THE REACTION OF ETHYLENE SULFIDE WITH ISOTHIOCYANATES

V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev

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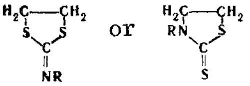
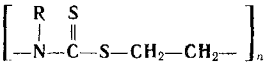
Ethylene sulfide reacts with isothiocyanates in the presence of triethylamine catalyst at 20° C, to give low-molecular copolymerization products having the general formula $[-C(NR)-S-CH_2-CH_2-S-]_n$. Their hydrolysis gives a salt of the amine and $[-C(O)-S-CH_2CH_2S-]_n$. Vacuum-heating the latter gives ethylenedithiocarbonate, and hydrogen peroxide oxidation in formic acid gives ethane disulfonic acid. Treatment of the copolymer from phenyl isothiocyanate and ethylene sulfide with liquid ammonia, amines, or aqueous alkali results in splitting and formation of 2-phenylimino-1, 3-dithiolane, while its reaction with ethylene oxide in the presence of triethylamine gives 3-phenyloxazolid-2-one.

Developing work on the reaction of alkene oxides with isothiocyanates [1, 2], we have investigated the reaction of the latter with the sulfur analog of ethylene oxide, ethylene sulfide. The catalyst used was triethylamine, as the more usual tetraethylammonium bromide is not soluble in the particular system. The main reaction products might have been expected to be N-alkyl(aryl)imino-1, 3-dithiolanes or N-substituted thiathiozolid-2-ones:



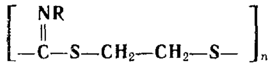
However on mixing equimolecular quantities of ethylene sulfide and methyl-, ethyl-, n-butyl-, p-tolyl-, α-naphthylisothiocyanates at 20° C, white precipitates are formed, while phenylisothiocyanate gives a transparent solid block. They are insoluble in ethanol, ether, benzene, but are easily soluble in chloroform, and moderately soluble in chlorobenzene. The compounds synthesized are low-molecular products of the unusual copolymerization of isothiocyanates with ethylene sulfide. To prove their structures we proceeded as described below.

Since the isothiocyanate molecule possesses a system of double bonds, formation of two compounds could have been postulated, depending on the type of bond opened: I from the opening of the N=C bond, II from the opening of the C=S one:



$$\left[-\overset{\overset{R}{|}}{N}-\overset{\overset{S}{\|}}{C}-S-CH_2-CH_2-\right]_n$$

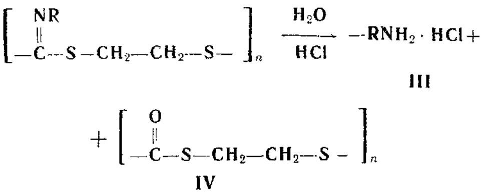
I



$$\left[-\overset{\overset{NR}{\|}}{C}-S-CH_2-CH_2-S-\right]_n$$

II

Study of the copolymers of ethylene sulfide with methyl-, ethyl-, and phenylisothiocyanates, using IR spectroscopy, showed intense absorption bands at respectively the 1582, 1571, and 1566 cm^{-1} regions. This indicated that they contained the same group $-S-\overset{|}{C}=N-$; the absorption band of the so-called thioureide group $>N-\overset{|}{C}=S$ should lie in the longer wave region at 1513–1470 cm^{-1} [3]. The results obtained favor structure II. The latter is also confirmed by hydrolyzing the copolymers with hydrochloric acid:

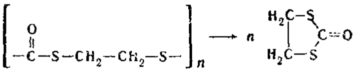


$$\left[-\overset{\overset{NR}{\|}}{C}-S-CH_2-CH_2-S-\right]_n \xrightarrow[HCl]{H_2O} \underset{III}{-RNH_2\cdot HCl}+\underset{IV}{\left[-\overset{\overset{O}{\|}}{C}-S-CH_2-CH_2-S-\right]_n}$$

The copolymers of ethylene sulfide with methyl-, ethyl-, and phenylisothiocyanates gave respectively the hydrochlorides of methylamine, ethylamine, and aniline (III), along with white products with melting point 165–170°, of identical structure, and exhibiting the characteristic intense absorption band of the carbonyl group.

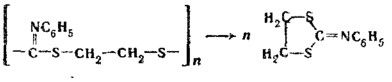
The compound isolated can consequently be regarded as a copolymer of carbonyl sulfide and ethylene sulfide (IV). Such a copolymer has not hitherto been described. Only its sulfur analog, the copolymer between carbon disulfide and ethylene sulfide [4] $[-C(S)-S-CH_2-CH_2-S-]_n$, is known, and this, when vacuum-heated above its melting point, is converted into ethylene trithiocarbonate.

Starting from the structure of the hydrolysis product given above, it might have been expected to give a cyclic product also, but actually when we vacuum-heated it at 200°, we obtained ethylenediothiol carbonate.



In addition the structure of the hydrolysis product was confirmed by oxidizing it with hydrogen peroxide in formic acid to ethane disulfonic acid.

In addition to the above proofs of the structure of the copolymers of ethylene disulfide with isothiocyanates, we made use of splitting of the copolymer with liquid ammonia. The presence of the C=S group (structure I) should have resulted in formation of ammonium thiocyanate. When we carried out this reaction on the copolymer of phenylisothiocyanate with ethylene sulfide, we did not find ammonium thiocyanate, but isolated a white crystalline substance melting point 43–44°. The same compound is obtained by heating the copolymer with primary, secondary, and tertiary amines, aqueous alkali, and aqueous ammonia. The elementary analysis and molecular weight of the compound correspond to the formula $C_9H_9NS_2$, the same as that of the basic unit of the copolymer, and agrees with that of 2-phenylimino-1,3-dithiolane:



Hydrochloric acid hydrolysis of the compound obtained gives ethylenedithiol carbonate and aniline hydrochloride. The cyclization product gave an undepressed mixed melting point with 2-phenylimino-1,3-dithiolane, which we previously synthesized from phenylisocyanide dichloride and ethanedithiol in the presence of triethylamine as a hydrogen chloride acceptor [5].

The copolymer from phenylisothiocyanate and ethylene sulfide reacts with ethylene oxide in the presence of triethylamine catalyst to give 3-phenyloxazolid-2-one. Evidently under the conditions of reaction, the copolymer first undergoes cyclization to 2-phenylimino-1,3-dithiolane; the latter on reaction with ethylene oxide gives 3-phenyloxazolid-2-one, by the equation which we previously gave [5]. Thus copolymers from ethylene sulfide and isothiocyanates can serve as starting materials for the preparative method of synthesis of derivatives of 1,3-dithiolanes and oxazolid-2-ones.

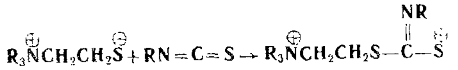
The high yield of heterocyclic compounds obtained from the copolymers and their hydrolysis products, indicates regularity of structure of the copolymers and regular alternation of the elementary units in their molecules. Confirmation of the structural regularity is also given by the X-ray diagrams, which indicate that the copolymers are crystalline in structure. Study of the thermomechanical properties of the copolymer from phenylisothiocyanate and ethylene sulfide shows that when it is heated above its melting point it becomes amorphous. Then if pressed tablets of the copolymer are rapidly cooled, they do not have time to crystallize, and remain amorphous. But if cooling is carried out slowly, the copolymer again assumes a crystalline structure.

The mechanism of copolymerization of ethylene sulfide with isothiocyanates can probably be explained as follows. The first stage is reaction of triethylamine with ethylene sulfide to give a bipolar ion with negatively charged sulfur:

$$R_3N + CH_2CH_2S \rightleftarrows R_3\overset{\oplus}{N}CH_2CH_2\overset{\ominus}{S}$$

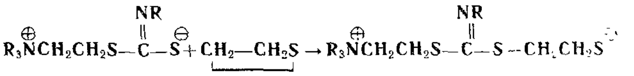
The occurrence of such a stage has previously been shown experimentally for alkene oxides [6].

The resultant ion attacks a molecule of isothiocyanate at a C=S bond:



$$R_3\overset{\oplus}{N}CH_2CH_2\overset{\ominus}{S} + RN{=}C{=}S \rightarrow R_3\overset{\oplus}{N}CH_2CH_2S{-}\overset{\overset{\large NR}{\|}}{C}{-}\overset{\ominus}{S}$$

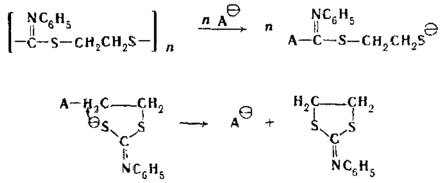
The new ion is less active, since the negative charge is delocalized by conjugation. Further reaction is found to take place with the more reactive ethylene sulfide molecule, and not with isothiocyanate:



$$R_3\overset{\oplus}{N}CH_2CH_2S{-}\overset{\overset{\large NR}{\|}}{C}{-}\overset{\ominus}{S} + \underbrace{CH_2{-}CH_2S} \rightarrow R_3\overset{\oplus}{N}CH_2CH_2S{-}\overset{\overset{\large NR}{\|}}{C}{-}S{-}CH_2CH_2\overset{\ominus}{S}$$

Chain growth proceeds with alternating addition of molecules of isothiocyanate and ethylene sulfide.

Conversion of the copolymer of phenylisothiocyanate into 2-phenylimino-1,3-dithiolane under the action of base (A^-) probably involves their reaction with a carbon atom linked to a phenylimino group. Here the copolymer molecule is split into separate units, which undergo cyclization with liberation of the base causing decomposition:



EXPERIMENTAL*

Preparation of copolymers of ethylene sulfide and isothiocyanates. a) With methyl isothiocyanate. 1.2 g methyl isothiocyanate, 1.0 g ethylene sulfide, and 0.01 g triethylamine were kept together for 22 hr at 20°, in an ampul. The contents polymerized completely; they were washed with ether, yield 2.0 g (91%), mp 60°. Found: C 36.01; 36.05; H 5.08; 5.10; N 10.60; 10.50; S 48.43; 48.30%. Calculated for $[C_4H_7NS_2]_n$: C 36.10; H 5.26; N 10.52; S 48.12%.

b) With ethyl isothiocyanate. 1.8 g ethyl isothiocyanate, 1.2 g ethylene sulfide, and 0.02 g triethylamine were stored together in an ampule for 25 hr. There was obtained 2.6 g (85%) of a white powder, mp 60–70°. Found: C 40.72; 40.70; H 6.10; 6.08; N 9.41; 9.45; S 43.42; 43.45%. Calculated for $[C_5H_9NS_2]_n$: C 40.82; H 6.12; N 9.53; S 43.53%.

c) With phenylisothiocyanate. 2.7 g phenylisothiocyanate, 1.2 g ethylene sulfide, and 0.02 g triethylamine were dissolved in 5 ml o-xylene, and the solution stored in an ampule at 20°. After 16 hr the white polymer was filtered off, and washed with ether. Yield 3.5 g (90%), mp 110°. Found: C 55.67; 55.50; H 4.69; 4.52; N 7.38; 7.20; S 32.77; 32.74%. Calculated for $[C_9H_9NS_2]_n$: C 55.38; H 4.62; N 7.18; S 32.82%.

Bulk polymerization was also effected. 2.7 g phenylisothiocyanate, 1.2 g ethylene sulfide, and 0.01 g triethylamine gave, in 20 hr at 20°, a transparent yellowish glassy polymer.

Copolymers of ethylene sulfide with n-butyl-, p-tolyl-, and α-naphthylisothiocyanate were prepared similarly, with melting points respectively 100°, 110°, and 135°.

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*With N. B. Novikova

IR spectra of the copolymers were measured with a 2-beam IKS-14 IR spectrophotometer, using a NaCl prism, in the 1700–1450 cm^{-1} region. The materials were tabletted with KBr (concentration 1–2%).

Cyclizing the phenylisothiocyanate-ethylene sulfide copolymer. a) With ammonia. 10 g copolymer and 20 ml liquid ammonia were sealed together in an ampule, and left for 24 hr at 20°. The ammonia was then evaporated off and the contents of the ampule treated with water. The water was analyzed for ammonium thiocyanate (none found). The precipitate insoluble in water was recrystallized from methanol, with strong cooling, to give white crystals, yield 0.9 g (90%), mp 43–44°, undepressed mixed mp with 2-phenylimino-1, 3-dithiolane. Found: C 55.47; 55.40; H 4.74; 4.70; N 6.90; 7.00; S 32.65; 32.71%; M 192 (cryoscopic). Calculated for $C_9H_9NS_2$: C 55.38; H 4.62; N 7.18; S 32.82%; M 195.

Cyclization with 30% aqueous ammonia proceeded similarly.

b) By amines. 1.0 g copolymer was put in an ampule with 2.01 ml ethylamine and kept for 24 hr at 20°. Yield of 2-phenylimino-1, 3-dithiolane 0.8 g (80%), mp 43–44°.

1.0 g copolymer was heated at 80–90° in a sealed tube with 2.0 ml diethylamine for 2 hr. Yield of 2-phenylimino-1, 3-dithiolane 0.8 g mp 43–44°.

1.0 g copolymer was heated with 2 ml triethylamine for 2 days at 80–90°. The triethylamine was distilled off under vacuum, to give a residue containing a viscous mass, which was crystallized. Yield of 2-phenyl-imino-1, 3-dithiolane, mp 43–44° 0.5 g (50%).

1.0 g copolymer was heated for 80–90° in MeOH solution with a catalytic quantity of butylamine for 2 days. Yield of 2-phenylimino-1, 3-dithiolane, mp 43–44°, 0.2 g.

c) By aqueous alkali. A reaction vessel fitted with a mechanical stirrer was charged with 23.4 g copolymer and 100 ml 40% aqueous NaOH, and the mixture heated for 7 hr at 100°, when the liquid split up into layers. The unreacted polymer was filtered off, and the solution extracted with ether. The ether solution gave 10.4 g (44.4%) white crystals mp 43–44° (ex MeOH with strong cooling). Undepressed mixed mp with 2-phenylimino-1, 3-dithiolane.

Hydrolysis of copolymers of ethylene sulfide with isothiocyanates. a) 10.0 g copolymer of phenylisothiocyanate with ethylene sulfide and 50 ml 35% HCl were stirred together at 100° for 1 hr. When the HCl was added to the polymer, a viscous sticky mass formed, which in the course of time disintegrated into a powder. The powder was filtered off from the liquid, and washed with water until neutral, mass 5.0 g (81%) mp 160–165°. The filtrate was evaporated on a water-bath, and the residue thus obtained contained white crystals, mass 4.0 g, mp 198°. Undepressed mixed mp with aniline hydrochloride. Neutralization equivalent 132. Calculated for $C_6H_7N \cdot HCl$: 129.5.

b) 2.0 g copolymer from ethyl isothiocyanate and ethylene sulfide was heated and stirred with 20 ml 36% HCl for 1 hr at 100°. The viscous mass disintegrated to a powder. Yield 1.4 g, mp 160–165°. Evaporation of the aqueous solution gave 0.6 g crystals of ethylamine hydrochloride. Neutralization equivalent 78. Calculation for $C_2H_7N \cdot HCl$: 81.5.

c) 2.0 g methyl isothiocyanate copolymer was heated and stirred with 20 ml 36% HCl at 90° for 1 hr. Mass of powder filtered off 1.7 g (94%), mp 150–160°. Evaporation of the aqueous solution gave 0.5 g methylamine hydrochloride. Neutralization equivalent 70. Calculated for $CH_5N \cdot HCl$: 67.5.

Hydrolysis of 2-phenylimino-1, 3-dithiolane. 1.0 g products was refluxed in a flask with 30 ml 10% HCl for 5 hr. The products were extracted with ether and dried. Evaporation of the ether gave 0.5 g crystals mp 33–34° (ex $CHCl_3$). Undepressed mixed mp with ethylenedithiocarbonate. The aqueous solution was evaporated. Yield of aniline HCl 0.5 g, mp 198°, undepressed mixed up with a pure specimen.

Oxidation of polymer IV. 5.0 g polymer was placed in a reaction vessel fitted with a stirrer and reflux condenser, 30 ml 30% H_2O_2 and 30 ml 85% formic acid run in, and the whole vigorously stirred for 3 hr. There was vigorous evolution of CO_2 and marked evolution of heat.

The contents of the reaction vessel were transferred to a porcelain cup, unreacted H_2O_2 destroyed by heating in the presence of Pt, and the formic acid evaporated off. The oxidation gave a small amount of H_2SO_4 which was neutralized with lead carbonate. The $PbSO_4$ was filtered off and the lead salt of ethane disulfonic acid, which was water-soluble, treated with H_2S to obtain the free acid. The PbS was filtered off, and washed with hot water. The aqueous solution was concentrated and phenylhydrazine then added. The ethane disulfonic acid salt of phenylhydrazine was precipitated, and recrystallized from EtOH (4.5 g). Neutralization equivalent 200. Calculated for $1/2(C_2H_6O_6S_2 \cdot C_6H_8N_2)$: 203. Free ethane disulfonic acid could also be isolated. Thus 3.7 g polymer when oxidized with hydrogen peroxide in formic acid gave 1.5 g ethane disulfonic acid, mp 104–105° (the literature gives [7] 104°).

Cyclizing polymer IV. 1.0 g polymer was placed in an ampule, which was evacuated and sealed, then heated for 1 hr in an oil bath at 200°. After cooling crystals were isolated, mass 0.8 g (80%), mp 33–34° (ex $CHCl_3$ on cooling). Undepressed mixed mp with ethylenedithiocarbonate.

Reaction of ethylene oxide with the copolymer from phenylisothiocyanate and ethylene sulfide. 2.0 g polymer, 3 ml ethylene oxide, and 1 g triethylaniline were heated together in an ampule for 6 hr at 80–90°, when a viscous mass formed, which was dissolved in MeOH; on cooling the solution gave white crystals mp 121°, mass 0.9 g (53.8%). Undepressed mixed mp with 3-phenyloxazolid-2-one.

REFERENCES

1. V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev, Izv. AN SSSR, ser. khim., 737, 1964.

2. V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev, Izv. AN SSSR, ser. khim., 2051, 1964.
3. L. J. Bellamy, The Infra-red Spectra of Complex Molecules [Russian translation], 414, IL, 1957.
4. V. S. Etlis, L. N. Grobov, and G. A. Razuvaev, DAN, **140**, no. 3, 1961.
5. V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev, ZhOKh, **34**, 4018, 1964.
6. W. Bradley, J. Forrest, and O. Stephenson, J. Chem. Soc., 1589, 1951.
7. C. Suter, Chemistry of the Organic Sulfur Compounds [Russian translation], Part 1, 186, IL, 1950.

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