a little to $0.889 \cdot 10^{-6} s^{-1}$.

In the second step of numerical calculations an attempt was made to remove the remaining uncertainty by postulating that the resulting concentration of thiosulphate for the decomposition of dithionite alone should be approximately $T_f \approx 0.1$ over the whole experimental concentration range D_0 . This postulate was not met in any of the examined cases for which $K_c = 0$. Except for the lowest concentration $D_0 = 10^{-3}M$ (calculated value of $T_f = 0.07$) it was fulfilled fairly well over the whole remaining concentration range up to $D_0 = 10^{-2}M$ when also the direct reaction (H2) of hydrogen sulphide with sulphite under the formation of sulphur was considered with the parameter $K_c = 5 \cdot 10^{-5}$. The finally adopted parameters, consistent with the observed dependences in the decomposition of dithionite, related to the initial concentration of $D_0 = 2.5 \cdot 10^{-3}M$, were the following:

$$K_m = 1.6 \cdot 10^{-4}; K_2 = 2.5 \cdot 10^{-4}; K_3 = 10; K_4 = 0.004; K_5 = 7.5 \cdot 10^{-5}; K_c = 100; K_c = 5 \cdot 10^{-5}; K_T = 0.105; k_2 = 0.50032,$$

which corresponds to the real rate constants:

$$k'_2 = 3.33_5 M^{-1} s^{-1}$$

$$k'_m = 0.889 \cdot 10^{-6} s^{-1}$$

$$k'_3 = 1.33_4 \cdot 10^5 M^{-1} s^{-1}$$

for reaction (D1), decomposition D + C
for the initial decomposition reaction of the type (A)

for reaction (E1), decomposition D + E

$$\begin{array}{ll}
 k'_4 = 1.33_4 \cdot 10^{-2} \text{M}^{-1} \text{s}^{-1} & \text{for reaction (F), decomposition D + T} \\
 k'_5 = 1.00_1 \text{M}^{-1} \text{s}^{-1} \text{ and } k'_6 = 33.3_5 \text{s}^{-1} & \text{for equilibrium reactions (L)} \\
 k'_c = 266.8 \text{M}^{-2} \text{s}^{-1} & \text{for reaction (H2), i.e. } 2 \text{C} + \text{B} \rightarrow 3 \text{S} \\
 k'_e = 1.33_4 \cdot 10^6 \text{M}^{-1} \text{s}^{-1} & \text{for reaction (H1), i.e. } \text{C} + \text{E} \rightarrow 3 \text{S}
 \end{array}$$

These values are only of informative value, since it is in the nature of the correlation procedure that the variation width of the set up parameters increases strongly with their number.

A common feature of models including participation of thiosulphate is that in contradiction to measurements the decomposition rate decreases in all cases at the end of the process. This indicates that on the one hand the compliance of simple models neglecting the formation of thiosulphate with experimental results is incidental, on the other hand that the system cannot be competently treated only in terms of homogeneous reactions. That the experimentally found course of the final phases of the reaction is faster than the calculated one, can easily be explained by adsorption of dithionite on the agglomerates of colloidal sulphur.

The model course of dependence of the concentration of thiosulphate on the degree of decomposition agrees fairly well with experiments in which sulphite was added. In this model a monotonous increase of this concentration is assumed, even in the case of decomposition of dithionite alone. However, the concentration of thiosulphate cannot be reliably evaluated from polarograms, as it is too low under the given conditions and consequently also the verification of the model predictions is impossible.

The last discrepancy between the experimental results and the model is the observed decrease in the final relative concentration of hydrogen sulphide with increasing initial concentration of dithionite. As already mentioned, this is probably due to the fact that the model does not respect that the assumption about the dominating rate of reaction (C1) for dithionite with active sulphur ceases to be valid towards the end of the decomposition. This assumption made is possible to apply the quasi-stationary relation (I). Also the growing amount of colloidal sulphur causes that the rate of formation of hydrogen sulphide decreases less than the rate of its removal. The material balance which includes the formation of colloidal sulphur leads also to lower values of the final concentration of hydrogen sulphide.

CONCLUSION

Mathematical treatment of a model system of reactions involved in the decomposition of dithionite in acidic aqueous solutions has shown that the observed dependences are consistent with the assumption that the main decomposition mechanism is a two-step cycle of reactions (C), (D1) and (E1) of dithionite with sulphur and with hydrogen sulphide, possibly also bound to sulphite. In these reactions the

attack of dithionite by the complex $\text{H}_2\text{S}\cdot\text{SO}_2$ is more productive than the attack merely by hydrogen sulphide. The most rapid reaction in the system is, with the possible exception of sulphur polymerization, the reaction of dithionite with active sulphur. It is approximately ten times faster than the reaction of active sulphur with sulphite under the formation of thiosulphate. An important participation of reactions (*D2*) and (*E2*), leading directly to thiosulphate in the course of dithionite decomposition could be eliminated, as well as the significance of the reaction of thiosulphate with dithionite (*F*) and its decomposition with hydrogen sulphide (*I*). On the other hand, in order to express the dependence of the final concentration of dithionite, also the direct reaction (*H2*) of $2 \text{H}_2\text{S} + \text{SO}_2$ had to be taken into account in addition to reaction (*H1*) of hydrogen sulphide with $\text{H}_2\text{S}\cdot\text{SO}_2$.

The variability of the adjustable parameters is wide, owing to their great number and only a single set is presented which is consistent with experimental results.

The model is able to reflect essentially all the observed dependences on the initial concentration of dithionite, sulphite and hydrogen sulphide. Its principal drawback can be seen in that it does not express the experimentally found decomposition course near its end. The model leads to a considerable slowing down of the reaction for the last 5–10%, whereas the experiments show at most a slight slow-down. This is probably due to the participation of a heterogeneous reaction of dithionite adsorbed on colloidal sulphur.

REFERENCES

1. Čermák V., Smutek M.: This Journal 40, 3241 (1975).
2. Lem W. J., Wayman M.: Can. J. Chem. 48, 776 (1969).
3. Wayman M., Lem W. J.: Can. J. Chem. 48, 782 (1969).
4. Goehring M.: Fortschr. Chem. Forsch. 2, 444 (1952).
5. Goehring M.: Z. Anorg. Allg. Chem. 253, 313 (1947).
6. Stamm H., Goehring M.: Chemie 58, 52 (1945).
7. Rinker R. G., Lynn S., Mason D. M., Corcoran W. H.: Ind. Eng. Chem., Fundam. 4, 282 (1965).

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