Notes

The Reaction of Sulfur Compound Activated by Amine. II.[1] Reaction of Sulfur and Some Aliphatic Primary Amines

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The interaction of sulfur and an amino group has not been fully elucidated as some of the reaction products are unstable and none was isolated which suggests a complex reaction mechanism. Davis[2] and Hodgson[3] suggested the formation of open-chain ionic polysulfur compounds on the basis of data of several physical methods including examination of the electron spin resonance, spectra, and conductance of the solutions of sulfur in amine solvents. Although ammonia, hydrogen sulfide, and ethylenediammonium thiosulfate were detected in the reaction of sulfur with ethylenediamine (EN), the interaction of sulfur and amine was not confirmed upon a total conspectus of these reaction products.

In the present study some new reaction products have been detected, and a reaction has been postulated which is in good agreement with the yields of the products of EN with sulfur.

Immediately after the addition of sulfur to EN, generation of heat and ammonia gas was observed.[2] In the present study, yellow crystals of ethylenediamine hydrotrisulfide were obtained in 98% yield based on sulfur by diluting the reaction mixture with ethanol. Similar reactions were observed with other primary diamines, and crystalline hexamethylenediamine hydropentasulfide could be prepared. Only unstable oily hydropolysulfides from 1,3-propanediamine (PN) and diethylenetriamine (DETN) were produced, which were not characterized except by the fact that with *n*-butyl chloride they gave mixtures of higher dibutyl polysulfides. No such reaction products, however, were obtained from *n*-butylamine (BN), *n*-dibutylamine, morpholine, and tributylamine.

Addition of *n*-butyl chloride to the solutions of amine hydropolysulfide resulted in the production of dibutyl polysulfide (Table I). In the protonated amino groups such as EN, mainly dibutyl disulfide was formed, but, in dimethylformamide (DMF), dibutyl polysulfides of the sulfur chain corresponding to that of the amine hydropolysulfide were produced. Therefore, the length of the sulfur chain of amine hydropolysulfide can be determined by identifying dibutyl polysulfide obtained in DMF. Thus, ethylenediamine hydrotrisulfide ($EN \cdot H_2S_3$) was confirmed to be a single compound because only dibutyl trisulfide was given in DMF.

Other amine hydropolysulfides were estimated to be mixtures, but the average of the length of the sulfur chain of dibutyl polysulfide determined by nmr analysis was almost similar to the sulfur chain length of amine hydropolysulfide by elemental analysis.

In the direct reaction of *n*-butyl chloride with the solutions of sulfur in the listed primary amines, dibutyl di- and trisulfides were selectively obtained, but no monosulfide was recovered (Table II). This was also the case with BN. Therefore, amine hydropolysulfide may be formed in BN solutions of sulfur, although not isolated. No dibutyl polysulfide was isolated with *n*-dibutylamine, tributylamine, or morpholine. Increasing the reaction time and temperature resulted in decreased trisulfide–disulfide ratios. Therefore, polysulfides, except disulfide, are desulfurized by the amines, and the sulfur chain length of dibutyl polysulfides obtained in this reaction system does not agree with that of the corresponding amine hydropolysulfides. The identification of dibutyl polysulfide is strong evidence for the formation of amine polysulfide in sulfur solution of the listed primary amine.

The amount of ammonia generated by the reaction of sulfur with excess EN was 0.322 mol per g-atom of sulfur, which approximately agrees with the calculated value (0.33 mol) from the equation which will be shown later, as well as with the result by Davis.[2] However, the amounts of ammonia formed from PN, BN, and hexamethylenediamine (HN) were smaller, *i.e.*, 0.28, 0.14, and 0.07 mol, respectively. The amount was related to the length of the sulfur chain of the corresponding amine hydropolysulfide—the shorter the sulfur chain length the more the amount of ammonia.

After separating ammonia and $EN \cdot H_2S_3$ from the reaction mixture of sulfur and EN, an imino compound, probably that indicated in the following equation, was isolated by recrystallizing the neutralized residue. This unique imino compound, which will be better characterized for future publication, is of importance in understanding the interaction of sulfur and EN.

$$3NH_2CH_2CH_2NH_2 + 3S \longrightarrow NH_2CH_2CH_2NH_2 \cdot H_2S_3 + NH_3 + NH_2CH_2CH_2N{=}CHCH_2NH_2$$

Although no imino compound was isolated in the case with PN, HN, and BN, similar reactions are assumed, as amine hydropolysulfide and NH_3 were detected. It is expected that some new reaction, involving oxidation and reduction of organic compounds by polysulfide radical ions and hydropolysulfide in sulfur solution of amines as in Willgerodt reaction, will be further examined.

Experimental Section

Materials.—Sublimed sulfur was recrystallized twice from benzene. The sulfur, mp 112–113°, was free from hydrogen sulfide and sulfur dioxide. Amines were purified in a manner previously described.[2]

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[1] Paper I: K. Mori and Y. Nakamura, *J. Org. Chem.*, **34**, 4170 (1969).

[2] R. E. Davis and H. F. Nakshbendi, *J. Amer. Chem. Soc.*, **84**, 2085 (1962).

[3] W. G. Hodgson, S. A. Buckler, and G. Peters, *ibid.*, **85**, 543 (1963).

TABLE I[a]

AMINE HYDROPOLYSULFIDE + n-$C_4H_9Cl \rightarrow (C_4H_9)_2S_x$

Amine hydropolysulfide	g	Solvent	Reaction conditions Temp, °C	Reaction conditions Time, hr	Yields of $(C_4H_9)_2S_x$,[b] g $x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
EN.H_2S_3	7.9	DMF	30	2	0	6.5	0	0	0
EN·H_2S_3	7.9	DMF	50	2	0	7.5	0	0	0
EN·H_2S_3	7.9	EN	30	2	9.6	0.3	0	0	0
EN·H_2S_3	7.9	EN	50	2	10.1	0.2	0	0	0
EN·H_2S_3	7.9	BN	50	2	8.4	0.8	0	0	0
1,3-PN·H_2S_x	4.2	DMF	30	2	0	1.2[c]	1.4[c]	1.4[c]	0
HN·H_2S_5	8.8	DMF	30	2	0	0	0.4[c]	2.2[c]	0.4[c]

[a] EN, ethylenediamine; PN, propanediamine; HN, hexamethylenediamine; BN, n-buthlamine; DMF, dimethylformamide. [b] $(C_4H_9)_2S_x$ ($x = 1$) not isolated. [c] Value from nmr analysis.

TABLE II[a]

AMINE + S_8 + n-$C_4H_9Cl \rightarrow (C_4H_9)_2S_x$

Amine	Reaction condition Temp, °C	Reaction condition Time, hr	Yields of $(C_4H_9)_2S_x$,[b] g $x = 2$	$x = 3$
EN	30	1	4.7	2.2
EN	30	8	9.2	0.5
EN	50	3	10.6	0.2
1,3-PN	30	1	4.2	2.5
1,3-PN	50	3	9.4	0.4
HN	60	3	9.2	0.6
DETN	30	1	3.4	2.8
DETN	50	3	8.6	0.9
XDN	50	3	5.2	2.4
BN	30	1	1.8	2.0
BN	50	3	5.9	3.6

[a] DETN, diethylenetriamine; XDN, p-xylylenediamine. [b] $(C_4H_9)_2S_x$ ($x = 1$, $x \geqq 4$) not isolated.

Isolation of Hydropolysulfides of Amines. A. EN·H_2S_3.—A solution of 7.8 g of sulfur in 30 ml of EN was heated for about 2 hr at 50° under nitrogen until evolution of ammonia gas ceased, cooled, and diluted with 100 ml of ethanol to yield yellow, crystalline solid, which is soluble in DMF. The crystals were collected by filtration, washed with ethanol and benzene, and then dried in a desiccator: 98% yield (12.6 g) based on sulfur. The yield of the product recrystallized from EN–ethanol (1:3) was 92% (11.8 g); decomposition temperature, 116–120°; ir (KBr) SH–H_2N at 3000–3700 cm^{-1}, S–S at 480 cm^{-1}.

Anal. Calcd for EN·H_2S_3: C, 15.17; H, 6.37; N, 17.70; S, 60.76. Found: C, 15.44; H, 5.57; N, 17.33; S, 61.06.

B. HN·H_2S_5.—A solution of 7.8 g of sulfur in 30 ml of HN was heated for about 2 hr at 80° under nitrogen, and then treated in a similar manner as above. The yield of the product recrystallized from HN–ethanol (1:3) was 75% (9.1 g); decomposition temperature, 140–145°.

Anal. Calcd for HN·H_2S_5: C, 25.87; H, 6.51; N, 10.06; S, 57.56. Found: C, 25.59; H, 6.27; N, 9.67; S, 57.45.

C. Other Hydropolysulfides.—By adding 100 ml of ethanol to the reaction mixture of 7.8 g of sulfur with 30 ml of 1,3-PN or DETN, no crystalline products were obtained but a dark red oil deposited. The oily products were unable to be purified, as thermal decomposition was noted on distillation *in vacuo*. From the reaction mixtures of sulfur with BN, tributylamine, and morpholine, no reaction products were separated.

Dibutylpolysulfides from Amine Hydropolysulfides and Butyl Chloride.—Ten grams of n-butyl chloride was added dropwise to the solution of 7.9 g of EN·H_2S_3 in 50 ml of the solvent indicated in Table I. The mixture was stirred for 2 hr at the indicated temperature under nitrogen and then poured into ice–water containing an excess of sulfuric acid. The solution was extracted with benzene, and the extracts were washed with water and dried over anhydrous sodium sulfate. It was then evaporated to recover the crude product, which was distilled under a reduced pressure in a current of nitrogen. Dibutyl disulfide [bp 113–115° (15 mm),[4] ir S–S at 480 cm^{-1}] and dibutyl trisulfide [bp 73–75° (0.1 mm),[4] ir S–S at 480 cm^{-1}] were obtained, as shown in Table I.

Anal. Calcd for $(C_4H_9)_2S_2$: S, 35.95. Found: S, 35.48. Calcd. for $(C_4H_9)_2S_3$: S, 45.71; S, 45.71. Found: S, 45.29.

Similarly, dibutyl polysulfides were obtained from the hydropolysulfides of other primary diamines as summarized in Table I. Some of the dibutyl polysulfides were detected by the proton nmr spectrum analyses as previously reported.[5]

Dibutyl Polysulfides from Butyl Chloride and Amine Solutions of Sulfur.—To the solution of 5.2 g of sulfur in 50 ml of various amines, 12.5 g of n-butyl chloride was added dropwise with stirring at the temperature indicated in Table II. The mixture was cooked in a nitrogen atmosphere. The reaction mixture was treated similarly as described in the previous section and dibutyl polysulfides were isolated which are summarized in Table II.

Desulfurization of Dibutyl Trisulfide in EN.—To 20 ml of EN, 15.8 g of dibutyl trisulfide was added and the mixture was stirred for 2 hr at 30° under nitrogen. The reaction mixture was treated similarly as described previously and 9.6 g of dibutyl disulfide was obtained.

Isolation of $H_2NCH_2CH_2N{=}CHCH_2NH_2 \cdot 3HCl$.—The cooled filtrate from EN·H_2S_3 described before was neutralized with concentrated hydrochloric acid and allowed to settle the precipitates of EN·2HCl. The filtrate was then evaporated to dryness under reduced pressure, and the residue was extracted with the mixture of C_2H_5OH–H_2O (1:1). Removal of the solvent of the extracts left 2 g of colorless, crystalline product in needles which began to decompose on heating, ir (KBr) 1660 cm^{-1} (C=N).

Anal. Calcd for $H_2NCH_2CH_2N{=}CHCH_2NH_2 \cdot 3HCl$: C, 22.82; H, 6.70; N, 19.96; Cl, 50.52. Found: C, 22.56; H, 6.95; N, 20.29; Cl, 50.48.

Determination of Ammonia from Amine Solution of Sulfur.—Ammonia, generated from the mixture of 30 ml of amine and 9.6 g of sulfur at 50–80°, was determined by alkalimetry after separating amine through a trap at −10°.

Registry No.—S_8, 10544-50-0; EN·H_2S_3, 31044-74-3; HN·H_2S_5, 31044-75-4; ethylenediamine, 107-15-3; 1,3-propanediamine, 109-76-2; hexamethylenediamine, 124-09-4; diethylenetriamine, 111-40-0; p-xylylenediamine, 539-48-0; n-butylamine, 109-73-9; n-butyl chloride, 109-69-3; $H_2N(CH_2)_2N{=}CHCH_2NH_2 \cdot 3HCl$, 31044-76-5.

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[4] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., New York, N. Y., 1960, p 387.

[5] B. D. Vineyard, *J. Org. Chem.*, **31**, 601 (1966).

Conversion of Aliphatic and Alicyclic Polyalcohols to the Corresponding Primary Polyamines

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As part of a study of complexes of transition metal ions which is presently being conducted in this labora-