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Structure and Kinetic Stability of 1-Hydroxy- and Aminoalkalnesulfinates in Aqueous Solutions

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Abstract — The structural parameters of the molecules of sodium hydroxymethane-, 1-hydroxyethane-, 1-hydroxypropane-, aminomethane-, and dimethylaminomethanesulfinates, aminoiminomethanesulfinic acid, and thiourea dioxide were studied by Hartree–Fock–Roothaan and DFT quantum-chemical calculations. The C–S bond length in these molecules varies in the same direction as the constants characterizing their decomposition in aqueous solutions.

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1-Hydroxy- and aminoalkanesulfinates in solutions exhibit high reducing power correlating with their stability. In most cases, this is associated with the formation from alkanesulfinate molecules of active intermediate species: sulfoxylic acid or its anions, sulfur dioxide radical anions, and dithionite anions. The mechanism of their formation is complex and depends on various factors: temperature, pH of solution, content of impurities of sulfur compounds, and solvent [1]. In all the cases, the primary step of the decomposition in aqueous solution is the decomposition of sodium hydroxy- and aminoalkanesulfinate molecules. The decomposition of sodium hydroxyalkanesulfinates in neutral media yields, along with sulfoxylic acid anions, also aldehydes, as, e.g., in the case of decomposition of sodium hydroxymethanesulfinate:

$$HOCH_2SO_2^- \rightleftarrows HSO_2^- + CH_2O. \quad (1)$$

The decomposition of aminoalkanesulfinates yields instead of aldehydes unidentified amino derivatives.

Molecules of aminoiminomethanesulfinic acid or thiourea dioxide in neutral media decompose by the following reaction:

$$(NH_2)_2CSO_2 + H_2O \longrightarrow H_2SO_2 + (NH_2)_2CO. \quad (2)$$

In reactions (1) and (2), anions or molecules of sulfoxylic acid are formed by heterolytic cleavage of the C–S bond.

The available quantitative data on the stability of alkanesulfinates in aqueous solutions [2, 3] allow consideration of the relationship between these characteristics and structural parameters of the molecules. The structure of the first representative of this class, sodium hydroxymethanesulfinate, was studied in [4]. X-ray diffraction studies showed that the CSO_2 group forms a pyramid with the sulfur atom in the apex. The unit cell parameters, interatomic distances, and bond angles were determined. The C–S bond is the longest among covalent bonds (1.838 Å).

X-ray diffraction analysis of thiourea dioxide was made in [5]; later the data obtained were refined [6]. Thiourea dioxide exists in the solid phase in the form of $(NH_2)_2CSO_2$; the CSO_2 group, as in rongalite, has a pyramidal configuration. The C–S bond is also the longest (1.8615 Å). Kharitonov and Prokof'eva [7] examined the IR spectra of crystalline thiourea dioxide and suggested on their basis a zwitterionic structure with two amino groups one of which forms a double bond with the carbon atom. De Filippo et al. [8] suggested that thiourea dioxide exists in the form of formamidinesulfinic acid $HNC(NH_2)SO_2H$ with a strong hydrogen bond between the molecules in the crystal. However, later ^1H NMR and IR studies [9] proved that the thiourea dioxide molecule contains no O–H groups. The structure of thiourea dioxide is essentially influenced by the solvent. As follows from ^1H NMR data, in aqueous solution thiourea dioxide exists as two tautomers, and in an aprotic solvent, as a single tautomer [10].

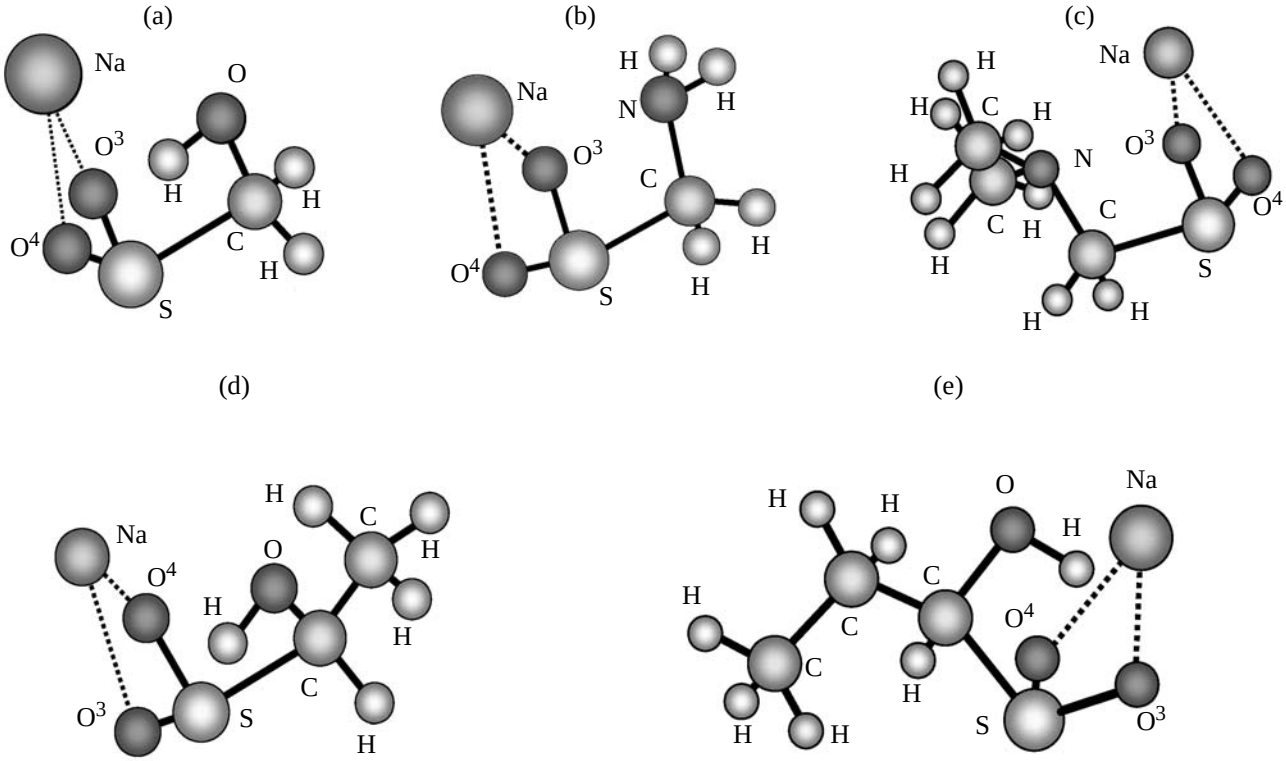

Fig. 1. Geometric configurations of molecules: (a) sodium hydroxymethanesulfinate, (b) sodium aminomethanesulfinate, (c) sodium dimethylaminomethanesulfinate, (d) sodium hydroxyethanesulfinate, and (e) sodium hydroxypropanesulfinate.

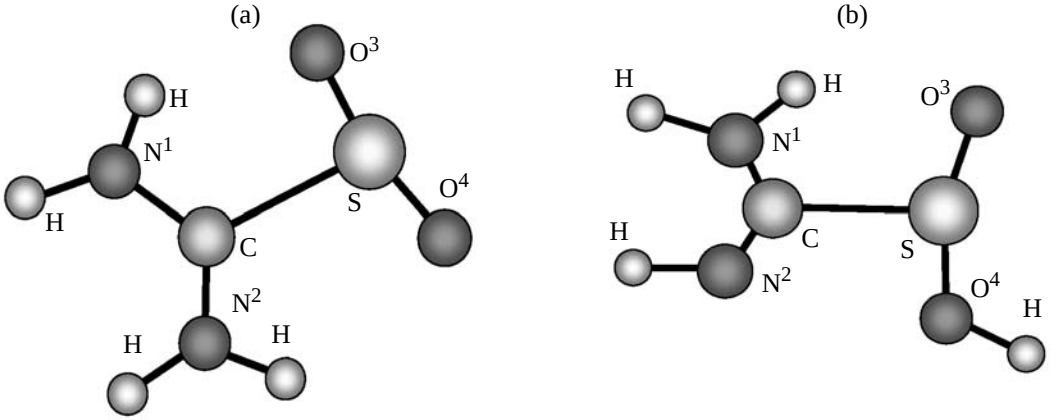

Fig. 2. Geometric configurations of molecules: (a) thiourea dioxide and (b) aminoiminomethanesulfinic acid.

Thus, data are avaliable on the structure of sodium hydroxymethanesulfinate and thiourea dioxide, but for other 1-hydroxy- and aminoalkanesulfinates such data are lacking.

We calculated molecular geometry of a series of sulfinic acid derivatives by the Hartree–Fock–Roothaan ab initio method (RFH) and by the density functional theory (DFT/B3LYP version [11]) using 6-31G** two-exponent valence set supplemented with polarization functions of the *d* and *p*(H) type [12]. The RHF and DFT/B3LYP calculations were performed using the GAMESS program [13]. The molecular geometries were optimized by the gradient method for all the considered configurations. For each structure, at optimized geometric parameters, we analytically calculated the force field and then calculated in the harmonic approximation the normal mode frequencies and the band intensities in the IR spectra. The calculations showed that all the configurations (Figs. 1, 2) correspond to a minimum on the potential energy surface. The theoretically calculated main geometric parameters are given in Tables 1 and 2 (the results of the RHF calculations, in the numerator, and the results of the DFT calculations, in the denominator). All the calculations were performed for the gas phase.

Table 1. Calculated geometric parameters (R_e, Å; α_e; χ_e, deg) of sodium 1-hydroxy- and aminoalkanesulfinates

Molecule	R_e(C–S)	R_e(S=O^3)	R_e(S–O^4)	R_e(O^3–Na)	R_e(O^3–Na)	α_e(C–S=O^3)	α_e(O^4–S^4=O^3)	α_e(SO^{4}Na)	χ_e(NaO^{4}SO^3)
$HOCH_2SO_2Na$	1.826	1.513	1.521	2.272	2.192	100.5	107.0	88.4	–22.5
	1.909	1.548	1.568	2.307	2.210	100.4	107.6	86.4	–24.8
$NH_2CH_2SO_2Na$	1.824	1.512	1.514	2.266	2.207	100.6	107.3	87.9	25.9
	1.896	1.550	1.547	2.223	2.280	98.8	108.0	88.4	–28.1
$(CH_3)_2NCH_2\cdot$	1.823	1.514	1.515	2.237	2.211	100.1	107.2	88.6	25.3
SO_2Na	1.898	1.551	1.548	2.225	2.255	100.7	107.8	87.8	–27.9
$HOCH(CH_3)\cdot$	1.836	1.514	1.522	2.267	2.190	101.3	106.7	88.6	–22.1
SO_2Na	1.928	1.549	1.570	2.206	2.300	101.2	107.5	86.7	–24.0
$HOCH(C_2H_5)\cdot$	1.841	1.514	1.522	2.270	2.192	101.2	107.0	88.5	–22.6
SO_2Na	1.934	1.550	1.570	2.302	2.208	101.1	107.5	86.6	–24.2

Table 2. Calculated geometric parameters (R_e, Å; α_e, deg) of thiourea dioxide and aminoiminomethanesulfinic acid

Molecule	R_e(C–S)	R_e(S=O^3)	R_e(S–O^4)	R_e(O–H)	R_e(C–N^1)	R_e(C–N^2)	α_e(C–S=O^3)	α_e(O^4–S=O^3)	α_e(N^{1}CN^2)	α_e(SO^{4}H)
$(NH_2)_2CSO_2$	1.901	1.470		1.470	1.302	1.302	97.0	117.2	125.4	–
	2.018	1.500	1.514		1.305	1.317	93.8	117.7	127.4	
$HNC(NH_2)\cdot$	1.824	1.462	1.600	0.959	1.354	1.252	102.4	111.5	131.5	110.9
SOOH	1.859	1.498	1.689	0.971	1.356 (for NH_2)	1.270 (for NH)	104.1	109.7	135.1	106.3

Table 3. C–S bond lengths, apparent rate constants (k_{dec}) of decomposition of sodium 1-hydroxy- and aminoalkanesulfinates and thiourea dioxide, and parameters θ_1 characterizing the equilibrium constants of steps (1)

Compound	R_e(C–S), Å	$k_{dec}\times 10^3$, min^{-1}	$\theta_1\times 10^3$, l mol^{-1} min^{-1}
$HOCH_2SO_2Na$	1.909	0.75 ± 0.02	1.315 ± 0.043
$H_2\cdot NCH_2SO_2Na$	1.896	0.65 ± 0.02	–
$(CH_3)_2NCH_2SO_2Na$	1.898	0.9 ± 0.03	0.75 ± 0.02
$HOCH(CH_3)SO_2Na$	1.928	2.5 ± 0.1	9.78 ± 0.23
$HOCH(C_2H_5)SO_2Na$	1.934	5.0 ± 0.2	47.19 ± 1.60
$(NH_2)_2CSO_2$	2.018	150 ± 6	–

In aqueous solutions, the molecules under consideration dissociate into sodium ions and the corresponding alkanesulfinate anions, and the ionic bond between the sodium and oxygen atoms is broken. Comparison of the covalent bond lengths in the molecules under consideration shows that the longest bond is that between the C and S atoms, which is cleaved at heterolysis. Presumably, the trends in the bond lengths in the molecules will be preserved in solutions; then the C–S bond length can be considered as a characteristic of the stability of 1-hydroxy- and aminoalkanesulfinate molecules. The C–S bond lengths are compared in Table 3 with the kinetic parameters of decomposition of various alkanesulfinates and of reduction of a dye, Red 11-80 f vat dye precursor, with these compounds.

The apparent rate constants of the decomposition of sodium hydroxy- and aminoalkanesulfinates were taken from the literature [2] (353 K, pH 11.2), and those for thiourea dioxide were determined in this study under the same conditions. The parameters θ_1 were taken for 333 K from [3]; they characterize the concentration equilibrium constants of steps (1) for the compounds listed in Table 3. These results show that the C–S bond length varies in the same direction as the kinetic parameters of the decomposition of alkanesulfinates. The different stability of two tautomers of thiourea dioxide can be attributed to the difference in the C–S bond lengths.

Figure 3 shows the kinetic dependences for thiourea dioxide, obtained in this study for aqueous solutions with various pH values. The induction periods observed in acidic solutions decrease with increasing pH and disappear in alkaline solutions. The decomposition rate increases with pH. The reaction order with

respect to thiourea dioxide also changes; in alkaline solutions it approaches unity.

The presence of an induction period in the kinetic curve and the low rate of thiourea dioxide decomposition in acid solutions can be accounted for by the occurrence of a reversible tautomeric rearrangement mentioned above:

$$(NH_2)_2CSO_2 \rightleftarrows HNC(NH_2)SO_2H. \quad (3)$$

Apparently, in acidic solutions the equilibrium of reaction (3) is shifted to the right, and thiourea dioxide exists in the solution in the form of stable aminoiminomethanesulfinic acid (C–S bond length 1.859 Å, Table 2). In alkaline solutions, the equilibrium is shifted to the left, toward the less stable thiourea dioxide form (C–S bond length 2.018 Å, Table 2). The monoanion $HNC(NH_2)SO_2^-$, as shown in [14], mainly exists in acidic solutions.

EXPERIMENTAL

Thiourea dioxide taken for decomposition experiments was prepared from analytically pure grade thiourea (main substance content ≥97%) and a hydrogen peroxide solution as described in [15].

The decomposition of thiourea dioxide in aqueous solution was studied in a temperature-controlled glass vessel under argon in Robinson–Britton universal buffer solution. From the reaction mixture, we took samples at regular intervals and determined in them the total content of thiourea and impurities by iodometric titration [16]. To plot the kinetic curves shown in Fig. 3, we analyzed polarographically the amount of impurities formed by decomposition of thiourea dioxide (mainly dithionite, sulfite, and thiosulfate).

As supporting electrolytes used in polarographic analysis we used solutions of the Robinson–Britton universal buffer mixture. The polarographic analysis of the above-mentioned intermediates was performed in a glass two-electrode electrochemical cell. A mercury dropping electrode was the working electrode, and bottom mercury was the reference electrode. To eliminate the disturbing effect of oxygen on the polarographic waves, the supporting electrolyte was purged with argon. The potential sweeping rate was 4 mV s^{-1}, and the mercury dropping period, 3 s.

When determining the dithionite content, we used as supporting electrolyte the universal buffer solution with pH 9.0. The polarogram was taken in the classical mode from the initial potential of –0.3 V to the final potential of –0.9 V; the half-wave potential vs. bottom mercury was –0.68 V. Preliminarily we constructed the calibration dependence of the height (limiting current) of the polarographic wave on the dithionite solution concentration.

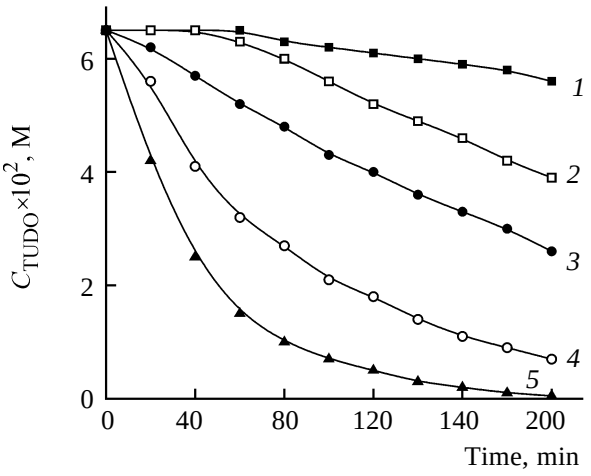

Fig. 3. Variation with time of the thiourea dioxide concentration C_{TUDO} at 308 K and various pH values of the aqueous solution. pH: (*1*) 1.76, (*2*) 3.98, (*3*) 6.8, (*4*) 8.85, and (*5*) 12.2.

Polarographic determination of the thiosulfate and sulfite concentrations was performed in the universal buffer solution at pH 4.7. The polarogram was taken in the differential mode from the initial potential of +0.3 V to the final potential of –1 V, at the sweeping amplitude of +11 mV. The polarographic peak potentials were –0.15 and –0.70 V for thiosulfate and sulfite, respectively. Preliminarily we determined the dependences of the peak heights on the thiosulfate and sulfite concentrations.

To construct the calibration plots, we used the following chemicals: sodium dithionite $Na_2S_2O_4$, main substance content 85±5%, monitored by iodometric titration [17]; analytically pure grade sodium sulfite Na_2SO_3, main substance content ≥97%; and chemically pure grade sodium thiosulfate $Na_2S_2O_3\cdot5H_2O$, main substance content 99%.

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