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Recent trends in the chemistry of sulfur-containing reducing agents

S V Makarov

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Abstract. Data on the structure, synthesis, stability and reactivity of sulfur-containing reducing agents with C – S or S – S bonds — sodium dithionite, sodium hydroxymethanesulfinate and thiourea oxides — are surveyed. Reactions of anaerobic and aerobic decomposition of sulfur-containing reducing agents are discussed. The applications of these compounds in the studies of non-linear phenomena in chemical kinetics and in guanidine syntheses are considered. The bibliography includes 165 references.

I. Introduction

Compounds containing an S – S or C – S bond, namely, sodium dithionite, sodium hydroxymethanesulfinate (HMS, commercial name rongalite) and thiourea dioxide (TUDO), have long been used in chemistry and chemical technology as reducing agents. The traditional fields of application including printing and dyeing of textiles,[1] production of synthetic rubber,[2] manufacture of uranium and transuranium element compounds,[3] preparative organic[4] and inorganic[5] chemistry have been covered fairly comprehensively in monographs.[6,7] In recent years, some new fields of application appeared and the above-mentioned fields (mainly, organic synthesis[8,9]) have been further developed. In particular, increasing numbers of publications are devoted to the use of these compounds in biochemistry,[10–12] in organofluorine chemistry,[13] and in investigations of non-linear phenomena in chemical kinetics.[14,15] A promising field of application of thiourea dioxides and the products of their oxidation, trioxides, is the synthesis of guanidines.[16–20] The researchers' interest in the guanidine properties, which has increased in recent years,[21,22] is due to the discovery of an important biological function of nitrogen oxide, the precursor of which in an organism is L-arginine (2-amino-5-guanidinovaleric acid), and to the search for new medical drugs.[18,20] Thus, there is a need for a review that would reflect the state-of-the-art of the chemistry of sulfur-containing reducing agents.

S V Makarov Ivanovo State University of Chemistry and Technology, prosp. F Engelsa 7, 153460 Ivanovo, Russian Federation.
Fax (7-093) 241 79 95. Tel. (7-093) 232 73 97.
E-mail: makarov@icti.ivanovo.su

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II. The structure of molecules of sulfur-containing reducing agents

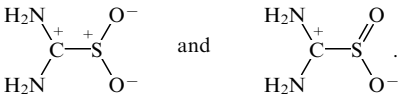
The molecular structures of sodium dithionite, HMS and TUDO have been studied in detail by IR and Raman spectroscopy and by X-ray diffraction analysis. The structure of sodium dithionite has aroused the greatest interest. Seemingly, the structure of the $S_2O_4^{2-}$ ion should resemble the structures of well-known sulfur-and-oxygen anions with the S – S bonds, *e.g.*, $S_2O_5^{2-}$ and $S_2O_6^{2-}$ (see Ref. 23). One might expect that $S_2O_4^{2-}$ and $S_2O_6^{2-}$ ions would correspond to D_{3d} and C_{2h} point groups of symmetry, respectively. This prediction came true only for the latter anion, while for sodium dithionite, unexpected results were obtained. According to X-ray diffraction data,[24,25] the $S_2O_4^{2-}$ ion belongs to the C_{2v} point group and contains an abnormally long S – S bond (2.39 Å). Later, it was shown by Raman spectroscopy[26,27] that in aqueous solutions of sodium dithionite, the structure of the $S_2O_4^{2-}$ ion changes, namely, it becomes centrosymmetrical and corresponds to the C_{2h} point group. The influence of the nature of the salt cation on the structure of the dithionite ion has been studied.[23] It was shown that the 'abnormal' eclipsed conformation (C_{2v}) of $S_2O_4^{2-}$ can be found in salts with small cations, for example, with sodium. In the salts with large cations, in particular, in tetraethylammonium dithionite, this anion is centrosymmetrical both in the solid state and in solution. Thus, the abnormal structure of sodium dithionite in the solid phase is due to the influence of the cation and to the associated packing effects[23] rather than to the properties of the $S_2O_4^{2-}$ anion itself. These experimental data were substantiated theoretically by the results of LCAO-X_α density functional calculations.[28] It was shown that the curve for the total energy *vs.* S – S bond length for dithionite ion, unlike these curves for $S_2O_6^{2-}$ or $S_2O_5^{2-}$ ions, has a very broad minimum. This indicates that the S – S bond length in $S_2O_4^{2-}$ depends appreciably on external factors, in particular, on the packing effects in the crystal. It was also found that the barrier to rotation in the dithionite ion is very low. This accounts for the easy dehydration of $Na_2S_2O_4 \cdot 2H_2O$ and the concomitant change in the dithionite structure (for example, the S – S bond length increases from 2.298 Å in the dihydrate to 2.393 Å in the anhydrous salt). Therefore, it can be expected that the properties of solid dithionites should depend on the nature of solvents from which they have been crystallised. Indeed, it has been demonstrated in relation to lithium dithionite[29] that the products isolated from aqueous and tetrahydrofuran solutions have different properties; in particular, the latter is extremely susceptible to oxidation and to self-ignition in air. When lithium dithionite is stored in a sealed capillary, its

crystal lattice is transformed giving rise to defects, and this accelerates solid-phase processes. A similar transformation but taking place at elevated temperatures was observed for the sodium salt. Thus, conditions used to prepare dithionites affect appreciably their properties. A substantial dependence of the stability on the nature of the solvent used for recrystallisation is also typical of solid sodium hydroxymethanesulfinate.[30]

Due to the long and rather weak S–S bond, dithionites tend to undergo homolytic decomposition giving rise to the $SO_2^{-\bullet}$ radical anions. The structural parameters of the $SO_2^{-\bullet}$ radical anion have been determined;[31] the (*r*) S–O distance is 1.523 ± 0.02 Å, the O–S–O angle (α_{O-S-O}) is $115.6 \pm 2.0^\circ$. The structures of the $SO_2^{-\bullet}$ radical anion and the $NaSO_2$ charge transfer complex were also determined by *ab initio* calculations.[32]

According to X-ray diffraction studies,[33] HMS is the sodium salt of hydroxymethanesulfinic acid, $HOCH_2SO_2Na$. The crystal lattice parameters of HMS and the interatomic distances in the $HOCH_2SO_2^-$ anion were determined; the C–S bond was found to be the longest one (1.838 Å).

X-Ray diffraction analysis of TUDO was first performed by Sullivan and Hargreaves;[34] later, the data were refined.[35,36] In the solid phase, TUDO exists as $(NH_2)_2CSO_2$. The CSO_2 group is pyramidal, the S–O and C–N bond lengths are 1.496 and 1.296 Å, respectively, and the C–S bond (1.867 Å) is much longer than this bond in the thiourea (1.716 Å) molecule. The bond lengths in the TUDO molecule found from X-ray diffraction data are in good agreement with the results of *ab initio* calculations.[36] It was suggested that TUDO is a combination of two zwitter-ion forms



In these ions, the negative charge is concentrated on the oxygen and nitrogen atoms and the positive charge is on the hydrogen, carbon and sulfur atoms, mainly, on sulfur. The results of calculations indicate that nucleophilic attack is directed at the carbon and sulfur atoms. The structure of thiourea dioxide depends substantially on the solvent. It was found[37] that after dissolution of TUDO in water, the acidity increases, a constant pH value being established very slowly. It was found in special experiments that these changes are not related to decomposition of TUDO or to the presence of oxygen. The ^1H NMR spectra of aqueous[38] and dimethyl sulfoxide[39] solutions of TUDO were found to vary with time. The peak observed initially in the TUDO spectrum is rapidly split into a doublet, these changes taking place only in the first minutes after dissolution of thiourea dioxide. Quantum-chemical calculations by the AM1 method for TUDO in the $(NH_2)_2CSO_2$ and $NH_2C(=NH)SO_2H$ (aminoiminomethanesulfinic acid) forms[40] showed that solvation with water or dimethyl sulfoxide decreases substantially the total energy of the system. Note that unlike the gas phase, in aqueous solutions, aminoiminomethanesulfinic acid is the thermodynamically more stable form. Thus, quantum-chemical calculations imply the possibility of TUDO tautomerisation in aqueous solutions. The tautomeric transformations of TUDO in aqueous solutions have been studied theoretically using the method of critical points on the potential energy surface.[41] The most probable mechanism of tautomerisation includes stages of successive intermolecular proton transfer in TUDO oligomers and decomposition of the oligomers to give solvated monomers of aminoiminomethanesulfinic acid.

The structure of thiourea trioxide (TUTO) has also been studied.[42] It was found that the C–N bonds in TUTO are virtually equivalent (1.298 and 1.297 Å) and are much shorter than the typical C–N single bond (1.470 Å), while the C–S bond length (1.815 Å) is slightly greater than the sum of the covalent radii of the S and C atoms (1.790 Å). The tetrahedral S atom forms three nearly equivalent S–O bonds (1.439, 1.431, and 1.446 Å). The structures of thiourea di- and trioxides are stabilised by intermolecular hydrogen bonds.[36,42] The unusually high density calculated[42] for TUTO, 1.948 g cm^{-3} (the density of thiourea dioxide is[36] 1.70 g cm^{-3}) points to a highly efficient packing of $(NH_2)_2CSO_3$ molecules in the crystal lattice. Apparently, the structure of TUTO is similar to that of TUDO.

The research into the structures of sodium dithionite, HMS and TUDO showed that each of these molecules contains an abnormally long bond, which is, hence, highly prone to rupture (S–S bond in the dithionite and C–S bonds in HMS and TUDO). It is this structural feature that accounts for the high reducing activities of these compounds. As will be shown below, the chemical reactivities of dithionites, HMS, TUDO and their analogues are governed by transformations of the same intermediates, namely, sulfoxylic acid H_2SO_2 or its anions and the $SO_2^{-\bullet}$ radical anion. This fact, together with the similarity of methods for the use of these compounds explain why they have been combined in one group.

III. Classification of sulfur-containing reducing agents and the fields of their application

The sulfur-containing reducing agents considered here (Table 1) can be classified into dithionites, α-hydroxyalkanesulfinates, and thiourea dioxides.

Thiourea trioxides are also included in Table 1. Data on α-aminoalkanesulfinates not reflected in the Table can be found in a monograph.[7] Note that the properties of most of compounds listed in Table 1 have been little studied. The only exceptions are sodium dithionite, HMS and TUDO, which have found wide practical use. Sodium dithionite and hydroxymethanesulfinate are used most often for the reduction of vat dyes in textile industry.[1] The processes involving these reducing agents form the basis of all industrial printing and vat dyeing techniques. The textile industry also makes use of zinc hydroxymethanesulfinates, which possess a lower reducing activity than HMS.[6] Conversely, α-hydroxyethanesulfinate is a stronger reducing agent than HMS.[7]

An important application of HMS and TUDO is the manufacture of synthetic rubber.[2] For instance, a mixture of HMS with isopropylbenzene hydroperoxide and ethylenediaminetetraacetatoferrate(III) initiates copolymerisation of butadiene with styrene. The Fe^{2+}–TUDO–H_2O_2 system is used to initiate polymerisation of various vinyl monomers.[59] Other effective initiating systems are TUDO–$KBrO_3$[60] and TUDO–$KMnO_4$.[61] In addition, TUDO is used for waste paper processing[62] and for wool bleaching.[63] Numerous publications have been devoted to the use of the reducing agents in question, mainly sodium dithionite, in biochemistry.[10–12,64–66] Sodium dithionite is used for the reduction of many natural and synthetic electron transfer agents including nicotinic acid derivatives, flavins and cytochromes;[64,65] TUDO is used for reduction of ferredoxin, cytochrome C and other substrates[66] and for inactivation and modification of cytidine triphosphate synthase.[11,12] *N*,*N*′-Dimethylthiourea is a highly efficient antioxidant, which has found wide use in biochemical and medical research.[67] Thus the reaction of hydrogen peroxide with *N*,*N*′-dimethylthiourea, resulting in the dioxide, can be used to determine the content of H_2O_2 in biological systems.[55]

Sulfur-containing reducing agents are widely used in organic synthesis. Thus sodium dithionite serves as the reagent for the reduction of nitro, nitroso, azido and azo compounds, aldehydes, ketones, keto esters, benzyls, quinones, heterocycles, and compounds with double bonds as well as for the synthesis of sulfones.[4] Hydroxymethanesulfinate and thiourea dioxide are used in similar processes, in particular, in the preparation of a light-stabiliser for plastics, Benazol P,[68] a stabiliser for motor oils called Diafen FP[69] and sulfones.[70–74] In recent years, the possibility of using these reducing agents in the chemistry of organofluorine compounds has been studied intensively.[13,75] Thiourea dioxide is also employed to reduce organosulfur compounds (sulfylimines, sulf-

Table 1. Sulfur-containing reducing agents.

Name of compound	Formula	Ref.
Dithionites		
Sodium dithionite	$Na_2S_2O_4$	7
Potassium dithionite	$K_2S_2O_4$	43
Lithium dithionite	$Li_2S_2O_4$	29
Zinc dithionite	ZnS_2O_4	44
Tin dithionite	$Sn(S_2O_4)_2$	25
Tetraethylammonium dithionite	$(Et_4N)_2S_2O_4$	45
α-Hydroxyalkanesulfinates		
Sodium hydroxymethanesulfinate (rongalite)	$HOCH_2SO_2Na$	7
Disodium hydroxymethanesulfinate	$NaOCH_2SO_2Na$	6
Zinc hydroxymethanesulfinate	$(HOCH_2SO_2)_2Zn$	46
Zinc hydroxyl hydroxymethanesulfinate	$HOCH_2SO_2Zn(OH)$	47
Zinc hydroxymethanesulfinate, disubstituted	$\overline{OCH_2SO_2Zn}$	6
Calcium hydroxymethanesulfinate, disubstituted	$\overline{OCH_2SO_2Ca}$	6
Titanium hydroxymethanesulfinate	$(HOCH_2SO_2)_4Ti$	6
Barium hydroxymethanesulfinate, disubstituted	$\overline{OCH_2SO_2Ba}$	6
Lead(II) hydroxymethanesulfinate, disubstituted	$\overline{OCH_2SO_2Pb}$	6
Mercury(II) hydroxymethanesulfinate, disubstituted	$\overline{OCH_2SO_2Hg}$	6
Sodium α-hydroxyethanesulfinate	$MeCH(OH)SO_2Na$	48
Sodium α-hydroxytrifluoroethanesulfinate	$CF_3CH(OH)SO_2Na$	49
Potassium α-hydroxyethanesulfinate	$MeCH(OH)SO_2K$	6
Sodium α-hydroxypropanesulfinate	$EtCH(OH)SO_2Na$	7
Potassium α-hydroxy-2-propanesulfinate	$Me_2C(OH)SO_2K$	6
Sodium α-hydroxy-n-butanesulfinate	$Pr^nCH(OH)SO_2Na$	6
Thiourea dioxides		
Thiourea dioxide	$(NH_2)_2CSO_2$	36
N-Methylthiourea dioxide	$MeNHC(NH_2)SO_2$	50
N-Propylthiourea dioxide	$Pr^nNHC(NH_2)SO_2$	50
N-Isopropylthiourea dioxide	$Me_2CHNHC(NH_2)SO_2$	50
N-Butylthiourea dioxide	$Bu^nNHC(NH_2)SO_2$	50
N-But-2-ylthiourea dioxide	$Et(Me)CHNHC(NH_2)SO_2$	50
N-*tert*-Butylthiourea dioxide	$Me_3CNHC(NH_2)SO_2$	50
N-Neopentylthiourea dioxide	$Me_3CCH_2NHC(NH_2)SO_2$	50
N-Hydroxymethylthiourea dioxide	$HOCH_2NHC(NH_2)SO_2$	51
N-Hexylthiourea dioxide	$C_6H_{13}NHC(NH_2)SO_2$	52
N-Dodecylthiourea dioxide	$C_{12}H_{25}NHC(NH_2)SO_2$	52
N-Phenylthiourea dioxide	$PhNHC(NH_2)SO_2$	51
N-*p*-methylphenylthiourea dioxide	p-$MeC_6H_4NHC(NH_2)SO_2$	53
N-*o*-hydroxyphenylthiourea dioxide	o-$HOC_6H_4NHC(NH_2)SO_2$	51
N-*o*-methoxyphenylthiourea dioxide	o-$MeOC_6H_4NHC(NH_2)SO_2$	51
N-2,6-Dimethylphenylthiourea dioxide	2,6-$Me_2C_6H_3NHC(NH_2)SO_2$	50
Thiourea dioxides		
N-2,6-Diethylphenylthiourea dioxide	2,6-$Et_2C_6H_3NHC(NH_2)SO_2$	50
N-2,6-Diisopropylphenylthiourea dioxide	2,6-$Pr^i_2C_6H_3NHC(NH_2)SO_2$	50
N-Guanylthiourea dioxide	$NH_2CNC(SO_2H)NH_2$ (NH)	54
N-Diphenylmethylthiourea dioxide	$Ph_2CHNHC(NH_2)SO_2$	50
N-Triphenylmethylthiourea dioxide	$Ph_3CNHC(NH_2)SO_2$	50
N,*N*-Dimethylthiourea dioxide	$Me_2NC(NH_2)SO_2$	50
N,*N*-Dipropylthiourea dioxide	$Pr^n_2NC(NH_2)SO_2$	50
N,*N*-Dibutylthiourea dioxide	$Bu^n_2NC(NH_2)SO_2$	50
N,*N*-Di(2-methylpropyl)thiourea dioxide	$(Me_2CHCH_2)_2NC(NH_2)SO_2$	50
N,*N*′-Dimethylthiourea dioxide	$(MeNH)_2CSO_2$	55
N,*N*′-Dibut-2-ylthiourea dioxide	$[Et(Me)CHNH]_2CSO_2$	50
N,*N*′-Diphenylthiourea dioxide	$(PhNH)_2CSO_2$	51
N,*N*′-Di-*o*-methylphenylthiourea dioxide	$(o$-$MeC_6H_4NH)_2CSO_2$	53
N,*N*′-Dicyclohexylthiourea dioxide	$(cyclo$-$C_6H_{11}NH)_2CSO_2$	50
Thiourea trioxides		
Thiourea trioxide	$(NH_2)_2CSO_3$	17
N-Methylthiourea trioxide	$MeNHC(NH_2)SO_3$	56
N-Propylthiourea trioxide	$Pr^nNHC(NH_2)SO_3$	56
N-But-2-ylthiourea trioxide	$Et(Me)CHNHC(NH_2)SO_3$	56
N-*tert*-Butylthiourea trioxide	$Me_3CNHC(NH_2)SO_3$	56
N-Allylthiourea trioxide		56
N-Phenylthiourea trioxide	$PhNHC(NH_2)SO_3$	56
N-Benzylthiourea trioxide	$PhCH_2NHC(NH_2)SO_3$	56
N-*o*-Methylphenylthiourea trioxide	o-$MeC_6H_4NHC(NH_2)SO_3$	17
N-*o*-Chlorophenylthiourea trioxide	o-$ClC_6H_4NHC(NH_2)SO_3$	17
N-*p*-Fluorophenylthiourea trioxide	p-$FC_6H_4NHC(NH_2)SO_3$	16
N-2-Isopropylphenylthiourea trioxide	2-$Me_2CHC_6H_4NHC(NH_2)SO_3$	56
N-2,6-Dimethylphenylthiourea trioxide	2,6-$Me_2C_6H_3NHC(NH_2)SO_3$	56
N-2,6-Diethylphenylthiourea trioxide	2,6-$Et_2C_6H_3NHC(NH_2)SO_3$	17
N-2,6-Diisopropylphenylthiourea trioxide	2,6-$Pr^i_2C_6H_3NHC(NH_2)SO_3$	56
N-2,6-Dichlorophenylthiourea trioxide	2,6-$Cl_2C_6H_3NHC(NH_2)SO_3$	17
N,*N*-Dimethylthiourea trioxide	$Me_2NC(NH_2)SO_3$	56
N-Ethyl-*N*-phenylthiourea trioxide	$Ph(Et)NC(NH_2)SO_3$	57
N,*N*′-Diethylthiourea trioxide	$(EtNH)_2CSO_3$	57
N,*N*′-Diisopropylthiourea trioxide	$(Me_2CHNH)_2CSO_3$	56
N,*N*′-Dibut-2-ylthiourea trioxide	$[Et(Me)CHNH]_2CSO_3$	56
N,*N*′-Di-*tert*-butylthiourea trioxide	$(Me_3CNH)_2CSO_3$	56
N,*N*′-Dineopentylthiourea trioxide	$(Me_3CCH_2NH)_2CSO_3$	56
N,*N*′-Dicyclohexylthiourea trioxide	$(cyclo$-$C_6H_{11}NH)_2CSO_3$	56
N,*N*′-Diphenylthiourea trioxide	$(PhNH)_2CSO_3$	57
N,*N*′-Dibenzylthiourea trioxide	$(PhCH_2NH)_2CSO_3$	58

oxides, disulfides),[76,77] for the preparation of a number of compounds of selenium and tellurium[78,79] and deoxygenation of various heteroaromatic *N*-oxides;[8] in addition, it serves as a convenient reductant in phase transfer catalysis.[76,80] Sodium hydroxymethanesulfinate is also utilised in the syntheses of various compounds of selenium and tellurium[81,82] and for the preparation of sultins.[9]

An important application of thiourea oxides is the synthesis of guanidines and their derivatives,[16–20,83–85] which consists in the reaction of thiourea oxides with primary[83] or heterocyclic secondary amines, for example, morpholine,[85] or with amino acids[84] and other amino compounds. The reactions of thiourea oxides with amines are carried out in organic solvents (methanol,[83] acetonitrile[85]), while the reactions with amino acids take place in aqueous solutions.[84] The mechanism proposed for this reaction includes the addition of the nucleophile (*i.e.*, amine) to thiourea oxide and decomposition of the intermediate giving rise to guanidine.[85] The use of trioxides is more convenient because it permits the preparation of guanidines[85] and guanidine acids[84] in high yields. Currently, thiourea trioxide is among the most important guanidylating agents used in the syntheses of guanidines with various structures.[18–20,86–98] Unfortunately, the kinetics of the reactions of thiourea oxides with amino compounds has not yet been studied, despite the fact that the interest in guanidines is very high due to the discovery of the crucial role of nitrogen oxide in functioning of the vascular system.[99–101] It was found that it is the guanidine fragment of L-arginine that is oxidised *in vivo* to give citrulline and nitrogen oxide (in a recent publication,[87] the possibility of using thiourea trioxide in the syntheses of L-arginine derivatives is demonstrated). Guanidines have proved efficient in the treatment of cardiovascular diseases.[100] Thus chemists of the Du Pont company have developed the Du P 714 preparation,[18] which prevents thrombus formation; this synthesis was a success only when thiourea dioxide was used to introduce the guanidine group. The attempts to synthesise this preparation using other guanidylating agents failed. Thiourea trioxide[86–98] and *N*-phenylthiourea trioxide[16] have also been employed for the preparation of other medicinal drugs. Thiourea trioxides are the initial compounds in the syntheses of aminoiminoethanenitriles, 5-aminotetrazoles, *N*-cyanoguanidines and *N*-hydroxyguanidines.[57] The reaction of $(NH_2)_2CSO_3$ with methyl anthranylate affords 5*H*-quinazolino[3,2-*a*]quinazoline-5,12(6*H*)-dione.[102]

Numerous studies have been devoted to the use of reduction reactions involving HMS and TUDO to produce metals — silver,[103] cadmium,[104] technetium,[105] nickel,[106] and metallic coatings on fibres.[107]

IV. Methods of synthesis of sulfur-containing reducing agents

Metal dithionites are prepared by the reduction of sulfur dioxide with zinc, sodium formate[44] or borohydrides.[43] A method for the synthesis of extra pure sodium dithionite containing 99% of the required substance has been developed.[108] A procedure for the preparation of tetraethylammonium dithionite using ion exchange resins is documented.[45]

Several methods for the synthesis of sodium hydroxymethanesulfinate are known.[6] The preparation of HMS by the reduction of sodium hydroxymethanesulfonate with disperse zinc is used most often.

Thiourea mono-, di- and trioxides are produced upon the oxidation of thiourea with hydrogen peroxide in a neutral medium.[7] The synthesis of TUDO is performed at 0–5°C. Unlike the dioxide, thiourea monoxide is quite unstable. More stable monoxides are formed from thiourea derivatives containing bulky substituents at the nitrogen atoms. Thus *N*-phenyl- and ethylenethiourea monoxides have been prepared.[109] The formation of these compounds in solution was proved by the test reaction with $FeCl_3$, typical of mono-*S*-oxygenated thioamides and thiocarbamates. Neutral aqueous solutions of the monoxides synthesised are stable over a period of 24 h at 0 °C; however, these compounds are exceptionally unstable in the solid state. *N*-Phenyl-, *N*,*N*′-diphenyl-, *N*-*o*-hydroxyphenyl- and *N*-*o*-methoxyphenylthiourea dioxides have been prepared by using sodium molybdate[51] to catalyse the reaction between the corresponding thiourea derivative and H_2O_2. Dioxides of other *N*-aryl-substituted thioureas have also been prepared.[53] Syntheses of *N*-aryl- and *N*-alkyl-substituted thiourea dioxides in 80%–90% yields without catalysts have been reported.[50,110] In order to prepare *N*-phenylthiourea dioxide containing ~100% of the required substance, the synthesis should be carried out at −7 to 12 °C.[17] An attempt to prepare *N*,*N*′-diphenylthiourea dioxide by a procedure proposed previously[53] failed.[17] Thiourea trioxides can be synthesised by treatment of thioureas or thiourea dioxides with three or one equivalent of peracetic acid, respectively.[56] An electrochemical procedure for the synthesis of thiourea trioxides has been proposed.[111]

The major products formed in the reaction of thiourea with hydrogen peroxide in strongly acidic media and in the presence of metal ions are formamidine disulfide salts.[112] There is no consensus of opinion on the mechanism of the reaction between thiourea and H_2O_2. The kinetics and the mechanism of the reactions of thiourea and *N*,*N*′-dialkylthiourea with hydrogen peroxide in acid media have been studied.[113] Presumably, in this case, these thioureas act as nucleophiles by replacing the peroxide oxygen, *i.e.*, the reaction does not involve free radicals. However, the use of spin traps, namely, *N*-benzylidene-*tert*-*N*-butylamine *N*-oxide and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) allowed detection of the carbamidinothiyl radical $NH_2(=NH)CS^{\bullet}$ upon oxidation of thiourea with hydrogen peroxide.[114] The stability of this radical was found to depend substantially on the medium pH, the most intense EPR signal being observed at 2.5–3.0.

V. The kinetics and mechanisms of reactions involving sulfur-containing reducing agents

Decomposition of sulfur-containing reductants and their reactions with oxidants are closely interrelated because they proceed *via* the formation of the same intermediates. Therefore, we shall first consider the results of research into decomposition of sulfur-containing reducing agents. The stability of these compounds in aqueous solutions depends appreciably on the pH. Sodium dithionite and HMS are less stable in acid media.

Oxygen-free decomposition of sodium dithionite in acid solutions has been studied in detail.[115,116] Polarography was used to measure the time variation of the concentrations of dithionite and the products of its decomposition, which include sulfide, sulfite, thiosulfate, and active sulfur (S_a); the term 'active sulfur' implies atomic sulfur, the $S\cdot H_2O$ hydrate, the HSOH thioperoxide, the polymeric biradical and sulfur in a polysulfide chain.

Decomposition was found to be autocatalytic, active sulfur and sulfide functioning as the catalysts. The influence of sulfide, sulfite, thiosulfate and sulfur dichloride additives (and also of mixtures of these compounds) on the rate of dithionite decomposition has been studied.[115] On the basis of the results obtained, it was concluded that the following reactions are responsible for the dithionite decomposition:

— non-catalysed reaction proceeding during the induction period,

$$2\,H_2S_2O_4 \longrightarrow S_a + 3\,SO_2 + 2\,H_2O; \quad (1)$$

— autocatalytic reaction mainly proceeding at the fast decomposition stage,

$$3\,H_2S_2O_4 \longrightarrow H_2S + 5\,SO_2 + 2\,H_2O. \quad (2)$$

Simultaneously, a series of side reactions take place. On the basis of experimental data,[115] a mathematical model of the dithionite decomposition was proposed.[116] Calculations performed in terms of this model made it possible to estimate the

contribution of individual homogeneous reactions and to demonstrate that the proposed two-stage scheme is adequate to describe the real mechanism of decomposition.

Non-catalysed and catalysed decomposition of sodium dithionite in weakly acidic solutions in the presence of sulfur-containing admixtures has been investigated.[117] Particular attention is devoted to the influence of sulfite. In the opinion of the researchers cited,[117] in the case of a high sulfite concentration in the solution, decomposition of $S_2O_4^{2-}$ can follow two mechanisms, a heterolytic and a homolytic one. The former includes the following stages:

$$S_2O_4^{2-} + HSO_3^- \longrightarrow [O_2S(O_2)S-SO_2OH]^{3-}, \quad (3)$$

$$[O_2S(O_2)S-SO_2OH]^{3-} + H^+ \longrightarrow S_3O_6^{2-} + H_2O. \quad (4)$$

In this case, reaction (3) is the rate-determining stage. The trithionate formed in reaction (4) participates, together with the $SO_2^{-\bullet}$ radical ion, in the decomposition by the homolytic mechanism

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet}, \quad (5)$$

$$HSO_3^- + SO_2^{-\bullet} \rightleftharpoons S_2O_5H^{2-\bullet}, \quad (6)$$

$$S_2O_5H^{2-\bullet} + S_3O_6^{2-} \longrightarrow SO_2 + HSO_3^- + SO_3^{2-} + S_2O_3^{-\bullet}, \quad (7)$$

$$S_2O_3^{-\bullet} + SO_2^{-\bullet} \longrightarrow S_2O_3^{2-} + SO_2. \quad (8)$$

The reaction between two dianions [reaction (7)] determines the rate of the whole homolytic process.

When the sulfite concentration in the solution is low, the process follows a third pathway

$$S_2O_4^{2-} + HSO_3^- \longrightarrow [O_2S(O_2)S-OSOOH]^{3-}, \quad (9)$$

$$[O_2S(O_2)S-OSOOH]^{3-} \longrightarrow S_2O_5^{2-} + HSO_2^-, \quad (10)$$

$$2\,HSO_2^- \longrightarrow S_2O_3^{2-} + H_2O, \quad (11)$$

$$S_2O_5^{2-} + H_2O \rightleftharpoons 2\,HSO_3^-. \quad (12)$$

Unlike the heterolytic mechanism mentioned above, in this pathway, the initial reaction is the transfer of an oxygen atom from the bisulfite ion to the dithionite sulfur atom.

A serious drawback of the mechanisms proposed by Holman and Bennett [117] [see reactions (3)–(12)] is that nothing is said about the role of sulfur or sulfides in the dithionite decomposition. This is explainable for a large excess of sulfite present because in acid media, HSO_3^- rapidly reacts with sulfur and sulfides, which virtually cancels out their effect on the dithionite decomposition. However, in the case of low initial concentrations of sulfite in the solution, the influence of sulfur or sulfide, which are the main products of dithionite decomposition in acid media, cannot be neglected.

Decomposition of sodium hydroxymethanesulfinate in acid media has been studied.[118, 119] This process is autocatalytic, being accelerated by active sulfur. The catalytic effect of S_a is attributable to its influence on the decomposition of sodium dithionite, which is one of the main intermediate compounds formed upon decomposition of HMS. The following sequence of reactions was proposed as taking place during oxygen-free decomposition of HMS in acidic aqueous solutions:

$$HOCH_2SO_2^- \rightleftharpoons HSO_2^- + CH_2O, \quad (13)$$

$$2\,HSO_2^- \longrightarrow S_2O_3^{2-} + H_2O, \quad (11)$$

$$S_2O_3^{2-} \rightleftharpoons S_a + SO_3^{2-}, \quad (14)$$

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^-, \quad (15)$$

$$HSO_2^- + HSO_3^- \rightleftharpoons S_2O_4^{2-} + H_2O, \quad (16)$$

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet}. \quad (5)$$

An important role in the mechanisms of decomposition of sodium dithionite as well as HMS and TUDO is played by reaction (5), *i.e.*, the homolytic cleavage of $S_2O_4^{2-}$.

The equilibrium constant of reaction (5) at 298 K is equal to 1.4×10^{-9} mol litre^{-1} (see Ref. 120). Studies of the temperature dependence of this equilibrium constant gave quite contradictory results. Thus it has been found [121] that an increase in the temperature from 298 to 353 K results in a 10-fold increase in the concentration of the $SO_2^{-\bullet}$ radical anion, which entails an increase in the equilibrium constant of reaction (5) by a factor of 10. A similar pattern of dependence of the constant on the temperature was also indicated by other researchers.[122] However, according to some other studies,[120, 123, 124] the increase in the equilibrium constant upon an increase in the temperature is much more gradual.

In view of the inconsistency of the data on the temperature dependence of the equilibrium constant, the thermodynamic characteristics of reaction (5) were determined using other methods.

The standard enthalpies of formation (Δ_fH°) of the $SO_x^{-\bullet}$ ($x = 2-4$) radical anions were calculated.[125] The $\Delta_fH^\circ(SO_x^{-\bullet}, 298)$ values in an aqueous solution were determined on the basis of thermodynamics data for liquid-phase decomposition of ions of the $[R-R]^{2-}$ type including the dithionite ion:

$$[R-R]^{2-} \rightleftharpoons R^{-\bullet} + R^{-\bullet}. \quad (17)$$

The standard enthalpy of formation of the product of this reaction can be estimated using the following relation:

$$\Delta_fH^\circ(R^{-\bullet}, 298) = 0.5\,\{\Delta_rG^\circ(298) + T\Delta_rS^\circ(298) + \Delta_fH^\circ([R-R]^{2-}, 298)\}, \quad (18)$$

where $\Delta_rG^\circ(298)$ and $\Delta_rS^\circ(298)$ are the change in the standard Gibbs energy and the standard entropy in reaction (17) at 298 K, respectively, $\Delta_fH^\circ([R-R]^{2-}, 298)$ is the standard enthalpy of formation of the $[R-R]^{2-}$ ion at 298 K.

The $\Delta_rG^\circ(298)$ (52.3 ± 1.3 kJ mol^{-1}) and $\Delta_fH^\circ(S_2O_4^{2-}, 298)$ (-753.7 kJ mol^{-1}) values for the decomposition of $S_2O_4^{2-}$ are known. The uncertainty in $T\Delta_rS^\circ(298)$ is due to the absence of data on the standard entropy of formation of the $SO_x^{-\bullet}$ anion at 298 K [$S_f^\circ(SO_x^{-\bullet}, 298)$]. These values were estimated using the empirical dependence of the standard entropy of the $[R-R]^{2-}$ oxy anion on its mass (M), charge (Z), the distance between the central atom and the peripheral oxygen atoms (r), and the empirical factor (f) that takes into account the ion geometry

$$S_f^\circ(298) - 6.3\,R(\ln M) = 276 - 338.6\,(Z/\rho), \quad (19)$$

where R is the universal gas constant, ρ is an empirical variable equal to r/f. For $SO_2^{-\bullet}$, the ρ value was found proceeding from the values $r = 0.151$ nm, $f = 0.87 \pm 0.11$. The $S_f^\circ(SO_2^{-\bullet})$ value at 298 K found on the basis of relation (19) amounted to 134 ± 25 J mol^{-1} K^{-1} [for the dithionite ion, $S_f^\circ(S_2O_4^{2-}) = 104.5$ J mol^{-1} K^{-1}]. The $\Delta_rS^\circ(298)$ value for reaction (5) corresponding to these parameters is equal to 163.5 ± 50 J mol^{-1} K^{-1}. The $\Delta_fH^\circ(SO_2^{-\bullet}, 298)$ value determined from Eqn (18) amounts to -326.5 ± 8 kJ mol^{-1}. The researchers cited [125] did not compare the resulting $\Delta_rH^\circ(298)$ (100.7 ± 17 kJ mol^{-1}) with the values found from the temperature dependence of the equilibrium constant of reaction (5). It is noteworthy that this value is close to $\Delta_rH^\circ(298) = 89.1$ kJ mol^{-1}, presented in a publication.[122] Unfortunately, the standard enthalpies and entropies of formation of the sulfoxylate ion SO_2^{2-} have not been determined yet.

Equilibrium (5) in aprotic media has been studied using tetraethylammonium dithionite.[45] It was shown by EPR and UV spectroscopy that the $S_2O_4^{2-}$ dimer dissociates to give the $SO_2^{-\bullet}$ radical anions in DMF, DMSO and acetonitrile, the equilibrium constants in non-aqueous solvents being 10^7 times as high as that in water. Thus, the equilibrium constant for reaction (5) depends appreciably on the nature of the solvent.

Unlike HMS or sodium dithionite, TUDO is much less stable in alkaline solutions than in neutral or acidic solutions.

Comparative investigation of the composition of the products of decomposition of thio- and *N*-phenylthiourea di- and trioxides

and *N*,*N*′-diphenylthiourea trioxide in neutral and alkaline solutions has been carried out.[17] Ureas are the major products of thiourea dioxide decomposition in alkaline media. Conversely, decomposition of thio- and *N*-phenylthiourea trioxides affords mainly cyanamides (pH 13–14) (*N*,*N*′-diphenylthiourea trioxide is mainly converted into *N*,*N*′-diphenylurea). In less alkaline solutions (pH 10), the percentage of ureas in the products of dioxide decomposition decreases, while the content of cyanamides increases. Under similar conditions, thiourea trioxide gives melamine in 52% yield; the formation of cyanoguanidine (dicyanodiamide) was also detected (the formation of substituted triazine related to melamine has been observed previously in the decomposition of *N*-propylaminoiminomethanesulfonic acid in the presence of *tert*-butylamine[16]). Presumably, a product of self-condensation of TUTO is formed intermediately in the reaction of melamine formation.

The essentially different decomposition mechanisms of thiourea dioxides and trioxides and, as a consequence, different compositions of the reaction products have been attributed,[17] first of all, to the different stabilities of $NH_2NHRCSO_2$ and $NH_2NHRCSO_3$ in alkaline media (R = H, Ph). The trioxide is assumed to be much more stable in solution than the dioxide; however no experimental evidence supporting this assumption is available. No data on the sulfur-containing products of decomposition of thiourea oxides are available either.

It has been assumed[126] that an important role in the decomposition of TUDO is played by dithionite ions and the $SO_2^{-\bullet}$ radical anions. The appearance of these species in alkaline solutions of TUDO was detected by polarography and interpreted as being due to the reaction

$$(NH_2)_2CSO_2 + OH^- \longrightarrow HSO_2^- + (NH_2)_2CO, \quad (20)$$

as well as reactions (5) and (16) presented above. Presumably,[126] decomposition of TUDO gives sulfoxylate as the primary product [however, it is not indicated what process is responsible for the formation of sulfite needed for the formation of dithionite by reaction (16)]. Yet another mechanism of TUDO decomposition has also been proposed;[104] according to this mechanism, the strong reducing properties of TUDO in alkaline media are due to the homolytic decomposition of the $H_2N(=NH)CSO_2^-$ anion to give reactive species, $SO_2^{-\bullet}$ and $(NH_2)_2C^{\bullet}OH$. It has also been suggested[127] that the $SO_2^{-\bullet}$ radical anion (in the aqueous alkali–ethanol system) is formed as the primary product of TUDO decomposition.

Unfortunately, in most of the above-mentioned studies, no integrated approach is used to investigate the processes of decomposition of sulfur-containing reducing agents. This is especially true for thiourea oxides. The transformations of their 'sulfur' and 'nitrogen' components have been studied independently by chemists working in different fields. The former, 'sulfur' part has been studied by inorganic chemists and specialists in chemical kinetics, while the latter, 'nitrogen' part has been an object of investigations of organic chemists and biochemists. These investigations have not been connected with one another and, moreover, the results have been published in journals of different disciplines. The fewness of kinetic data concerning the processes of decomposition of sulfur-containing reducing agents also appears surprising. Data on the decomposition mechanisms are fragmentary and often contradictory. Unfortunately, in many publications, no attention is paid to the role of oxygen in the decomposition of the compounds in question. Often, it is even impossible to grasp whether the reaction was carried out in an inert atmosphere or in air (this is especially typical of papers in organic chemistry). It will be shown below that it is the effect of oxygen on the composition of the intermediate and final products in the decomposition of sulfur-containing reducing agents that is the main reason for the contradictions mentioned above.

Let us consider the reactions of sulfur-containing reductants with oxygen. Creutz and Sutin,[128] who confirmed the previously proposed[120] mechanism of the dithionite reaction with oxygen,

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet}, \quad (5)$$

$$SO_2^{-\bullet} + O_2 \longrightarrow \text{products}, \quad (21)$$

showed also that the process rate is determined by reaction (5), the rate constant for the forward reaction being virtually independent of the pH: $k = 2.5$ (pH 6.5) and 1.8 s^{-1} (pH 13). The researchers also determined the lower limit for the rate constant for reaction (21): $k_{21} \geqslant 1 \times 10^8$ litre mol^{-1} s^{-1}. Later, the value $k_{21} = 2.4 \times 10^9$ litre mol^{-1} s^{-1} was found.[129]

The kinetics of the reaction of sodium dithionite with hydrogen peroxide has been studied.[128] As in the case of oxygen, the $SO_2^{-\bullet}$ radical anion rather than the $S_2O_4^{2-}$ dithionite ion enters into the reaction with the oxidant. The influence of oxygen on the decomposition of HMS and TUDO has been studied.[119, 130] It was found that in the HMS decomposition under aerobic conditions, the appearance of dithionite is preceded by an induction period, which is missing when the experiment is carried out under an inert atmosphere.[119] Study of decomposition of HMS in the presence of superoxide dismutase, catalase and sodium formate showed that active forms of oxygen (superoxide, peroxide, hydroxyl radicals) have little influence on the rate of dithionite formation. Sulfite additives exert a much more pronounced influence under both anaerobic and aerobic conditions.

Decomposition of air-saturated alkaline solutions of thiourea dioxides is also accompanied by the formation of dithionite, preceded by an induction period.[130] However, unlike HMS, sulfite additives do not affect decomposition of TUDO. In addition, decomposition of thiourea dioxides under anaerobic conditions does not give dithionite. Thus, the $S_2O_4^{2-}$ ion and the $SO_2^{-\bullet}$ radical anion occurring in equilibrium arise upon the reaction of a sulfur-containing product of thiourea dioxide decomposition with oxygen. Apparently,[130] this sulfur-containing product is the sulfoxylate ion SO_2^{2-}. This species reacts with oxygen to give the $SO_2^{-\bullet}$ radical anion, which in turn reacts with oxygen [reaction (23)] and dimerises [back reaction (5)]:

$$SO_2^{2-} + O_2 \longrightarrow SO_2^{-\bullet} + O_2^{-\bullet}, \quad (22)$$

$$SO_2^{-\bullet} + O_2 \longrightarrow SO_2 + O_2^{-\bullet}, \quad (23)$$

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet} \quad (5)$$

These reactions occur during the induction period. Since dithionite ion is accumulated after the completion of the induction period, *i.e.*, after oxygen has disappeared, the sulfur-containing species react with superoxide or with the product of its dismutation, peroxide. However, it is known that superoxide is quite stable in strongly alkaline media[131] (most experiments were carried out in a solution of NaOH with a concentration of 0.5 mol $litre^{-1}$) and is unlikely to undergo dismutation over the period of TUDO decomposition. Thus, the peroxide can be formed only upon the reduction of superoxide. This was proved by an independent research of the reaction of TUDO with potassium superoxide in the absence of oxygen. The shape of the resulting kinetic curves was similar to that typical of the curves of TUDO decomposition and dithionite accumulation in the presence of oxygen. The same regularities were also observed in the reaction of TUDO with peroxide under anaerobic conditions; this is due to reactions of the sulfoxylate (arising upon decomposition of TUDO deprotonated in a strongly alkaline medium) and the $SO_2^{-\bullet}$ radical anion with peroxide, giving rise to a hydroxyl radical [represented in Eqns (25) and (26) as the deprotonated form $O^{-\bullet}$]:

$$(NH)_2CSO_2 \longrightarrow SO_2^{2-} + NH{=}C{=}NH, \quad (24)$$

$$SO_2^{2-} + HO_2^- \longrightarrow SO_2^{-\bullet} + O^{-\bullet} + OH^-, \quad (25)$$

$$SO_2^{-\bullet} + HO_2^- \longrightarrow SO_2 + O^{-\bullet} + OH^-, \quad (26)$$

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet}, \quad (5)$$

$$NH = C = NH + H_2O \longrightarrow (NH_2)_2CO. \quad (27)$$

Thus, study of the kinetics of reactions of thiourea dioxide with oxygen and its reduced forms made it possible to prove that

the sulfoxylate ion SO_2^{2-} rather than the $SO_2^{-\bullet}$ radical anion, as had been proposed previously,[104] is the primary sulfur-containing product of TUDO decomposition in strongly alkaline media. It is the formation of sulfoxylate that accounts for the strong reducing properties of TUDO in alkaline media.

The aerobic decomposition of *N*-methyl- and *N*,*N*′-dimethylthiourea dioxides follows regularities similar to those considered above for TUDO.[130] *N*,*N*′-Dimethylthiourea dioxide is the most reactive reductant, apparently due to the much higher stability of the intermediate formed primarily in its decomposition, namely, *N*,*N*′-dimethylcarbodiimide, compared to the stabilities of carbodiimide and *N*-methylcarbodiimide.[132] Conversely, the rates of the reactions of oxygen and its reduced forms with *N*-methylthiourea dioxide (MTUDO) are lower than those in the case of TUDO. Among the compounds considered, MTUDO is the most stable. *N*-Phenylthiourea dioxide (PTUDO) also exhibits a higher stability in solutions than TUDO.[133] Data on the reactivity of thiourea dioxides can be important for interpreting the toxicity of thioureas. Many thioureas, especially *N*-substituted ones, are known to be highly toxic. Thus lethal doses of α-naphthyl- and *N*-phenylthioureas amount to 0.5 and 5 mg kg^{-1}, respectively.[17] The toxicity of thioureas is supposed to be due to their oxidation [134–137] and the tendency of the resulting oxides to undergo desulfurisation;[17] the higher this tendency, the more toxic the compound. However, data of some publications [130, 133] are at variance with this conclusion:[17] the rates of desulfurisation of *N*-methyl- and *N*-phenylthiourea dioxides are lower than that of thiourea dioxide; nevertheless, *N*-methyl- and *N*-phenylthioureas are much more toxic than the unsubstituted thiourea. Apparently, there are also other reasons for the high toxicity of *N*-substituted thioureas. Therefore, the formation and the properties of adducts produced by thiourea oxides and proteins are being vigorously studied.[137]

In weakly alkaline solutions of thiourea dioxides, dithionite ions are accumulated much more slowly. Among other reasons, this is due to the sharp increase in the reactivity of hydrogen peroxide upon a decrease in the pH, which results in a change in the mechanism of interaction of H_2O_2 with TUDO. It was found that at pH < 13, TUDO reacts directly with the peroxide to give thiourea dioxide radicals and hydroxyl radicals.[138] The latter have been detected by EPR in the presence of DMPO. Yet another possible reason for the appreciable decrease in the rate of dithionite formation in solutions of thiourea dioxides is a change in the mechanism of their decomposition. To verify this, a comparative kinetic study [138] of the processes of TUDO decomposition and its reactions with oxygen at various pH has been carried out. The rate of the reaction of thiourea dioxide with oxygen at $[TUDO]_0 \gg [O_2]_0$ was found to be described by the equation $v = k[TUDO]$. In nearly neutral and in strongly alkaline media, the rate constants for both processes virtually coincide. However, in the pH range of 9–12, substantial differences are observed: the rate constant for TUDO decomposition increases much more rapidly and reaches a constant level at pH 10, whereas the rate constant for the reaction of thiourea dioxide with O_2 continues to grow even in the pH 10–13.7 range. The non-coincidence of the mechanisms of TUDO decomposition at pH 10 and 13 has been also discovered by other authors. Thus it has been found [139] that the reaction of glycine with TUDO in concentrated ammonium hydroxide solutions affords guanidinoacetic acid in 36% yield. When the reaction is carried out in a solution of K_2CO_3 with a concentration of 1 mol $litre^{-1}$ (pH 10), guanidineacetic acid is not formed.[17] In addition, ammonia was detected upon decomposition of TUDO in this solution [17] (ammonia is also formed when thiourea trioxide decomposes in weakly acidic media [42]). These facts led to the conclusion [138] that decomposition of thiourea dioxide at pH 9–12 follows two pathways. According to one of them, ammonia is eliminated (as this takes place, TUDO loses the guanidylating capacity towards glycine) but the C–S bond is not cleaved, the SO_2^{2-} anion is not formed, and the reaction with oxygen does not occur. Conversely, the second pathway includes a stage of formation of the SO_2^{2-} anion and the C–N bond remains intact; therefore, TUDO actively reacts with oxygen and glycine. It was found[138] that both pathways have a stage of TUDO ionisation. Since the dependence of the rate constant for the reaction of thiourea dioxide on pH is shifted to the region of high pH, the pathway involving the formation of sulfoxylate is assumed to result from decomposition of TUDO dianions. In the TUDO monoanion, the C–N bond is apparently much weaker than the C–S bond; hence, the primary decomposition stage yields ammonia.

In acid media, thiourea dioxide is very stable and barely decomposes at room temperature.[7] On heating in glacial acetic acid, TUDO and some its analogues decompose to give formamidine acetate and sulfur dioxide.[110]

The data presented here indicate that oxygen and active forms of oxygen (AFO) play an important role in the reactions with sulfur-containing reductants. Let us consider published data dealing with the reaction of the TUDO precursor, thiourea, with AFO (oxidation with peroxide has been mentioned above, in the discussion of the methods of synthesis of thiourea oxides). The strongest oxidant among the AFO is the hydroxyl radical.[140] The reaction of thiourea with the $OH^{\bullet}$ radicals proceeds at a very high rate [141] ($k = 1.2 \times 10^{10}$ litre mol^{-1} s^{-1}). The hydroxyl radicals also oxidise very effectively *N*,*N*′-dimethylthiourea [55] and tetramethylthiourea.[141]

The reactivity of the $O_2^{-\bullet}$ superoxide is substantially lower than that of $OH^{\bullet}$ radicals. In aqueous solvents, superoxide reacts with thiourea to give cyanamide.[142] It is assumed that TUDO is formed as an intermediate of this process. The reaction of superoxide with diarylthiourea follows a different pathway [143] giving rise to a substituted guanidine. In nonaqueous solutions, superoxide reduces sulfur dioxide

$$SO_2 + O_2^{-\bullet} \rightleftharpoons SO_2^{-\bullet} + O_2 . \quad (28)$$

The equilibrium constant for this reaction, calculated on the basis of redox potentials (E°) of the $O_2/O_2^{-\bullet}$ and $SO_2/SO_2^{-\bullet}$ couples, equals 4.8;[144] however, experimental data indicate that reaction (28) proceeds virtually to completion. This is due to the subsequent transformations of the $SO_2^{-\bullet}$ radical anion, namely, dimerisation to give $S_2O_4^{2-}$ and complexation with SO_2. In the aqueous medium, superoxide does not reduce sulfur dioxide: the redox potential of the $O_2/O_2^{-\bullet}$ couple at pH 7 and pH 14 equals −0.16 V; that at pH 0 is +0.12 V;[145] E° of the $SO_2/SO_2^{-\bullet}$ pair is −0.26 V.[146]

In some studies,[147–149] electron transfer reactions in the $O_2/O_2^{-\bullet}$–metal complex systems are considered in terms of the Marcus theory. The equations derived

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}} , \quad (29)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/z^2)} , \quad (30)$$

where z is a factor taking into account the frequency of collisions of the reacting species in solution, were used to determine the rate constant for the electron exchange in the $O_2/O_2^{-\bullet}$ system (k_{22}) on the basis of known constants for electron exchange in metal complexes (k_{11}) and the experimental rate constants for the reduction of metal complexes by superoxide (k_{12}), for example

$$Co(NH_3)_6^{3+} + O_2^{-\bullet} \longrightarrow Co(NH_3)_6^{2+} + O_2 \quad (31)$$

[in Eqns (29), (30), K_{12} is the equilibrium constant for reaction of type (31)].

However, the k_{22} values found in these calculations,[147] based on the data on the kinetics of reactions of $O_2^{-\bullet}$ with various metal complexes, varied in the range of 10^{-8}–$10^{5.7}$ litre mol^{-1} s^{-1}. In the opinion of the researchers cited,[145] the unsuitability of the Marcus theory for the calculation of k_{22} was due to the unequal solvations of O_2 and $O_2^{-\bullet}$. Later,[148] a different approach was used to determine the k_{22} values, namely, the kinetics of the reaction of metal complexes with oxygen

$$CrL_3^{2+} + O_2 \longrightarrow CrL_3^{3+} + O_2^{-\bullet}, \quad (32)$$

rather than with superoxide was studied (L is 2,2′-bipyridine, 1,10-phenanthroline and their derivatives).

The use of this approach provided the k_{22} values in the range of 1–10 litre mol^{-1} s^{-1} (in a later review,[150] a value of 10 litre mol^{-1} s^{-1} was recommended). The reasons for the so great difference between the k_{22} values calculated from the data on the kinetics of reduction of complexes with superoxide remain unknown. No corresponding data concerning the superoxide reduction to peroxide can be found from the literature.

Comparison of the rate constants for the reactions of the $O_2^{-\bullet}$ and $SO_2^{-\bullet}$ radical anions with identical oxidants, metal complexes, published in a study is of interest.[149] The ratio of the rate constants for the reactions involving $SO_2^{-\bullet}$ and $O_2^{-\bullet}$ was found to be approximately 10^3; it does not depend on the nature of the oxidant, which is consistent with the Marcus theory and the equation derived from it

$$\frac{k(SO_2^{-\bullet})}{k(O_2^{-\bullet})} = \sqrt{\frac{k(SO_2/SO_2^{-\bullet})}{k(O_2/O_2^{-\bullet})} \cdot 10^{16.9\,\Delta E}}, \quad (33)$$

where $k(SO_2^{-\bullet})$ and $k(O_2^{-\bullet})$ are the rate constants for the reaction of $SO_2^{-\bullet}$ and $O_2^{-\bullet}$ with the same substrate; ΔE is the difference between the reduction potentials of O_2 (−0.16 V) and SO_2 (−0.26 V), and $k(SO_2/SO_2^{-\bullet})$ and $k(O_2/O_2^{-\bullet})$ are the self-exchange rate constants of the $SO_2/SO_2^{-\bullet}$ and $O_2/O_2^{-\bullet}$ systems, respectively.

If we assume that $k(SO_2^{-\bullet})/k(O_2^{-\bullet}) = 10^3$, the $k(SO_2/SO_2^{-\bullet})/k(O_2/O_2^{-\bullet})$ ratio should be equal to $\sim 10^4$.

In most studies devoted to the electron exchange in the $SO_2/SO_2^{-\bullet}$ couple, dithionite served as the source of $SO_2^{-\bullet}$.[149] The $k(SO_2/SO_2^{-\bullet})$ values calculated for the outer-sphere oxidation of CrL_3^{2+} (L is bipyridine, phenanthroline, and their substituted derivatives) with sulfur dioxide were compared with the values determined previously in experiments using $SO_2^{-\bullet}$ as the reagent.[151] It was found that, unlike the $k(O_2/O_2^{-\bullet})$ values, the $k(SO_2/SO_2^{-\bullet})$ constants calculated from the kinetic data for reactions involving SO_2 and $SO_2^{-\bullet}$ are rather close: $k(SO_2/SO_2^{-\bullet}) = (1-18) \times 10^4$ litre mol^{-1} s^{-1} at 298 K. These values are approximately 10^4 times as high as the value $k(O_2/O_2^{-\bullet}) = 10$ litre mol^{-1} s^{-1} reported in a review,[150] which is consistent with the results cited above.[149]

Thus, the published data indicate that the Marcus theory is applicable to the $SO_2/SO_2^{-\bullet}$ and $O_2/O_2^{-\bullet}$ couples. It is noteworthy that the $SO_2^{-\bullet}/SO_2^{2-}$ couple in which $SO_2^{-\bullet}$ is the oxidised form has not been studied. Apparently, this is due to the difficulty of reduction of the $SO_2^{-\bullet}$ radical anion. Oxidation of sulfoxylate would be the preferred variant. The above data indicate that thiourea dioxides can be used as sources of SO_2^{2-}.

Let us consider data on the reactions of thioureas with yet another active form of oxygen, namely, singlet oxygen $^1O_2$. Thus oxidation of thiourea with photochemically generated singlet oxygen has been studied.[152] It was shown previously that solutions of thiourea do not undergo photolysis either in the absence or in the presence of oxygen even on prolonged exposure to UV light. Photooxidation of thioureas was observed when their alcohol solutions containing oxygen and a sensitiser (dye) were exposed to the visible light. The composition of photooxidised products depends on the nature of thiourea and, to a lesser extent, the dye. The major products formed in the reaction of thiourea with $^1O_2$ include SO_2, sulfur and TUDO (the sensitisers used are Methylene Blue or chlorophyll). In the presence of Rose Bengal, the formation of dicyanediamide was also observed.

Photochemical destruction of thiourea was discovered when titanium dioxide was used as the sensitiser.[153] The reaction yields cyanamide and dicyanamide.

The acid HOCl is also an active form of oxygen.[55] The kinetics of reactions of thiourea with oxohalogen compounds draws special attention.[14, 15, 154, 155] Until recently, studies of non-linear phenomena in chemical kinetics have been mainly related to the chemistry of halogens. However, at present, oscillators based on sulfur compounds are becoming more and more important. The combination of halogen and sulfur compounds in one reaction is rather attractive. However, data on the kinetics of such reactions are scarce.

One of the first chemical oscillators based on sulfur-containing compounds[156] is a mixture of sulfide, sulfite, oxygen and the Methylene Blue dye. It has been reported that the reaction between chlorite and thiourea is accompanied by oligo-oscillation.[154] Diverse non-linear effects have been discovered in the reactions of thiourea with iodate, bromate, chlorine dioxide, iodine and bromine.[155, 157, 158] However, the greatest attention of researchers is still attracted by the reaction with chlorite. Nevertheless, there is no consensus of opinion concerning the mechanism of the reaction between thiourea and chlorite. Thus it has been assumed[155] that the protonated form of the chlorite $HClO_2$ is much more reactive than the deprotonated form. However, other researchers[159] hold to the opposite opinion. They proposed a mechanism for the reaction of ClO_2 and $(NH_2)_2CS$, according to which two ClO_2 molecules successively transfer the oxygen atoms to $HOSCNHNH_2$ to give $HO_3SCNHNH_2$. However, other researchers[155] believe that the reaction between ClO_2 and the thiourea monoxide is accompanied by electron transfer giving rise to ClO_2^- and $H_2NNHCSO^\bullet$ (it has been assumed[60] that the reaction of thiourea dioxide with bromate also follows a radical mechanism). It was shown experimentally[155] that the rates of reactions of formamidine disulfide and thiourea dioxide with ClO_2 depend substantially on the time elapsed after the preparation of solutions of the sulfur-containing compounds. This was attributed[155] to accumulation of reactive aminoiminomethanesulfenic acid (thiourea monoxide) in the solution. However, this explanation can hardly be considered to be convincing because thiourea monoxide is exceptionally unstable at 298 K and can hardly be expected to accumulate in solution.

It was shown[158] that, among other reasons, non-coincidence of the kinetic data obtained by different researchers may be due to the influence of impurities of metal compounds, especially copper and iron compounds (Cu and Fe compounds are known to catalyse efficiently the processes of reduction by thiourea). However, the main reason for the inconsistency mentioned above is that no kinetic data concerning individual stages of the multistage reaction between thiourea and oxohalogen compounds have been available until recently. Only in 1993–1995, were reactions between an intermediate of $(NH_2)_2CS$ oxidation, *i.e.* thiourea dioxide, with iodate,[160] bromate[15] and chlorite[14] studied. The kinetic parameters thus found made it possible to correct (in some cases, the corrections were quite significant) the rate constants for the individual stages of thiourea oxidation published previously. However, the reported[14] ratios of the rate constants for reactions of thiourea di- and trioxides with the same oxidants raise doubts. Thus the rate constants for the reactions of TUDO and TUTO with HOCl are nearly equal (9.5×10^3 and 6.5×10^3 litre mol^{-1} s^{-1}) but those for the reaction with ClO_2 differ by a factor of 60 (6×10^2 and 10 litre mol^{-1} s^{-1}, respectively). The reasons for this discrepancy have not been elucidated. The interpretation[161, 162] of the results of kinetic studies of the reactions of hydroxymethanesulfinate with bromate and chlorite in acid media is even more objectionable. Presumably, the reactions of HMS with any oxohalogen compounds either present initially or formed at intermediate stages (BrO_3, $HBrO_2$, HOBr, ClO_2^-, HOCl, ClO_2, Cl_2O_2) afford hydroxymethanesulfonate.[161, 162] As a result of oxidation, this product gives sulfate, *i.e.*, as in the case of reactions involving thiourea, the C–S bond rupture takes place after the appearance of sulfonate. Meanwhile, it is known that hydroxymethanesulfonate is very stable in acid media and does not tend to participate in redox reactions.[7] Conversely, HMS rapidly decomposes in acid solutions, the products of its decomposition exhibiting strong reducing properties. Unfortunately, in the studies cited above,[161, 162] no mention is even made of the HMS decomposition or the role of its products —

sulfoxylate and formaldehyde (later, the same researchers demonstrated [163] that formaldehyde reacts with chlorite at a rather high rate). The results of study of Makarov *et al.*[164] made it possible to introduce substantial changes to the schemes of reactions of halogens and oxohalogen compounds with thiourea, thiourea dioxide and hydroxymethanesulfinate. It was shown [164] that the rates of oxidation of sulfonates (thiourea trioxide and hydroxymethanesulfonate) are much lower than the rates of oxidation of sulfinates (thiourea dioxide and hydroxymethanesulfinate) and even thiourea. Thus, it appears that thiourea trioxide and hydroxymethanesulfonate are not intermediates of the reactions of TUDO, thiourea and HMS with halogens and oxohalogen compounds. During the oxidation of sulfinates, rupture of the C–S bond takes place before the formation of sulfonates.[164] The active reducing agent thus formed, sulfoxylate, is then oxidised to sulfite and sulfate.

VI. Conclusion

The data on the properties of sodium dithionite, sodium hydroxymethanesulfinate and thiourea dioxides considered in the review provide a number of conclusions. An important feature common to these compounds is decomposition in solutions to give strong reducing agents. However, the opposite patterns of dependence of the stability of TUDO and HMS on the pH entail differences between the processes of their decomposition. Indeed, in solutions of HMS, the dithionite ion is formed predominantly according to an 'anaerobic' mechanism, whereas in solutions of TUDO, this occurs by an 'aerobic' mechanism. Sulfur-and-oxygen ions (sulfite, thiosulfate) barely affect the TUDO decomposition, whereas the mechanism of decomposition of hydroxymethanesulfinate largely depends on admixtures. Thus, in the case of HMS decomposition, the subsequent reactions of sulfur-containing compounds are much more significant than in the decomposition of TUDO. Decomposition of HMS is affected most appreciably by dithionite ions. The very low stability of these ions in acid media and the capability of decomposing in aqueous solutions by an autocatalytic mechanism account for the autocatalytic mode of HMS decomposition as a whole. The unique character of dithionite is due to the presence of the very long S–S bond. Therefore, insertion of monoatomic sulfur into the S–S bond becomes possible and, as a consequence, decomposition of dithionite and hydroxymethanesulfinate is accelerated. Conversely, in the thiourea dioxide molecule, direct insertion of sulfur into the shorter C–S bond is difficult. No conjugate pathway for dithionite destruction exists in the decomposition of TUDO (in alkaline solutions of thiourea dioxide under aerobic conditions, dithionite formation does take place but it is much more stable in these media than TUDO).

The following important circumstance should also be mentioned. Thiourea dioxides are the most convenient precursors of the little studied sulfoxylate ion (SO_2^{2-}). This sulfur-and-oxygen ion is quite interesting from both practical and theoretical standpoints. The need to study systematically its properties is due not only to its high reductive activity but also to the fact that sulfoxylate is the possible intermediate in the hydrogen sulfide oxidation.[165] The importance of this process as a part of natural sulfur cycle is beyond doubt.

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[f] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[g] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[h] — *Mendeleev Chem. J. (Engl. Transl.)*