

MECHANISM OF DECOMPOSITION OF DITHIONITE IN AQUEOUS SOLUTIONS

V. ČERMÁK and M. SMUTEK

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*



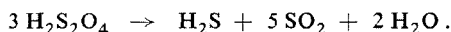
PE 1281

17.11.75

Received December 2nd, 1974

11-12.

Decomposition of aqueous solutions of dithionite was studied at pH c. 4 and at concentrations mostly $2.5 \cdot 10^{-3}$ M. Time changes of the concentration of dithionite, sulphide and thiosulphate were determined polarographically. Active sulphur and sulphide are formed in the induction period of the decomposition. In the fast period the decomposition is autocatalyzed by reactions of sulphide with dithionite, sulphite and thiosulphate under regeneration of active sulphur. Thio-sulphurous acid is also supposed to participate in these reactions. Both the inhibition and the acceleration effects of sulphite as well as the effects of thiosulphate, sulphide and sulphur dichloride were investigated. The decomposition can be described by equations



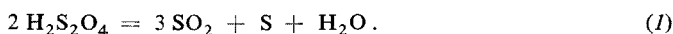
However, the final composition of the products is the result of parallel and consecutive reactions of intermediates H_2S and S with SO_2 which finally yield thiosulphate and/or polysulphides and polythionates.

The aim of the present publication is to give a critical survey of the studies of decomposition of aqueous solutions of dithionite published in the last 20 years and to propose a mechanism consistent with the found experimental data. The mechanism is based on a number of new results, making use also of the results of previous polarographic studies of dithionite solutions, which have remained either unknown or have not been taken into account.

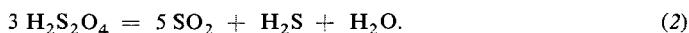
The hitherto published experimental material revealed a very complex behaviour of systems containing the decomposing dithionite which is strongly affected by the acidity of the solution^{1,2}. The rate of decomposition is markedly increased by increasing acidity and temperature. In the absence of components which activate or inhibit the decomposition an initial phase was observed of a slow, gradually accelerating reaction, which eventually turns into a more or less fast decomposition³. This behaviour is characteristic of autocatalytic reactions. In the absence of oxidizing agents, the highest oxidation state found is S(IV). Of the lower valence forms of sulphur were found thiosulphate, hydrogen sulphide and polythionates. The ratio of the concentrations of the products depends besides acidity, temperature and concentration also on the time of analysis from the beginning of the decomposition. This is the result of consecutive reactions of the primary

decomposition products. Because of this and also because unsatisfactory analytical procedures were often employed, the data on the products and mechanism of the decomposition are more than contradictory.*

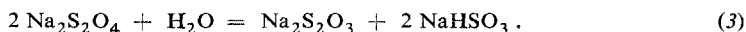
According to literature^{6,7}, the products of decompositions in acidic medium are SO₂ and S



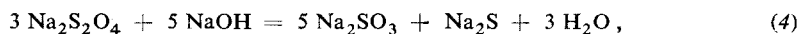
In extremely acidic medium (boiling 5M-HCl) the supposed products of the first step are SO₂ and H₂S (see^{7,8})



In weakly acidic to weakly alkaline medium the formation of thiosulphate is assumed according to papers^{3,9,10}

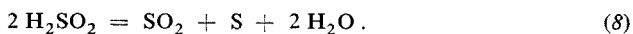
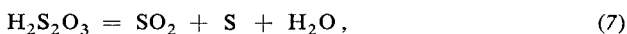
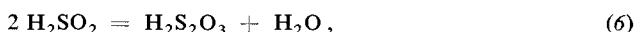
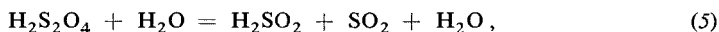


Sulphite and sulphide are formed in strongly alkaline medium^{8,10}



especially in the presence of ions of metals which easily form sulphides¹⁰. In concentrated solutions of dithionite also polythionates were detected as decomposition products⁷.

According to Scholder and Denk¹⁰, reaction (1) proceeds in three steps. The first of them is the hydrolysis of H₂S₂O₄ (reaction (5)), the second one the condensation of sulphylic acid (reaction (6)) and the last one is the decomposition of thiosulphuric acid (reaction (7)), or condensation of sulphylic acid according to equation (8)



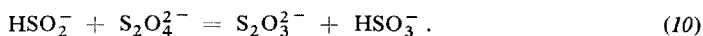
Formation of sulphide in alkaline medium was explained by disproportionation of sulphylyate anion⁸⁻¹⁰ according to equation (9)



* This is evident when reading the respective chapters, e.g., in *Gmelins Handbuch der anorganischen Chemie*¹. The decomposition was studied often in excessively concentrated solutions, at high temperatures and in a medium whose acidity varied in the course of decomposition. The products were analyzed sometimes only after several tens of hours. Consequently, the papers dealing with the decomposition of dithionite solutions give only a qualitative and often even uncorrect informations, which are then, in the lack of more accurate data, transferred also to modern textbooks of inorganic chemistry, e.g. Remy's⁴ or Cotton and Wilkinson's⁵ monographs.

Surprisingly enough, sulphide should be formed according to Eqs (2) and (4) only in extremely acidic or alkaline solutions.

A more recent study of the decomposition of dithionite solutions is that of Lister and Garvie¹² who worked in strongly alkaline medium (0.1M-NaOH) at concentrations $3 \cdot 10^{-2}$ –0.15M, at about 88°C. They found the decomposition to be a first-order reaction with respect to dithionite. The rate determining reaction is the hydrolysis of dithionite (reaction (5)). The authors supposed that only $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_3 are the reaction products. Thiosulphate is assumed to be the product of the reaction of sulphoxylate with dithionite



In his paper, Jouan¹³ presents the decomposition curves in a 0.1–0.4M aqueous solution of dithionite in water or in a buffer of pH 4.85 at 16 and 25°C. The curves reveal a distinct fast initial phase of decomposition, turning into the slow phase after about 20–30 min. The authors found the stabilization effect of NaHSO_3 . Their interpretation of the decomposition mechanism is based on the concepts of Scholder and Denk¹⁰.

Rinker and coworkers¹⁴ investigated the decomposition of dithionite at 60–80°C both in pure water and in buffer solutions. However, a complete analysis was carried out with only one sample, at 30°C and after an undefined time. The products found were HSO_3^- and $\text{S}_2\text{O}_3^{2-}$. In the induction period a fluctuation of the concentration of dithionite was found which disappeared at 80°C. A decomposition mechanism was proposed only for the initial phase, where the decomposition rate is governed by a radical reaction yielding thiosulphate

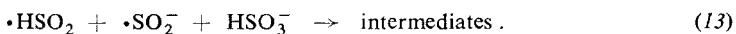


This reaction is followed by a faster reaction between two radicals, yielding sulphite



Rinker and coworkers proved that the decomposition is accelerated by a relatively stable decomposition product. They tentatively suggested sulphur as the active component. The presence of sulphide remained unnoticed. Their decomposition curves, determined by titration with methylene blue, had a convex shape without inflex, indicating that the decomposition rate either constantly increased or at least remained constant till the decomposition was complete.

The study by Spencer¹⁵ demonstrates that in concentrated solutions of NaHSO_3 , Na_2SO_3 and NaCl , used in electrolytical production of dithionite, and with concentrations of dithionite 0.2–1.5M, the decomposition proceeds at pH c. 5.2 as a 1st order reaction with respect to dithionite and bisulphite. The prevailing products are thiosulphate and trithionate. According to Spencer, the rate determining reaction is



The reaction is accelerated by thiosulphate in the concentration of 0.63M.

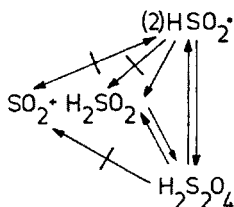
Burlamacchi and coworkers¹⁶ studied the decomposition in unbuffered solutions at higher temperature and at concentrations higher than $5 \cdot 10^{-2}$ M. Concentration of dithionite was measured by means of spin resonance. The decomposition curve had, at concentration $5 \cdot 10^{-2}$ M, a typical autocatalytic shape. Addition of bisulphite led to a decrease of the length of the induction period. The extent of the fast phase of the decomposition decreased and the decomposition

curve changed, at great concentrations of bisulphite, to the shape characteristic of a first-order reaction. The shape of the decomposition curve is governed by two reactions. The first one, catalyzed by bisulphite ion, is supposed to proceed as a normal, autocatalytic reaction of the 2nd order. The second reaction is assumed to be much faster, to be catalyzed by sulphur, to start after an induction period and to stop when a certain amount of the decomposition product is formed, by which the catalyst is removed. The rate of the slow reaction is governed by reaction (13).

Lem and Wayman¹⁷⁻¹⁹ investigated the decomposition of dithionite in buffered solutions at laboratory temperature at pH c. 4. Their results suffered from the fact that their polarographic decomposition curves did not represent the time dependence of the concentration of dithionite itself, as was supposed by the authors, but the dependence of the sum of the concentrations of dithionite and sulphide. The role of sulphide and of sulphur is limited to the function of electron carriers. The treatment of the experimental data on the reaction rate at the beginning of the reaction is semiquantitative, so that the proposed relation for the dependence of the decomposition rate on pH, concentrations of dithionite and of sulphoxylate is only of orientation value. However, this relation was used to set up a reaction mechanism. In the induction period the reaction rate is determined by the hydrolysis of dithionite (reaction (5)). In the fast phase the decomposition is governed by reaction (10). According to the authors, the reaction (10) is accelerated by H₂S and possibly also by sulphur by removal of an electron from HSO₂⁻ under the formation of the radical •HSO₂. This radical reacts with HS₂O₄⁻ faster, yielding the radical •HSO₃ instead of the anion HSO₃⁻. The radical •HSO₃ takes then one electron from H₂S⁻ or from S⁻. The authors also proposed an equation which should express the course of the whole decomposition curve. This equation yields an S-shaped curve. However, it totally differs from that obtained experimentally. Lem and Wayman proved that a distinct increase in the decomposition rate and the elimination of the induction period ensues after addition of H₂S. The decomposition is slightly accelerated by addition of Na₂S₂O₃, whereas addition of SO₂ in various forms has a negligible rate-decreasing effect. Zn²⁺, Cd²⁺ and In³⁺ salts are powerful inhibitors of the decomposition.

In the mentioned papers dithionite was determined mostly by chemical analysis and by the spin signal of its monomer. Neither of the methods is suitable for the determination of intermediates and of the fast changes of their concentrations. In contrast to this, polarography, when properly applied, has undoubtedly many advantages. It is very sensitive, fast and gives informations on the concentration of dithionite, sulphite, sulphide, thiosulphate, trithionate²⁰, tetrathionate and of polarographically active sulphur. In addition, some previously published polarographic studies contribute to the elucidation of the decomposition mechanism. These are: polarographic study of the electrochemical behaviour of dithionite²¹ which appeared in 1954, and the papers on electrode and chemical reactions in the system sulphurous acid-dithionic acid²²⁻²⁵. In 1958 polarographic curves of the solutions of decomposing dithionite were published²⁴ from which it can be seen that a product is formed in considerable amount which had been not identified at that time (Fig. 1). Later on, this substance was identified as sulphide. The decomposition curve of dithionite was without any inflex, which indicated that the decomposition rate did not decrease in the fast phase of the decomposition, until all dithionite disappeared (Fig. 2). Also of importance is the scheme of electrode reactions and chemical equilibria

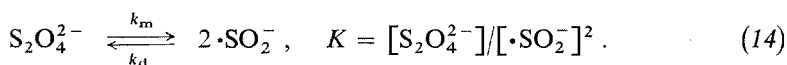
in the solution of dithionite²¹, published in 1954 (Scheme 1). The compounds are presented in non-dissociated form. The arrow \rightarrow means electrode reaction with electron transfer, the sign \leftrightarrow reversible electrode reaction, \rightarrow chemical reaction and \rightleftharpoons chemical equilibrium in the solution.



SCHEME 1

Electrode and Chemical Reactions and Equilibria in Solutions of Dithionite

Evidently, it was proved for the first time that a mobile equilibrium exists between the dithionite dimer and its two monomers, the free radicals $\cdot\text{HSO}_2$



The calculated value of k_m/\sqrt{K} was $6 \cdot 10^{-3} \text{ s}^{-1} \text{ mol}^{-1/2} \text{ l}^{1/2}$ (at 40°C)²¹. Further,

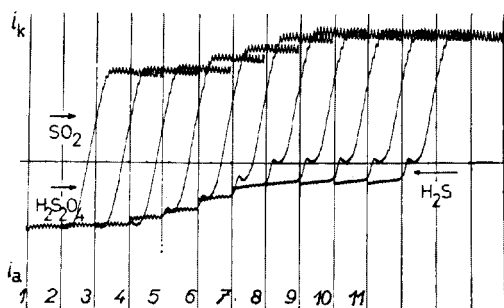
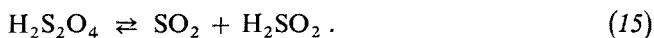


FIG. 1

Anodic and Cathodic Waves of Dithionite in Its Decomposition in Acidic Solution

$2 \cdot 10^{-4} \text{ M-Na}_2\text{S}_2\text{O}_4$, pH 2.7. Time after addition of dithionite at the moment of registration: 1 1 min, 2 4 min, 3 7 min, 4 13 min, 5 16 min, 6 18 min, 7 21 min, 8 27 min, 9 30 min, 10 34 min, 11 39 min.

the mobile disproportionation equilibrium* (15) was found



The mobility of this equilibrium in acidic medium, as well as the existence of mobile equilibrium (14) and of the radical $\cdot\text{SO}_2^-$ were reliably proved on the one hand on the basis of the dependence of the heights of polarographic kinetic currents of radical $\cdot\text{SO}_2^-$ and of SO_2 on temperature and concentration of dimer $\text{S}_2\text{O}_4^{2-}$, and, on the other hand, using special polarographic techniques^{21,23-25,27}. The equilibrium decomposition (14) in aqueous solutions of dithionite was found five years later again by Rinker and coworkers²⁸ by paramagnetic resonance measurements in solutions.**

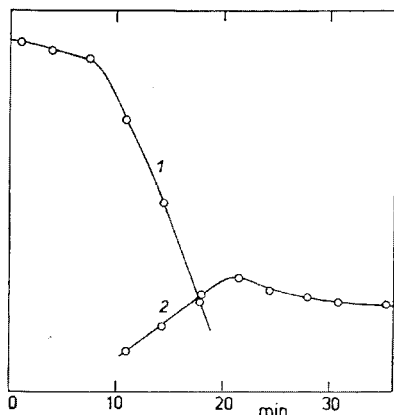


FIG. 2
Time Dependence of the Height of the Wave
of Dithionite (curve 1) and of Sulphite
(curve 2) in the Decomposition in Acidic
Medium
 $2 \cdot 10^{-4} \text{M} \cdot \text{Na}_2\text{S}_2\text{O}_4$, pH 2.7.

The mentioned earlier polarographic measurements demonstrated the following facts, important for suggesting mechanisms of the decomposition of dithionite: 1) H_2S is an important intermediate in the decomposition in acidic solutions. 2) The participants of equilibria (15) and (14) *i.e.* SO_2 and the radical $\cdot\text{SO}_2^-$ or $\cdot\text{HSO}_2$ yield measurable anodic and cathodic kinetic waves. Consequently, at least 1/10 of the dimer must decompose during the time of one drop, *c.* in 3 s, to the monomer or to SO_2 . This means that the rate constant of the formation of these components (*e.g.*

* The experimental evidence of the existence of disproportionation equilibrium (15) makes it possible to understand the decomposition of dithionite in the presence of formaldehyde to formaldehyde bisulphite and formaldehyde sulphonylate and the fast exchange of labelled sulphur between bisulphite and dithionite²⁶.

** In spite of the fact that polarographic study²¹ was the first paper to prove the existence of radical $\cdot\text{SO}_2^-$ and of the monomerization equilibrium (14) quite convincingly, the detection of the radical as well as of equilibrium (14) is now ascribed unjustly to Rinker and coworkers. Polarographic study²¹ has been abstracted in Chemical Abstracts²⁹. The other studies have also been abstracted³⁰, however, the abstracts contain gross errors made by the abstractor.

reaction (5)) is at least of the order of 10 s^{-1} . This was also verified by Lynn and co-workers³¹ who found the value of the monomerization rate constant $k_m = 40 \text{ s}^{-1}$, by using the mentioned polarographically determined value of k_m/\sqrt{K} .

In the present work use was made of polarography for a detailed study of the effects of different factors on the decomposition of dithionite in buffered solutions at various temperatures and various concentrations. However, most experiments were carried out at pH c. 4 and with dithionite concentrations up to $2.5 \cdot 10^{-3} \text{ M}$.

EXPERIMENTAL

The curves were recorded with the electronic polarograph LP 60 in a Kalousek vessel in the absence of air. The capillary used had a bent end according to Smoler³², ensuring that after each drop a fresh solution was electrolysed. The normal calomel electrode was used as reference. It has a sufficient layer of calomel, so that even in a long recording at constant potential its polarization did not occur which would have otherwise shifted the potential scale and change the recorded current.

In applying polarography to the investigation of the decomposition of dithionite it had always to be borne in mind that the half-wave potentials of both dithionite and sulphide change with pH according to Fig. 3. In a medium of pH between 4.5 and 5.5, both waves cannot be any more reliably separated. If the current is recorded at -0.2 V (NKE) at pH 4.5 in a solutions containing both dithionite and sulphide (as it was the case in the work of Lem and Wayman¹⁷), the measured current is the sum of waves of both components (Fig. 4). Therefore, to follow the time changes of the concentration of dithionite alone the current was recorded at a potential when the depolarization of hydrogen sulphide did not yet occur. At this potential, only a certain fraction of the limiting current is recorded, but this fraction being constant, the time change of the recorded current indicated directly the degree of decomposition of dithionite (the true decomposition curve, Fig. 5). If the time curves were recorded at more positive potentials, it was always clearly recognized that the actually recorded current is the sum of dithionite and sulphide waves, *i.e.* that the degree of decomposition is always higher than indicated by the recorded current (the additive decomposition curve). Concentration of thiosulphate was calculated from the difference

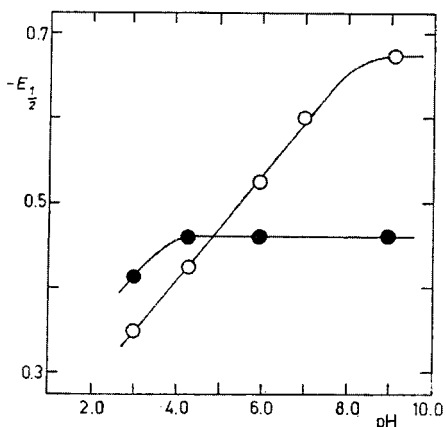


FIG. 3

Dependence of the Half-Wave Potential of Dithionite ● and of Sulphide ○ on pH

Potential is referred to saturated calomel electrode.

of the currents recorded at -0.3 and -0.05 V (Fig. 4). Polarographically active forms of sulphur or of polysulphides manifested themselves by the appearance of the anodic-cathodic sulphide wave^{33,34}.

The cathodic current, corresponding to the reduction of SO_2 , present in the solutions, is always increased in the presence of dithionite by a kinetic wave of SO_2 , formed by disturbing the mobile disproportionation equilibrium (15) (Fig. 1). Direct evaluation of the concentration of SO_2 , without correction for the mentioned contribution, can be made only after the dithionite is completely decomposed.

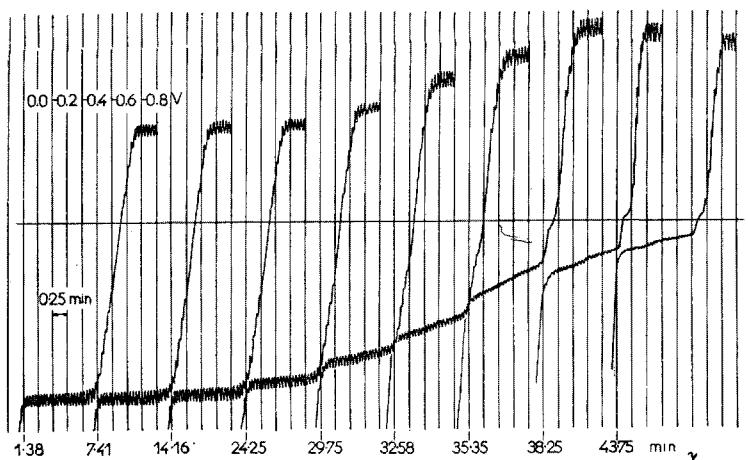


FIG. 4

Time Dependence of the Waves of Dithionite during Its Decomposition

$1 \cdot 10^{-3} \text{M-Na}_2\text{S}_2\text{O}_4$, pH 4.25, 20°C . 100 mV/absc., from +0.2 V. $E_{1/2}$ of dithionite -0.47 V, $E_{1/2}$ of sulphite -0.42 to -0.43 V, $E_{1/2}$ of thiosulphate -0.15 V.

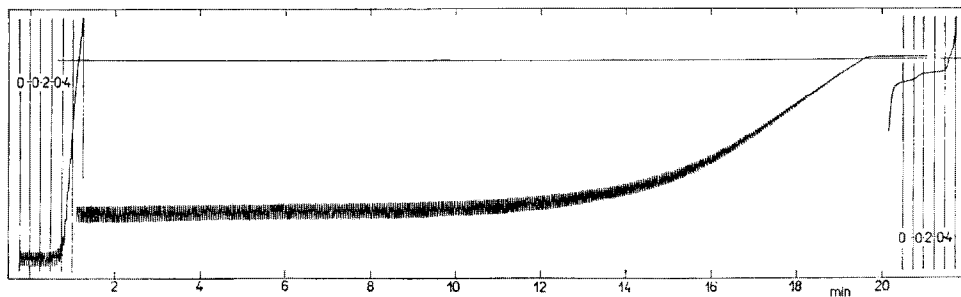


FIG. 5

True Decomposition Curve of Dithionite

$2.5 \cdot 10^{-3} \text{M-Na}_2\text{S}_2\text{O}_4$, pH 4.31, 20°C . Registered at constant potential -0.45 V. Left curve: the wave of non-decomposed dithionite. Right curve: Waves after decomposition. At -0.2 V the sum of waves of dithionite and sulphide would be registered.

Some experiments were made in strongly acidic and concentrated solutions of dithionite, using a small test tube, filled with the solution close up to the stopper to make sure that the decomposition proceeded in the absence of atmospheric oxygen. The sample taken for polarography was of course an appropriately diluted solution in a buffer of pH 6–9 in which the decomposition practically stopped. The waves of dithionite, thiosulphate, sulphide and active sulphur were sufficiently separated (Fig. 6).

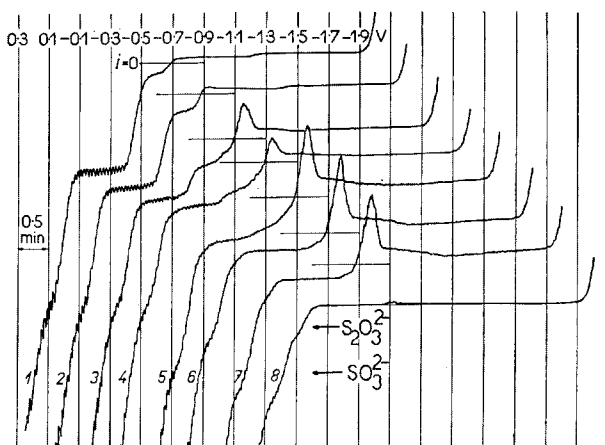


FIG. 6

Curves of Dithionite and of Intermediates after Various Times of Decomposition

Initial concentration of $\text{Na}_2\text{S}_2\text{O}_4$ 0.2M. Decomposed in 0.5M- H_3PO_4 . Pipetted into a buffer of pH 9.2 after: 1 0.5 min, 2 1.25 min, 3 5.5 min, 4 7.25 min, 5 9.5 min, 6 10.75 min, 7 11.75 min, 8 30 min. On the cathodic side of curve 1 the wave of monomer $\cdot\text{SO}_2^-$ at -1.22 V. $E_{1/2}$ of the wave of sulphide -0.67 V.

In following the catalytic effects of sulphide a certain amount of the dithionite solution was pipetted into the solution of sulphide or *vice versa*. During pipetting the solution in the vessel was bubbled with nitrogen. It was ascertained in separated experiments that the bubbling does not affect the concentration of sulphide or dithionite.

A mixture of 0.2M citric acid and 0.2M- Na_2HPO_4 was used as buffer solution. In studying the effect of addition of various substances the resulting pH of the solution was always determined and possible changes were taken into account when preparing the buffer. The dithionite used contained 96% of pure substance and a freshly prepared solution had pH ≈ 7 .^{*} The stock 0.1M solution was prepared by dissolving crystals of dithionite in 10^{-3} M- NaOH at 5°C in the absence of oxygen.

* The pH of the solutions used by Lem and Wayman¹⁷ in their studies of decomposition of dithionite in pure water was 3.5–4, at the beginning of the decomposition.

RESULTS

The new results are the following:

1) An anodic wave appears during the decomposition of dithionite, belonging to an intermediate whose half-wave potential is at pH up to 4.8 more positive, at higher pH values more negative than the half-wave potential of dithionite (Fig. 3). According to the shape of the wave and to the pH and concentration dependence of the halfwave potential it is the sulphide.

2) The wave of sulphide attains, after a longer time of decomposition an anodic-cathodic character (Figs 4, 6) which indicates the presence of polarographically active sulphur and/or polysulphides^{33,34}.

3) An opalescence appears in the solution at the beginning of the fast period of the decomposition, which is caused by the formation of sulphur in colloidal form. This finding is in accordance with previous studies. Sulphur disappears from the solution only after many hours.

4) The true decomposition curves of dithionite (without the contribution of sulphide) have, after the initial induction period, an almost linear course up to the complete disappearance of dithionite. In some cases a hardly distinguishable inflex can be seen, located close to the end of the dithionite decomposition (Fig. 5).

5) The presence of thiosulphate can be detected in the solution as late as in the fast phase of decomposition (Figs 4, 6).

6) Relative concentration of sulphide at the end of the decomposition decreases with increasing initial concentration of dithionite from 30% for 10^{-3} M solution to 2% for 10^{-2} M solutions. However, relative concentration of thiosulphate remains approximately constant, c. 10%.

7) With increasing concentration of dithionite the induction period becomes shorter and the rate of decomposition in the main phase increases (Fig. 7).*

8) The length of the induction period depends, when no other substances are added, on the purity of dithionite or its stock solutions.

9) At the beginning of the induction period dithionite decomposes probably in a reaction of the 1st order for dithionite. Since the length of the induction period is not precisely reproducible, this conclusion could not be taken as unambiguous. Nevertheless, the orders 2, or even 1.5, seem improbable.

10) The effect of sulphite on the decomposition depends on its relative concentration and on the moment of its addition. If it is added at pH 4 and at dithionite

* The length of the induction period is arbitrarily taken as the time in which 5% of the dithionite is decomposed. As will be demonstrated later, the shape of the decomposition curve is determined at 1% decomposition predominantly by gradual accumulation of reactive intermediates.

concentration $1 \cdot 10^{-3} \text{M}$ at the very beginning of the decomposition in a concentration lower than $1 \cdot 10^{-3} \text{M}$, it causes only a slight shortening of the induction period.

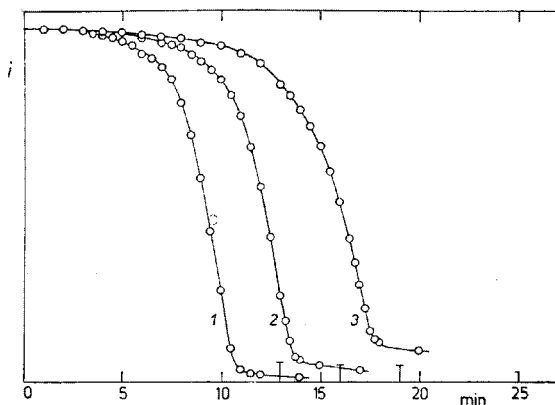


FIG. 7

Dependence of the Additive Decomposition Curve on the Concentration of Dithionite
 pH 4.05, 27°C . Constant potential -0.3 V . Concentration of dithionite: 1 $1 \cdot 10^{-2} \text{M}$, 2 $2.5 \cdot 10^{-3} \text{M}$, 3 $3.25 \cdot 10^{-3} \text{M}$. Vertical lines denote the height of thiosulphate wave.

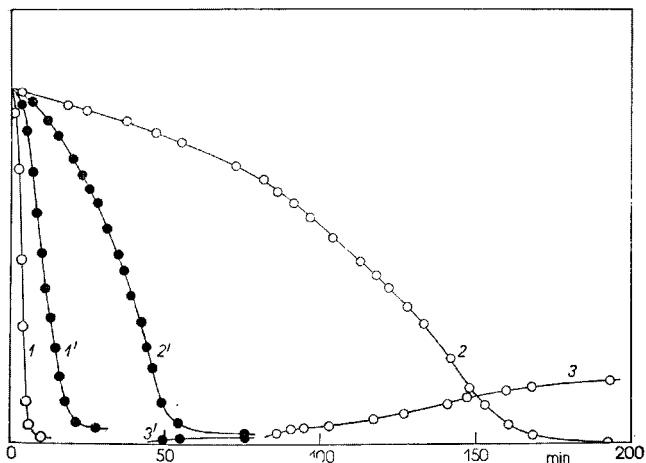


FIG. 8

Decomposition of Dithionite if Sulphite is Present in the Solution from the Beginning

$2 \cdot 10^{-3} \text{M-Na}_2\text{S}_2\text{O}_4$, pH 3.05. Registered at constant potential -0.3 V . 1 21°C , pure dithionite, 2 21°C , decomposition in the presence of $2 \cdot 10^{-2} \text{M-SO}_3^{2-}$, 3 21°C , time dependence of the height of the wave of thiosulphate. 1' 11°C , pure dithionite, 2' 11°C , decomposition in the presence of $2 \cdot 10^{-3} \text{M-SO}_3^{2-}$, 3' time dependence of the height of the wave of thiosulphate.

At higher relative concentrations ($5 \cdot 10^{-3}$ – $1 \cdot 10^{-2}M$) the decomposition is considerably inhibited (Fig. 8). No opalescence of the solution appears at all.

11) Contrary to this, addition of sulphite during the phase of fast decomposition increases the decomposition rate (Fig. 9).

12) If sulphite is present from the very beginning of the decomposition, thiosulphate is formed in measurable amounts already before the fast decomposition phase (Fig. 8).

13) At a great excess of sulphite the concentration of sulphide decreases very fastly to zero, as soon as the dithionite disappears.

14) Addition of thiosulphate at the beginning of the decomposition leads to a shortening of the induction period, whereas in the fast decomposition phase it has no visible effect (Fig. 10).

15) By addition of sulphur monochloride ($1 \cdot 10^{-3}M$) the rate of dithionite decomposition becomes immeasurably high. Sulphide and active sulphur are immediately formed and several minutes thereafter also thiosulphate appears.

16) Tetrathionate is fastly decomposed in the presence of dithionite. Thiosulphate and sulphite appear and the decomposition of dithionite is accelerated. Relative concentration of sulphide is lower and decreases fastly to zero.

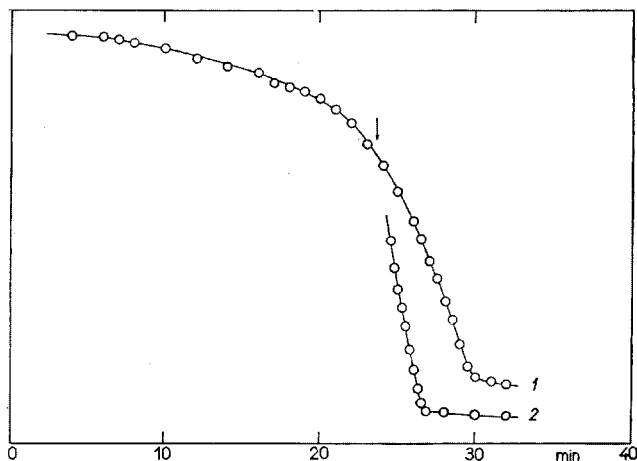


FIG. 9

Effect of Sulphite Added in the Phase of Fast Decomposition

$1 \cdot 10^{-3}M$ - $Na_2S_2O_4$, pH 4.17, $27^\circ C$, -0.3 V. Concentration of sulphite after its addition $1 \cdot 10^{-2}M$. 1 pure dithionite, 2 decomposition after addition of sulphite. The moment of addition is denoted by arrow.

17) The rate of dithionite decomposition is most effectively increased by the addition of sulphide (Fig. 11), especially in the presence of sulphite (Fig. 12). Already when 0.01% H_2S is added, the induction period of the decomposition of a $2.5 \cdot 10^{-3}\text{M}$ solution of dithionite is shortened by 15% at pH 4.3. At high concentration of sulphide a part of dithionite decomposes, during the addition, at immeasurably high rate, this part depending on the concentration of sulphide. Therefore, the height of the anodic wave, measured at the beginning of the decomposition, is not a sum of the heights of the sulphide and dithionite waves alone (Fig. 11). The remaining dithionite decomposes much more slowly. The fast decomposition is accompanied by immediate appearance of colloidal sulphur. At the same time, the concentration of thiosulphate increases steeply. Thiosulphate is formed probably in a secondary reaction of active sulphur with sulphite and of sulphide with dithionite, and is consumed in a reaction with sulphide. After the dithionite has disappeared, the remaining sulphide decomposes in a 2nd order reaction with sulphite (Figs 11, 12).

18) In the decomposition of dithionite under the experimental conditions used no measurable amount of polythionate is formed.

Sulphide as well as active sulphur are also observed in the decomposition of concentrated solutions of dithionite in strongly acidic medium (Fig. 6). In qualitative experiments a 0.5M solution was decomposed in 0.2M- H_3PO_4 . In accordance with earlier results^{3,10,35}, the colour of the solution became, after addition of the acid, dark orange-brown and gradually changed to light lemon-yellow. At the end of this

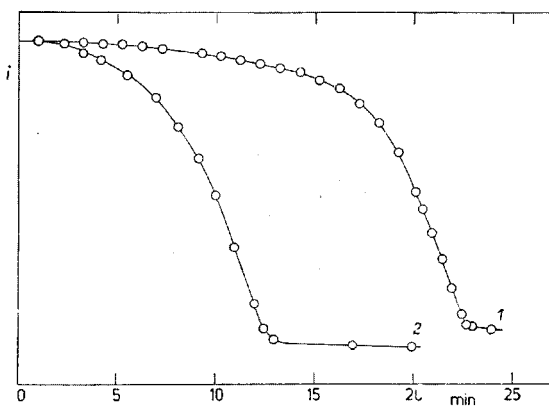


FIG. 10

Effect of Thiosulphate on the Decomposition of Dithionite

$1 \cdot 10^{-3}\text{M-Na}_2\text{S}_2\text{O}_4$, pH 4.11, 27°C , -0.35 V . 1 Pure dithionite, 2 decomposition in the presence of $1 \cdot 10^{-2}\text{M}$ thiosulphate from the beginning.

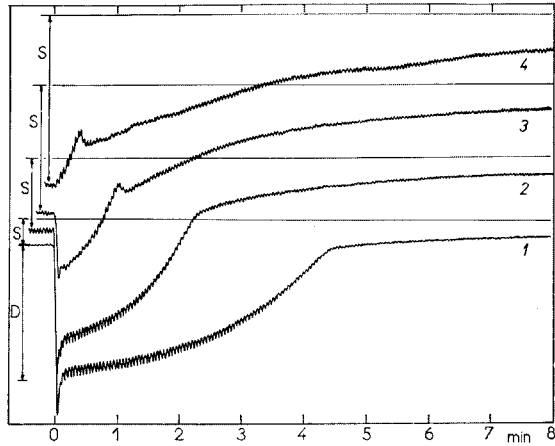


FIG. 11

Catalytic Effect of Hydrogen Sulphide on the Decomposition of Dithionite

The time dependence of the height of anodic wave was registered at constant potential of -0.25 V, pH 3.92, 27°C . Always the same amount of ditionite was added at time $t = 0$ into the solutions of sulphide whose concentration was: $1 \cdot 10^{-4}\text{M}$, $2 \cdot 10^{-3}\text{M}$, $3 \cdot 10^{-3}\text{M}$, $4 \cdot 10^{-3}\text{M}$. The height of the sulphide wave is denoted S, that of dithionite D. The height of the wave measured after mixing is not the sum of the $S + D$.

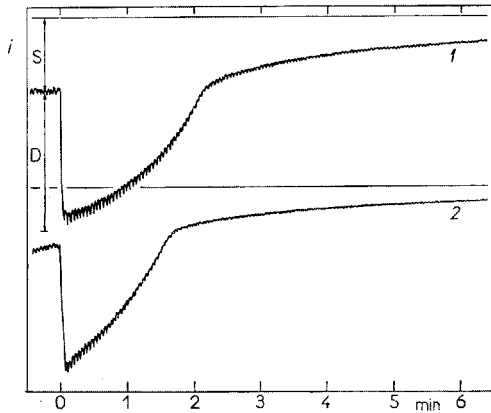


FIG. 12

Increase of the Catalytic Effect of Hydrogen Sulphide on the Decomposition of Dithionite in the Presence of Sulphite

The height of the anodic wave was registered at constant potential -0.25 V, pH 3.92, 27°C . Concentration of Sulphide $1 \cdot 10^{-3}\text{M}$ (wave height S). 1 dithionite was added to the solution in time $t = 0$. The resulting concentration of dithionite alone in the solution would be $2 \cdot 10^{-3}\text{M}$ (wave height D). 2 the solution before addition of dithionite contains $1 \cdot 10^{-3}\text{M}$ sulphide and $1.2 \cdot 10^{-3}\text{M}$ sulphite. Dithionite was added in time $t = 0$.

phase, an opalescence by the precipitated sulphur appeared in the middle of the test tube. Later on, the solution became milky, decolorized and the sulphur agglomerated. In the presence of air the solution became milky first at the boundary solution-air. The wave of sulphide could be observed already when the first sample was taken, *i.e.* 30 s after the addition of acid. Thiosulphate appeared in a measurable concentration only after 10 min. Opalescence appeared after c. 11 min. The sulphide concentration attained its maximum after 9 min and then decreased very fastly (Fig. 6). Dithionite disappeared after 8 min.

DISCUSSION

The new experimental results clearly reveal the drawbacks of the mechanisms of decomposition, suggested in previous publications. Obviously, the mechanism could hardly be derived only by analysing the final products after the time of several hours or even days. Many studies would have lead to other results, if their authors had known or respected the results of earlier publications.*

The papers, which appeared later on, brought many new data, however even here a number of lacks can be found which impair the interpretation of the decomposition mechanism. Rinker and coworkers¹⁴ limit their interpretation only to the induction period in which only a small fraction of the total amount of dithionite is decomposed. They postulate the formation of thiosulphate in the primary reaction (11) and of sulphite in reaction (12). This is in contradiction with the new data according to which thiosulphate is the product mainly of the subsequent secondary reaction, whereas sulphite is formed immediately in the first phase of the decomposition (results 5) and 12)). The decomposition reaction, suggested by Spencer¹⁵ (reaction (13)), is not an interpretation of the mechanism, but only a reaction scheme, satisfying the kinetics studied under the conditions when the secondary reactions completely obscure the picture of the decomposition. Burlamacchi and coworkers¹⁶ do not refer in their mechanism to any other reactions than Spencer. They do not try to propose any reactions leading to the formation of sulphur, neither those which play a role in the phase of fast decomposition. The reactions, suggested by Lister and Garvie¹² and by Lem and Wayman^{17,18}, cannot be correct without further specifications. Reaction (10) does not proceed as the main reaction in the fast phase

* So, *e.g.*, it was known that in the decomposing acidic solution of dithionite cadmium sulphide is precipitated upon addition of cadmium(II) salts^{1,3}. In the paper of Bernthsen⁶ it reads: "Finally it must be said that the solution of sodium dithionite does not give any precipitate after addition of CdSO_4 , however, CdS is formed very soon after addition of H_2SO_4 . The freed dithionic acid is evidently decomposed under the formation of H_2S which afterwards, if it is not removed from the reaction, reacts with a part of the obviously simultaneously formed sulphurous acid to yield sulphur and water." In spite of this, there exists a number of later papers in which nothing was known about sulphide as an important intermediate.

of the decomposition, since thiosulphate is not formed in this phase at a sufficient rate. The empirical decomposition reaction suggested by Lem and Wayman cannot be correct, as it leads to an S-shaped decomposition curve, *i.e.* to a shape principally different from the real one. Their decomposition curve does not give the true concentration change of dithionite, but the change of the sum of concentrations of dithionite and sulphide.

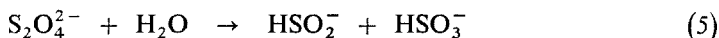
Mechanism of Decomposition

In our interpretation of the decomposition reactions we have deliberately limited ourselves to the analysis of homogeneous volume reactions which only can be taken into account in the induction period and at the beginning of the fast period of the decomposition. The scheme includes reactions of the formation of both intermediates and of final products and elucidates the mechanism of the reactions in the induction period as well as during autocatalytical phase. The intermediates are considered to be the result of a series of disproportionation reactions in which the valence of sulphur changes. Its highest oxidation state is IV, *i.e.* sulphite and compounds of lower valent sulphur are formed, so that the resulting formal valence of sulphur be S(III), the same as in dithionite. The scheme makes use of the available data of lower oxy-acids of sulphur from other papers^{1,2,8,36} and also of the picture supplied by polarography²¹⁻²⁵ on the decomposition and behaviour of dithionite. It differs from earlier schemes especially in that the formation of final products is not confined already to the primary reactions (except for sulphite), but only to the consecutive reactions of the intermediates. These are sulphonylic acid, active forms of sulphur, hydrogen sulphide, polysulphides, thiosulphurous acid^{1,2,36-38} and probably also sulphanemonosulphonic acids³⁹ in forms, determined by the pH of the solution. The proposed reactions are of course only schematic, in the sense, that they do not specify the structures of isomeric acids, and the given ionization degrees are purely formal. Also the active forms of sulphur are not specified which can be the following: atomic sulphur, hydrate $S \cdot H_2O$, thioperoxide $HSOH$ (see^{1,8,40}), polymeric diradical⁴¹, sulphur in the polysulphidic chain or even sulphur in the chain of sulphanemonosulphonic acids. The reactions also do not involve other species with lower oxidation degree of sulphur, as *e.g.* the experimentally proved, but unidentified substance, which is oxidized at the potential of -1.1 V at pH 6.3 (NCE). This substance must have very strong reduction properties²⁵. Further it is assumed that a weak polymerization of sulphur or its incorporation into linear chains does not decrease its reactivity and the denotation S_n is used for all types of reactive sulphur.*

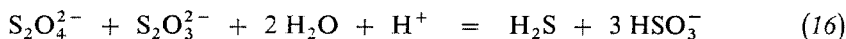
* The present mechanism does not exclude the possibility of radical reactions. However, a reaction mechanism, based only on radical reactions, would be far more hypothetical than that based on non-radical reactions.

Induction Period

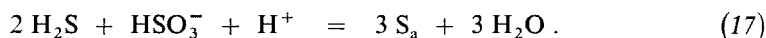
At the very beginning of the induction period dithionite decomposes in a reaction probably of the 1st order. The rate determining reaction could be either disproportionation of dithionite



or its monomerization (reaction (14)). Polarographic measurements have shown that such reactions take place, however, that their rates are much higher than the rate of the decomposition reaction. Not even the radical reactions proposed by Rinker and coworkers (11) determines the rate, since this reaction is of the order 1.5. It has been also proved that thiosulphate is not detectable in the induction period. It could be, however, removed in the reactions with dithionite, yielding hydrogen sulphide

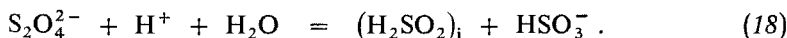


and sulphur in a consecutive reaction



As will be shown further, both H_2S and S_8 have a catalytic effect on the decomposition, but thiosulphate decreases the induction period only at relatively high concentration (Fig. 10). If it is present in small amounts, the rate of production of H_2S and S_8 is so small that it does not affect the subsequent processes to a decisive extent. Neither does it seem that the interaction of dithionite with one of the components of the equilibrium (15), sulphylic acid, can be the desired reaction, as the rate of this reaction should be strongly inhibited by increasing the concentration of HSO_3^- , e.g. by lowering the equilibrium concentration of sulphylic acid in the solution.

Therefore it seems probable that the decomposition reaction of the first order is the slow formation of sulphylic acid in the reactive isomeric form



In this form, sulphylic acid does not recombine fastly with HSO_3^- and it is not in a mobile equilibrium with that form which participates in equilibrium (15).*

The main reactions of the isomeric form of sulphylic acid are, under our experimental conditions, reactions with dithionite, resulting in the formation of active

* The proposed reaction (18) is not identical with reaction (5), since in (5) different forms of sulphylic acid were not distinguished and the existence of disproportionation equilibrium (15) was not taken into account.

sulphur*

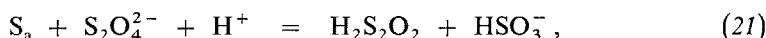


and probably also, to a much less extent, of thiosulphate

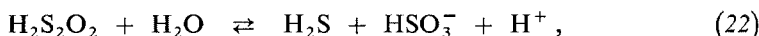


Development of the Decomposition Reactions

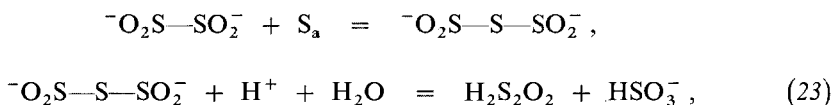
The irreversible formation of active sulphur according to (19) starts the decomposition chain of dithionite. In the first step the most probable partner of active sulphur is dithionite and reaction (21) takes place



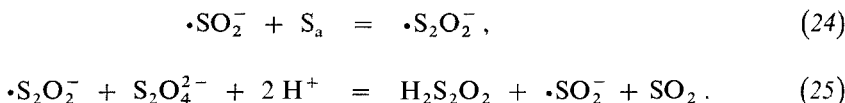
which yields hydrogen sulphide because of the existence of equilibrium



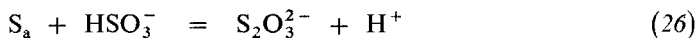
which is shifted markedly to the side of dissociation^{37,39,42-44}. Reaction (21) proceeds probably *via* insertion of sulphur into the S-S bond which may be described as follows



or *via* a reaction of a radical type, initiated by a reaction with the monomer of dithionite

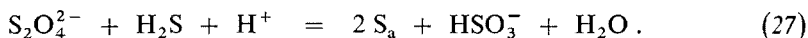


In this initial phase polymerization of sulphur can be neglected. If any active sulphur is formed, *e.g.* in the form of a low polymerized diradical, it collides more probably with dithionite than with further sulphur to form a higher polymer. No colloidal sulphur appears, nor the reversible reaction leading to thiosulphate

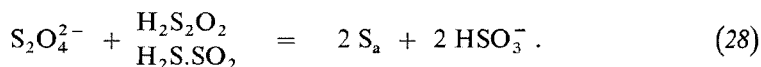


* Reactions (19) and (20) are, from a purely schematic point of view, reactions of two forms of sulphylic acid, one of which participates in equilibrium (15) or is formed from dithionite in the moment of the reaction by the shift of the electron pair of the S-S bond.

is manifested as yet. Reactions (21) and (22) lead to the formation of further active compounds, thiosulphurous acid and hydrogen sulphide. Their formation initiates the autocatalytic phase of the decomposition. The decomposition reaction is accelerated by reaction of hydrogen sulphide with dithionite, *i.e.* by the reaction of one of the products with the substrate

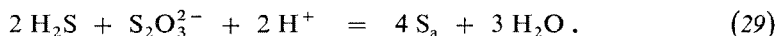


Experimental results show that the decomposition of dithionite is accelerated in the presence of sulphite (result 11)). The rate increase may be caused by the formation of active complex $\text{H}_2\text{S}\cdot\text{SO}_2$, if this complex attacks the dithionite easier than hydrogen sulphide alone, or by influencing the equilibrium (22) in favour of the unstable thiosulphurous acid, or, eventually, by the reaction of H_2S with HSO_3^- yielding active sulphur according to Eq. (17) which probably proceeds *via* the same complex $\text{H}_2\text{S}\cdot\text{SO}_2$. Thus, the effect of sulphite allows to conclude that also the reaction of dithionite with thiosulphurous acid or the complex $\text{H}_2\text{S}\cdot\text{SO}_2$ is important in the autocatalytic process



In reactions (27) and (28) active sulphur which is consumed in reaction (21) is regenerated always in amounts which allow its reaction with a two-fold amount of dithionite.

The decomposition reactions are also accompanied by the increase of the concentration of sulphite. Consequently, sulphur becomes deactivated by the parallel reaction (26), yielding thiosulphate. The steadily increasing amount of sulphite is consumed in its reaction with sulphide (17) and new active sulphur enters the system. Its another source is the fast reaction of sulphide with thiosulphate

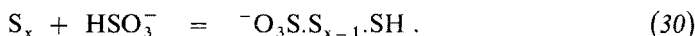


Reactions (22), (27), (28), (17) and (29) thus form a cycle, leading to fast autocatalytic decomposition.

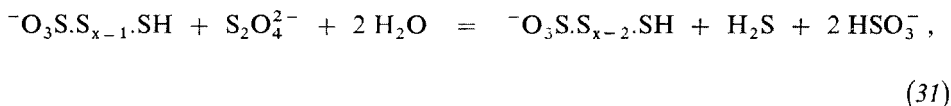
At the beginning of the fast decomposition phase agglomeration of sulphur appears and opalescence of the solution becomes apparent.* The polymerized sulphur

* Effective participation of sulphur agglomerates in the decomposition process can manifest itself by the formation of microheterogeneous structures on the interphase of which the decomposition of dithionite may be accelerated. The constant or only slightly retarded rate of decomposition up to the end of the decomposition is probably determined to a great extent by adsorption of dithionite on colloidal sulphur.

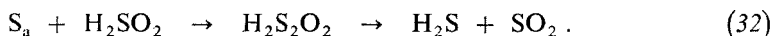
can most probably be partly reactivated by reaction with HSO_3^- by incorporation into the chain of unstable sulphane monosulphonic acids or their anions



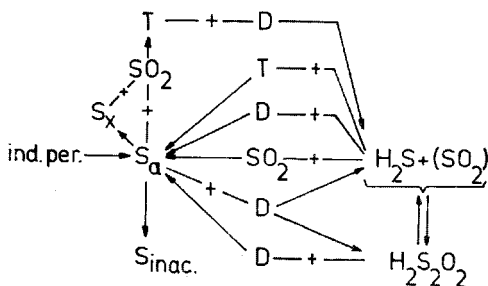
These compounds could react with dithionite according to equation



which is, in the sense of the earlier note, pure formally the sulphuration of sulphylic acid:



Analysis of experimental data leads to the conclusion that the main reactions, proceeding in the fast decomposition phase, can be summarized as in Scheme 2:



SCHEME 2

Decomposition Reactions of Dithionite in the Fast Decomposition Phase after the Induction Period Has Been Completed

Here S_a is active sulphur, S_x polymeric biradical or active sulphur incorporated in chains, S_{inac} inactivated sulphur, D dithionite and T thiosulphite.

Discussion of the Decomposition Mechanism

According to the above proposed Scheme 2 the autocatalytic decomposition of dilute acidic solutions of dithionite proceeds in the fast period predominantly through several simultaneous cycles under the participation of non-specified active forms

of sulphur S_a , H_2S , SO_2 , of some of the forms of thiosulphurous acid and of dithionite. If the only autocatalytic reaction were the direct reaction of only one reaction product, e.g. H_2S , with dithionite, the decomposition curve would necessarily be S-shaped. However, the experimentally found shape is different. It shows that the reaction rate does not decrease during decomposition or it does so only close to its end. The decomposition curves must consequently be governed by consecutive reactions in which more than one decomposition product participate.

Reactions of this kind are the reactions of H_2S with HSO_3^- (17) and reaction of H_2S with $S_2O_3^{2-}$ (29). Both these reactions yield active sulphur in such amount that the decomposition is steadily accelerated by regeneration of reactants in reaction (21). Both products, H_2S and HSO_3^- contribute to the autocatalysis also as participants of equilibrium (22) shifting it towards the very reactive thiosulphurous acid, which yields further active sulphur by reacting with dithionite (reaction (28)). The increased formation of active sulphur by these reactions compensates also for its losses by agglomeration* or by the formation of thiosulphate according to reaction (26).

Direct participation of hydrogen sulphide in the decomposition of dithionite has been proved in two ways: by following the effect of addition of H_2S into the system (result 17)) and by analysis of the obtained kinetic curves which are in contradiction with the assumption that hydrogen sulphide formed in reactions (21) and (22) is removed from the system only by parallel reaction (17) yielding sulphur.

The catalytic effect depending on the product of concentrations of two decomposition products is demonstrated by experimental results 1) and 17). It agrees with the kinetic analysis in the following paper⁴⁵ and with other experimental data on the system H_2S-SO_2 which postulate the existence of thiosulphurous acid and of equilibrium (22) (see^{36,42}).

We were not able to prove experimentally which of the active forms of sulphur participates in the decomposition of dithionite. Only the formation of polarographically active sulphur was detected (result 2)). Experiments with freshly generated emulsion of colloidal sulphur resulting from decomposition of thiosulphate in acidic solutions gave no decisive results. Thus this part of the concepts on the decomposition is not supported by experimental evidence, however, it seems to be an unambiguous result of the kinetic behaviour of the system.

The problem of the formation of thiosulphate, which was discussed in all previous interpretations, is closer to its solution now. Under our experimental conditions thiosulphate can be detected only in the last decomposition stages (results 5) and 6)), but it appears earlier in the presence of excess HSO_3^- in the solution (result 12)).

* Agglomerated sulphur is probably activated by reactions (30) and (31). However, it necessarily can reenter the reactions only to a small extent because of the low concentration of agglomerates. Their effect can be increased if dithionite is effectively adsorbed on them.

Obviously it is not a major primary product, but a product of consecutive reactions of HSO_3^- with sulphur, whose reaction rate is low in comparison with the processes in the main decomposition phase. Decrease of the induction period by addition of thiosulphate at the beginning of the decomposition can be explained by the slow formation of H_2S and S_a (reactions (16) and (17)).

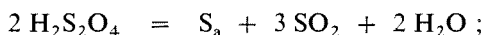
The mechanism proposed here is able to explain also further effects found. The inhibiting effect of HSO_3^- , added at the very beginning of the decomposition, which is connected with the appearance of thiosulphate and with the absence of colloidal sulphur in the solution, is that HSO_3^- adds the reactive sulphur S_a under the formation of thiosulphate according to equation (26) and thus interrupts the sequence of reactions, leading to catalysing products. The strong effect of S_2Cl_2 is due to its primary hydrolysis to sulphurous acid which decomposes to H_2S and HSO_3^- , *i.e.* to compounds which also have an catalytic effect³⁷. The catalytic effect of decomposition products, also described by Rinker and coworkers as well as by Lem and Wayman, can be accounted for the presence of H_2S together with excess HSO_3^- , *i.e.* to reactions (27) and (28), since the concentration of active sulphur is necessarily already very low. The stabilization effect of Zn^{2+} , Cd^{2+} , and In^{3+} ions is due to the fact that they lower the concentration of hydrogen sulphide by forming salts with low solubility product¹⁹. The fast decomposition of tetrathionate in the presence of dithionite allows to suppose that probably also other polythionates are not stable in the presence of dithionite. If they are formed during decomposition then it is only in consecutive reactions of the products.

CONCLUSION

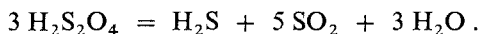
It follows from the above results that hydrogen sulphide is always present in the decomposition of dithionite. Therefore, all attempts to interpret the mechanism of decomposition must explain its formation. The decomposition scheme prior to total decomposition is principally the same in differently acidic and probably also in alkaline solutions. The discrepancies in the earlier results can be explained by the fact that the decomposition was followed mostly after a considerable time had elapsed, often even after all the consecutive reactions of the primary products had been completed which of course proceeded at different rates according to acidity and concentrations.

As a general conclusion, there are two fundamental primary reactions:

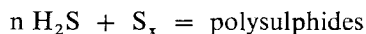
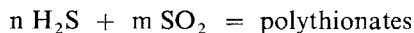
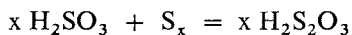
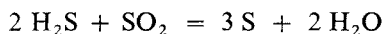
1) Non-catalyzed reaction in which active (non-colloidal) sulphur is formed and which is effective mainly in the induction period:



2) Autocatalyzed reaction, proceeding mainly in the fast decomposition phase:



The reaction in the fast phase is accompanied by secondary reactions of the decomposition products:



Just these parallel and consecutive reactions determine, after total decomposition of dithionite, the final composition of the products.

REFERENCES

1. *Gmelins Handbuch der Anorganischen Chemie, Schwefel*, Teil B, Lief. 2, System Nummer 9, p. 373. Verlag Chemie, Weinheim 1960.
2. Lyons D., Nickless G. in the book: *Inorganic Sulphur Chemistry* (G. Nickless, Ed.), p. 509. Elsevier, Amsterdam 1968.
3. Meyer J.: *Z. Anorg. Allg. Chem.* 34, 43 (1903).
4. Remy H.: *Lehrbuch der Anorganischen Chemie*, Bd. I, p. 875. Geest und Portig, Leipzig 1963.
5. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*, 2nd Ed., p. 552. Wiley, New York 1966.
6. Bernthsen A.: *Ann.* 208, 161 (1881).
7. Deines O. V., Elstner G.: *Z. Anorg. Allg. Chem.* 191, 340 (1930).
8. Marshak E. M.: *Khim. Nauka Prom.* 2, 524 (1957).
9. Jellinek K., Jellinek J.: *Z. Phys. Chem.* 84, 325 (1919).
10. Scholder R., Denk G.: *Z. Anorg. Allg. Chem.* 222, 48 (1935).
11. Breatly G., Starkie J.: *J. Soc. Dyers Colourists* 64, 278 (1948).
12. Lister M. W., Garvie R. L.: *Can. J. Chem.* 37, 1547 (1959).
13. Jouan R.: *J. Chim. Phys. Physicochim. Biol.* 56, 327 (1959).
14. Rinker R. G., Lynn S., Mason D. M., Corcoran W. H.: *Ind. Eng. Chem. Fundam.* 4, 282 (1965).
15. Spencer M. S.: *Trans. Faraday Soc.* 63, 2510 (1967).
16. Burlamacchi L., Guardini G., Tiezzi E.: *Trans. Faraday Soc.* 65, 496 (1969).
17. Lem W. J., Wayman M.: *Can. J. Chem.* 48, 776 (1969).
18. Wayman M., Lem W. J.: *Can. J. Chem.* 48, 782 (1969).
19. Lem W. J., Wayman M.: *Can. J. Chem.* 48, 2778 (1969).
20. Furness W.: *J. Soc. Dyers Colourists* 66, 270 (1950).

21. Čermák V.: Chem. Zvesti 8, 714 (1954).
22. Čermák V.: This Journal 20, 983 (1955).
23. Čermák V.: This Journal 23, 1471 (1958).
24. Čermák V.: This Journal 23, 1871 (1958).
25. Čermák V.: This Journal 24, 831 (1959).
26. Van der Heijde H. B.: Rec. Trav. Chim. Pays-Bas 72, 95 (1953).
27. Fischer O., Dračka D., Fischerová D.: This Journal 25, 323 (1960).
28. Rinker R. G., Gordon T. P., Mason D. M., Corcoran W. H.: J. Phys. Chem. 63, 302 (1959).
29. Chem. Abstr. 49, 14532 (1955).
30. Chem. Abstr. 52, 13482 (1958).
31. Lynn S., Rinker R. G., Corcoran W. H.: J. Phys. Chem. 68, 2363 (1964).
32. Smoler I.: J. Electroanal. Chem. Interfacial Electrochem. 6, 465 (1963).
33. Hall M. E.: Anal. Chem. 22, 1137 (1950).
34. Kalvoda M.: This Journal 21, 825 (1956).
35. Basset B. H., Durrant R. G.: J. Chem. Soc. 1927, 1401.
36. Goehring M.: Fortschr. Chem. Forsch. 2, 444 (1952).
37. Stamm H., Goehring M.: Angew. Chem. 58, 52 (1945).
38. Stamm H., Becke-Goehring M., Schmidt M.: Angew. Chem. 72, 34 (1960).
39. Schmidt M.: Angew. Chem. 73, 394 (1961).
40. Silbermann J. I.: Zh. Obshch. Khim. 10, 1257 (1940).
41. Pollard F. H., Jones D. J.: Chem. Soc. Symposia, Bristol 1958, p. 389. Chem. Soc. Spec. Publ. No 12, Chem. Soc. London 1958.
42. Goehring M.: Z. Anorg. Chem. 253, 313 (1947).
43. Van der Heijde H. B.: *IUPAC Colloquium, Münster 1954*. Verlag Chemie, Weinheim 1955.
44. Stamm H., Goehring M.: Ber. Deut. Chem. Ges. 76, 737 (1943).
45. Smutek M., Čermák V.: This Journal 40, 3265 (1975).

Translated by V. Čermáková