A STUDY OF THE FORMATION REACTIONS OF AMIDES OF 2-BENZTHIAZOLYLSULPHENIC ACID FROM N-CHLORAMINES AND 2-MERCAPTO BENZTHIAZONE

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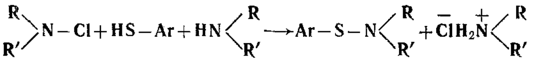
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 1, pp. 89–92, 1970

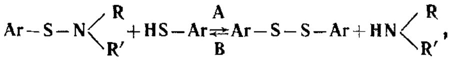
UDC 547.583:2

A study was made of the mechanism of the reaction between N-chloramines and 2-mercapto benzthiazole in water and in inert solvents. It was shown that in water and alcohol, in addition to the formation of sulfenamides, there is an oxidation reaction of 2-mercapto benzthiazole by hypochlorous acid to the disulfide.

In a previous study, it was shown that benzthiazolyl-2-sulfenamides are formed through the intermediate formation of N-chloramines on oxidation of 2-mercapto benzthiazole or its salts and amines [1]. It was of interest to study the reaction between N-chloramines and 2-mercapto benzthiazole in water and organic solvents. The interaction between N-chloramines and 2-mercapto benzthiazole or its salt may be described by the following equation:



$$ {}^{R}_{R'}\!\!>N-Cl+HS-Ar+HN<^{R}_{R'} \longrightarrow Ar-S-N<^{R}_{R'}+\overset{-}{Cl}H_2\overset{+}{N}<^{R}_{R'} \qquad (1)$$



$$ Ar-S-N<^{R}_{R'}+HS-Ar \underset{B}{\overset{A}{\rightleftarrows}} Ar-S-S-Ar+HN<^{R}_{R'}, \qquad (2)$$

where Ar = 2-benzthiazolyl, R = alkyl, R' = alkyl or H; A = forward reaction; B = reverse reaction.

It has been shown that the effect of solvents on the equilibrium (2) is in agreement with the Hughes-Ingold theory, i. e., for the given type of reagents an increase in polarity of the medium leads to a strong increase in the rate of the reverse reaction (B) and to a slight decrease in the rate of the forward reaction (A) [1, 2]. In relation to this theory, the rate of reaction (1) must fall slightly with increase in polarity of the medium. Thus, an increase in polarity of the medium must lead to a decrease in the quantity of disulfide formed during the course of reaction (1) and (2).

Thus, during the interaction between the chloramines studied and 2-mercapto benzthiazole were found the corresponding benzthiazolyl-2-sulfenamines and bis(2-benzthiazolyl)disulfide, the ratio of which is dependent on the nature of the solvent. However, increase in polarity of the solvent leads to an increase in quantity of bis(2-benzthiazolyl)disulfide in the products of the reaction (Table 1, which is in contradiction with the Hughes-Ingold theory and previously obtained data [1]. This may be explained by the fact that formation of disulfide in water and alcohol proceeds via a different pathway to that presented in equations (1) and (2).

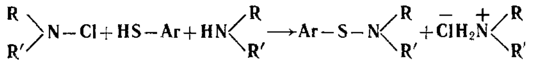
One of the possible pathways for the formation of bis(2-benzothiazolyl) disulfide is the oxidation of 2-mercapto benzthiazole by hypochlorous acid, which is formed as a result of the hydrolysis of N-chloramines [3]. Formation of hypochlorous acid or its sodium salts was determined according to the quantity of iodine formed from potassium iodide. The stability of chloramines in organic inert solvents and their inertness toward the stable radical, di-tert-butyliminoxyl, provides a basis for proposing that hypochlorous acid is only formed by an ionic mechanism. 2-Mercapto benzthiazole in acid or in slightly alkaline medium (in the presence of amines) under the action of hypochlorous acid and during the interaction with an aqueous solution of the products of hydrolysis of N-chloramines forms bis(2-benzthiazolyl)disulfide.

An increase in excess amine above that calculated by the stoichiometry of the equation in water and in alcohol leads to a change in the ratios of benzthiazolyl-2-sulfenamides and bis(2-benzothiazolyl)disulfide in the direction of increase of the first compound (Table 1). In benzene, even with equimolar quantities of chloramine, 2-mercapto benzthiazole, and amine, benzthiazolyl-2-sulfenamides are mainly obtained.

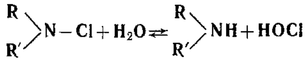
Thus, from the experimental data the interaction between N-chloramines and 2-mercapto benzthiazole in water and alcohol may be represented as follows.

Table 1. Interaction Between 2-Mercapto Benzthiazole and N-Chloramines in the Presence of Amines

Solvent	Quantity of amine in relation to 2-mercapto benzthiazole	Temperature, ° C	Duration of the reaction, min	Yield of bis(2-benzthiazolyl) disulfide, %	Yield of amide, %
Reaction containing N-chloromorpholine					
Water	1	22	30	89.9	—
	3	22	30	90.2	—
	5	22	30	78.3	14.3
	10	22	30	58.1	33.2
	15	22	30	47.1	42.1
	20	22	30	32.0	63.4
Ethyl alcohol	1	22	30	56.4	25.8
	2	22	30	46.6	45.5
	5	22	20	7.6	74.8
	7	22	20	—	93.5
	9	22	20	—	91.8
	1	50	30	8.6	78.3
	1	65	30	—	84.9
	1	−3	30	68.3	21.4
Benzene	1	22	20	8.3	73.4
	2	22	20	5.4	81.3
	3	22	20	—	86.8
	4	22	20	—	92.3
	1	50	20	—	91.3
	3	50	20	—	92.4
Reaction containing isopropyl-N-chloramine					
Water	1	22	30	57.1	26.6
	5	22	30	12.2	71.4
	7	22	30	8.0	75.0
	9	22	30	6.0	77.1
	1	0	30	67.0	15.3
	5	0	30	48.4	37.0
	1	30	20	—	86.0
	5	30	20	—	85.3
Ethyl alcohol	1	22	30	76.4	14.9
	5	22	30	44.4	46.6
	7	22	30	—	84.4
	9	22	30	—	88.3
	1	30	30	33.4	52.8
	5	30	30	—	97.0
	1	0	40	82.2	8.3
	5	0	40	51.0	42.1
Benzene	1	22	30	—	88.0
	5	22	30	—	91.4
	7	22	30	—	93.0
	9	22	30	—	93.2
	1	0	40	30.0	48.0
	5	0	40	38.4	54.0
	1	30	20	—	91.3
	5	30	20	—	92.0

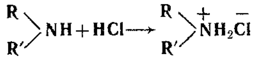


$$\mathrm{\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!N-Cl+HS-Ar+HN\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}\longrightarrow Ar-S-N\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}+\overset{-}{Cl}H_2\overset{+}{N}\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}} \qquad (3)$$



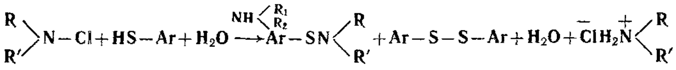
$$\mathrm{\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!N-Cl+H_2O\rightleftarrows\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!NH+HOCl} \qquad (4)$$

$$\mathrm{2Ar-SH+HOCl\longrightarrow Ar-S-S-Ar+HCl+H_2O} \qquad (5)$$



$$\mathrm{\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!NH+HCl\longrightarrow\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!\overset{+}{N}H_2\overset{-}{Cl}} \qquad (6)$$

Over-all scheme of the reaction



$$\mathrm{\begin{smallmatrix}R\\R'\end{smallmatrix}\!>\!N-Cl+HS-Ar+H_2O\xrightarrow{NH<\begin{smallmatrix}R_1\\R_2\end{smallmatrix}}Ar-SN\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}+Ar-S-S-Ar+H_2O+\overset{-}{Cl}H_2\overset{+}{N}\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}} \qquad (7)$$

Excess amine displaced the equilibrium of the reaction (4) in the direction of the formation of chloramine and moreover promotes the formation of benzthiazolyl-2-sulfenoamides. In benzene and in other inert solvents the reaction between N-chloramines and 2-mercapto benzthiazole proceeds according to equations (1) and (2).

EXPERIMENTAL

The N-chloramines used were obtained according to a previously described method [1]. 2-Mercapto benzthiazole with a mp of 181.5° C was used. Amines and all solvents were analytical grade.

Interaction of N-chloramines with 2-mercapto benzthiazole. A) In water. A 10 ml volume of a 0.1 N solution of the sodium salt of 2-mercapto benzthiazole and chloramine (and the amine corresponding to chloramine) were placed in a reactor provided with a stirrer, a reflux condenser, and thermometer. The mass was stirred for 20–30 min. At the end of the reaction, the resultant precipitate of disulfide and sulfenamide was removed by filtration, dried, and the sulfenamide (which dissolves in alcohol) was separated from bis(2-benzthiazolyl)disulfide. The compounds isolated were characterized according to melting point and UV spectra.

B) In alcohol.* At the end of the reaction the resulting precipitate of bis (2-benzthiazolyl)disulfide was removed by filtration, the filtrate was diluted with water, and a precipitate of sulfenamide was formed.

C) In benzene.* At the end of the reaction, benzene was removed by distillation in a water bath, and the precipitate remaining was washed with alcohol. The sulfenamides were found in the solution and bis(2-benzthiazole)disulfide was in the precipitate. The results of all the experiments are presented in Tables 1 and 2.

Interaction between 2-mercapto benzthiazole and hypochlorous acid. A) Hydrochloric acid and sodium hypochlorite were added with stirring to a solution of 0.5 g of 2-mercapto benzthiazole in 25 ml of water so that the pH of the solution was 2–3. Termination of the reaction was controlled by starch iodine paper. The precipitate was removed by filtration, and 0.49 g of bis(2-benzthiazolyl)disulfide was obtained.

B) A 0.2 ml volume of morpholine was added to a solution of 0.5 g of 2-mercapto benzthiazole in 25 ml water and then (with stirring) HCl and sodium hypochlorite were added in such ratios so that the acid neutralized the base in a solution of sodium hypochlorite. The resulting precipitate of bis(2-benzthiazolyl) disulfide was removed by filtration.

Determination of the stability of N-chloromorpholine in water and benzene. A) A 1-g quantity of N-chloromorpholine was transferred into 50 ml of water and benzene. After 10 min, potassium iodide was added to an aqueous solution of chloramine and the iodine liberated was titrated with thiosulfate. The content of iodine was 100% calculating for N-chloromorpholine.

The benzene solution was analyzed by IR spectroscopy after 24 hr. No increase in the intensity of the band characteristic for the N—H bond or decrease in the intensity of the band characteristic for the N—Cl bond was found.

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*When the reaction proceeded in alcohol and benzene, solutions of 2-mercapto benzthiazole were used.

B) A 0.5 g quantity of the sodium salt of 2-mercapto benzthiazole was added to an aqueous solution of chloramine after 10 mins, and the resulting precipitate of bis(2-benzthiazolyl)disulfide was removed by filtration and dried.

Table 2. Interaction between 2-Mercapto Benzthiazole and N-Chloramines (in the absence of amines)

Solvent	Quantity of chloramine according to the ratio to 2-mercapto benzthiazole, mole	Temperature, ° C	Duration of the reaction, min	Yield* of bis(2-benzthiazolyl)-disulfide, %	Yield* of sulfenamide, %
Reaction with N-chloromorpholine					
Water	1	22	30	91	
Alcohol				89	12
Benzene				75	
Water	2	22	20	93	
Alcohol				90	14
Benzene				71	
Water	5	22	10	94	
Alcohol				93	
Benzene				73	14
Alcohol	2	50	10	84	Traces
Reaction with isopropyl-N-chloramine					
Water	2	22	20	92	—
Alcohol				93	—
Benzene				95	—
Water	2	30	10	90	—
Alcohol				90	—
Benzene				91	—

*Calculated for 2-mercapto benzthiazole.

Interaction between 2-mercapto benzthiazole with di-tert-butyliminoxyl*. To 10 ml of 0.1 N N-chloromorpholine in benzene was added an equivalent quantity of di-tert-butyliminoxyl and the mixture was maintained for 10 hrs during which the intensity of the color of the solution of di-tert-butyliminoxyl, was measured every hour. There was no change in intensity. The sulphenamide was then synthesized by a previously described method, and N-oxydiethylene-benzthiazolyl-2-sulfenamide was obtained.

REFERENCES

1. V. A. Ignatov, P. A. Pirogov, and M. S. Fel'dshtein, ZhOrKh, 4, 2025, 1968.
2. K. K. Ingold, Mechanism of Reactions and Structure of Organic Compounds [Russian translation], IL, Moscow, 279, 1959.
3. B. V. Nekrasov, A Course in General Chemistry [in Russian], GKhI, Moscow-Leningrad, 349, 1954.

6 March 1968

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*Di-tert-butyliminoxyl was synthesized by R. S. Burmistrova.