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THE REDUCTION OF ORGANIC COMPOUNDS OF SULFUR BY METALS IN LIQUID AMMONIA

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No information has been reported concerning the effects of different metal-ammonia systems, as such, upon the carbon-sulfur bond. Moreover, there are no data available concerning the reactivity of unsaturated sulfides in such systems. It was the direct purpose of this work to investigate the extent and course of reduction of certain organic sulfur compounds and to learn the effect of molecular structure on the stability of the carbon-sulfur bond under such conditions. The working hypothesis which guided this investigation is that the reduction of organic compounds at a given temperature and given solute to solvent ratio is dependent upon the half-cell potential of the metal and the concentration of the proton donor. The three metals studied are lithium, sodium, and beryllium having standard half-cell potentials in liquid ammonia at $-50°$ of 3.0, 2.6, and 1.2 volts, respectively. The values for sodium and lithium are those of Pleskov (5, 6), while the value for beryllium is an estimate based on that of calcium and sodium. Ammonium salts used in this work were the sulfate, chloride, and bromide, whose solubilities (7) in ammonia at $-40°$ are 0.0, 1.4, and 2.0 moles/liter, respectively. Since two equivalents of ammonium salt are employed for each liter of ammonia, the solubilities of the sulfate and chloride being exceeded, initial concentrations of these salts in the liquid ammonia were the same as the solubilities. A reservoir of ammonium ions was available from the undissolved solid in the reactor in the case of these two proton donors, as contrasted to ammonium bromide which dissolved completely in ammonia to give a concentration of two moles per liter.

Saturated sulfides. n-Propyl, *n*-butyl, and *n*-hexyl sulfides were employed in this phase of the work, and the data obtained on the reduction of these substances are given in Table III. With the system $Li—(NH_4)_2SO_4—NH_3$ it is found that *n*-propyl sulfide undergoes reduction to the mercaptan in greater yield than does *n*-butyl or *n*-hexyl sulfide. Thus, as the molecular weight of the sulfide increases (solubility in ammonia decreasing), the extent of reduction decreases. The mercaptan formed is not reduced, as evidenced by the absence of hydrogen sulfide or sulfide ion in the products. In the case of ammonium sulfate as a proton donor, lithium, which has the highest electrode reduction potential of the metals used, effected a 13% reduction of *n*-propyl sulfide, while sodium and beryllium caused no reduction of the sulfide. Sodium did react with the ammonium sulfate to give the theoretical volume of hydrogen. In the absence of a proton donor

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[1] Taken from a portion of the thesis submitted by Stanley Tocker in partial fulfillment of the requirements for the M.S. degree.

n-propyl sulfide was reduced to the mercaptan by lithium in 35% yield. With sodium in the presence of a proton donor the volume of hydrogen evolved approximated that calculated from the assumption that all metal was consumed in the reduction of the ammonium ion. It was noted in the lithium runs that the volume of hydrogen evolved decreased as the reduction of the sulfide increased. As the concentration of the ammonium ions (dissolved in the liquid ammonia) increased, it was apparent that the reduction of these ions exceeded the competitive reduction cleavage of the carbon-sulfur bond. It is of interest to note that Henne and Greenlee (3) reported that the sodium-liquid ammonia system which contained added ammonium sulfate was more effective in reducing acetylene to ethylene than that employing the more soluble ammonium chloride.

Unsaturated sulfide. The greater reactivity of allyl sulfide as compared with the previously mentioned saturated sulfides was immediately apparent. Reactivity was not only increased but reduction was more extensive as witnessed by the formation of appreciable amounts of hydrogen sulfide. In the presence of ammonium sulfate as a proton donor, sodium and lithium effected complete conversion of allyl sulfide to give 85–92% allyl mercaptan and 8–15% hydrogen sulfide. In the presence of the same proton donor beryllium did not reduce allyl sulfide but did react slowly with the donor to give 15% of the theoretical volume of hydrogen. Using ammonium chloride the conversion of allyl sulfide was 100% with lithium, 40% with sodium, and 0% with beryllium. However, the latter metal reacted with this proton donor to give 73% of the theoretical amount of hydrogen, the remainder of the beryllium being recovered unreacted. This result demonstrates the ability of beryllium to react more readily with the more soluble ammonium salt. The influence of the proton donor on the conversion of allyl sulfide is illustrated by the values given in Table I.

A comparison of the results of the reductive-cleavage of the carbon-sulfur bond in alkyl and allyl type compounds reveals the tremendous effect of the double bond. The greater reactivity of allyl sulfide is not unexpected in view of the known polar effects of the allyl group.

Mercaptans. *n*-Propyl mercaptan did not undergo reduction either in the presence or absence of a proton donor. This stability was expected in view of the experiments with *n*-propyl sulfide where *n*-propyl mercaptan was the ultimate product of reduction.

Allyl mercaptan in the presence of lithium and ammonium sulfate was converted to hydrogen sulfide in 71% yield. This experiment further demonstrated the susceptibility to cleavage of the carbon-sulfur bond in an allylic type struc-

TABLE I

ALLYL SULFIDE-SODIUM-AMMONIA

Proton Donor	Conversion, %
$(NH_4)_2SO_4$	100
NH_4Cl	40
NH_4Br	19

TABLE II

REDUCTIVE CLEAVAGE OF THE CARBON-SULFUR BOND IN THE $Li—(NH_4)_2SO_4—NH_3$ SYSTEM

Compound	Reactivity
$CH_3CH_2CH_2—S—CH_2CH_2CH_3$	1.0
$CH_2{=}CH—CH_2—SH$	5.5
$CH_2{=}CH—CH_2—S—CH_2—CH{=}CH_2$	7.7

ture. For a given metal and proton donor, the effect of the introduction of a double bond in the β-position is shown in Table II. The numbers in the second column represent relative ease of reaction as indicated by the per cent conversions under the experimental conditions.

Thiophene. The results of the experiments with thiophene may best be summarized by a consideration of the proton donor employed. In the presence of ammonium sulfate or chloride lithium reduced thiophene to give 25–26% hydrogen sulfide and 74–75% sulfur-containing polymer including a small amount of a mercaptan not further identified. Under similar conditions, reduction with sodium gave 5–6% hydrogen sulfide and 94–95% polymer including a trace of mercaptan. With the above proton donors present beryllium did not effect the reduction of thiophene; however, 74% of the theoretical amount of hydrogen was evolved in the run using ammonium chloride as compared with 15% in the case of ammonium sulfate. These results are quite similar to those reported for beryllium in Table IV. The ammonium bromide-lithium system gave a large amount of hydrogen, 53% polymer and 47% unreacted thiophene. Sodium with ammonium bromide effected 43% conversion of thiophene yielding isomeric 2,3- and 2,5-dihydrothiophenes as the principal products. A trace of hydrogen sulfide was detected, and very little polymer was obtained. On the basis of 100% conversion, the yield of the dihydrothiophenes was 86% and polymer 14%. Physical constants (boiling point, refractive index) for the dihydrothiophenes are in excellent agreement with the recently published data of Birch and McAllan (1), who employed sodium and methanol in ammonia as the reducing system. Hydrogen sulfide, crotyl mercaptan, and 2-butene were also obtained in that reduction. The use of ammonium bromide in the present investigation holds promise of an excellent method of synthesis of dihydrothiophenes since side reactions are minimized. It should be noted that again the metal of greatest reducing potential effects the most extensive reduction and the greater the concentration of ammonium ion the lower the percentage reduction of the organic compound.

Theoretical aspects. The experimental evidence in this work is in opposition to the concept of reduction by nascent hydrogen. The results of the factors studied in the present investigation lead the authors to suggest that the reduction of the simpler organic sulfur compounds may proceed according to the following equations using allyl sulfide as an example.

$$\begin{array}{rl}
\text{(I)} & \mathrm{M + xNH_3 \rightarrow M^+ + e^-(NH_3)_x} \\
\text{(II)} & \mathrm{CH_2{=}CH{-}CH_2{-}S{-}CH_2{-}CH{=}CH_2 + 2e^-(NH_3)_x} \\
 & \qquad\qquad\qquad\qquad\downarrow \\
 & \mathrm{CH_2{=}CH{-}CH_2{-}S^-{:} + CH_2{=}CH{-}CH_2^-{:} + 2\ x\ NH_3} \\
\text{(III)} & \mathrm{CH_2{=}CH{-}CH_2^-{:} + NH_4^+ \rightarrow CH_2{=}CH{-}CH_3 + NH_3} \\
\text{(IV)} & \mathrm{CH_2{=}CH{-}CH_2{-}S^-{:} + NH_4^+ \rightarrow CH_2{=}CH{-}CH_2{-}SH + NH_3} \\
\text{(V)} & \mathrm{CH_2{=}CH{-}CH_2{-}S^-{:} + 2e^-\ (NH_3)_x + 2NH_4^+} \\
 & \qquad\qquad\qquad\quad\downarrow \\
 & \mathrm{CH_2{=}CH{-}CH_3 + H_2S + (2x + 2)\ NH_3}
\end{array}$$

Evidence for equation (I) is found in the works of Kraus (4) and others (2). In the case of the reduction of the saturated aliphatic sulfides no hydrogen sulfide was detected, *i.e.*, reduction was less extensive. The solvated electrons (I) could reduce the ammonium ions to yield hydrogen and ammonia. Thus, equation (VI) competes for electrons with equations (II) and (V).

$$\text{(VI)}\ \mathrm{2NH_4^+ + 2e^-\ (NH_3)_x \rightarrow H_2 + (2x + 2)\ NH_3}$$

The greater the concentration of the ammonium ions, the more predominant becomes equation (VI). Similarly, it was evident from the volume of hydrogen produced in specific runs that more emphasis can be placed on equation (VI) as the organic sulfur compounds become more difficult to reduce. The greater the electron release of the metal, *i.e.*, availability of solvated electrons for reaction (II), the greater will be the reduction of the sulfur compound.

EXPERIMENTAL

GENERAL

Apparatus. The liquid ammonia reactor system included a one-liter, round-bottomed, three-necked flask, one neck of which was connected to an ethanol-Dry Ice-cooled condenser. A rubber-sealed glass stirrer was attached to the middle neck of the flask, while the third neck was available for the addition of reagents. The gas train leading from the condenser consisted of a trap, an acid scrubber for ammonia, and a wet test meter for the measurement of the volume of gas evolved in the reaction.

The column employed for the fractionation of products was a vacuum-jacketed, silvered column 24" x ½", packed with ⅛" glass helices. It could not be used without flooding for materials which boiled above 100°. Using a test mixture of benzene and carbon tetrachloride, this column was rated at 15 theoretical plates under total reflux. An electrically lagged column was constructed for the fractionation of substances which boiled above 100°. It measured 31" x ½", and was packed with ⅛" glass helices. The column was rated at 20 theoretical plates under total reflux.

A modified 125-ml. Claisen flask was also utilized for the rapid distillation of relatively unstable liquids at atmospheric or reduced pressures. The arm containing the delivery tube was lengthened by the insertion of a 6½" glass section which was indented so as to increase the vapor-liquid contact.

The rate of stirring of the reaction mixture was maintained at 125 to 150 r.p.m. Such control made for a more even flow of gas through the traps and wet test meter.

Materials. The anhydrous ammonia from the du Pont Company was used directly from the 52 pound cylinder.

All organic sulfides and *n*-propyl mercaptan were Eastman grade, obtained from the Eastman Kodak Company. The allyl mercaptan, C.P. grade, was obtained from Edwal Laboratories.

Crude thiophene was generously supplied through the courtesy of the Socony Vacuum

Oil Co., Inc. The compound was purified by fractional distillation, the fraction distilling at 82° under 712 mm. pressure being employed in the investigation.

The sodium was C.P. grade metal stored under oil and cut as needed. Petroleum ether was used to remove the oil and the residual petroleum ether was evaporated in a stream of nitrogen. Lithium was treated in a similar manner.

Beryllium spheres of 97% minimum purity were acquired from the Beryllium Corporation. The metal was shattered into small fragments by a heavy hammer, washed in petroleum ether, and dried in a stream of nitrogen prior to use.

The ammonium chloride, ammonium sulfate, and ammonium bromide were C.P. grade.

SATURATED ALIPHATIC SULFIDES

General procedure. After the system was opened between the trap and the ethanol-Dry Ice condenser, ammonia (500 ml./equivalent weight of ammonium salt) was run into the flask. The ammonium salt and organic sulfide then were added in that order, and the contents were stirred for several minutes. A 125-ml. Erlenmeyer flask containing the small pieces of metal was attached to a neck of the reaction flask by means of Gooch tubing. The system then was closed and the metal was added *slowly* while stirring the contents of the reactor at a uniform rate. An effort was made to regulate the addition of metal so as to insure the smooth gas flow necessary for an accurate gas volume reading on the wet test meter. A blue color, which disappeared with stirring, appeared around the sodium or lithium metal suspended in the ammonia solution. No color was noted in the beryllium experiments. When reaction was complete, as indicated by the cessation of gas flow after all metal was added, the system was opened. In the lengthy beryllium runs, the stirring rate was periodically increased to 250 r.p.m. for a few seconds when unreacted metal was noted in the reactor and gas evolution had diminished. No attempt was made to isolate the relatively small amount of hydrocarbon resulting from the partial reduction of the saturated sulfides.

The data presented in Table III are based on recoveries obtained through the following preferred procedure. Ten grams of ammonium chloride were added to the reactor after a run. One volume of water then was added, the system being under reflux conditions as in a run. All water-soluble salts were dissolved by stirring and the use of more water, if necessary. The resultant solution was extracted with successive 50-ml. portions of ethyl ether. The combined ether extractions were dried and fractionally distilled, the fractions conforming to the boiling points of the sulfide and corresponding mercaptan being separated and weighed.

ALLYL SULFIDE

General procedure. The runs were carried out in a manner similar to that used for the saturated sulfides taking care that the metal was added slowly so as to favor a steady flow of gas. Although the reduction product propene was not identified as such, the exhaust gases from the sodium and lithium runs decolorized bromine dissolved in carbon tetrachloride.

Method of recovery for allyl sulfide runs. An iodometric method for the determination of allyl mercaptan and hydrogen sulfide was applied in the following manner with satisfactory results. (a) Two hundred milliliters of dried ether were added to the material in the reactor after a run and the ammonia allowed to evaporate through a drying tube. (b) The supernatant liquid and subsequent ether extractions of the solid material were combined and stoppered. (c) The solid materials in the cooled reactor were slowly acidified and the evolved hydrogen sulfide led into a standardized iodine solution. (d) Organic phases of (b) and that which separated out upon the acidification in (c) were combined. Ether was stripped off into the iodine solution of (c), which was subsequently titrated with standard thiosulfate solution for the iodometric determination of hydrogen sulfide. (e) The liquid remaining in the still pot was extracted with three 20-ml. portions of 40% potassium hydroxide, which dissolved the mercaptan by forming the water soluble mercaptide.

TABLE III

REDUCTION OF SATURATED ALIPHATIC SULFIDES

Number	1	2	3	4	5	6	7	8	9
Reagents									
n-Alkyl sulfide									
Form	$C_6H_{14}S$					$C_8H_{18}S$		$C_{12}H_{26}S$	
Moles	0.212	0.212	0.212	0.212	0.212	0.171	0.171	0.100	0.100
Metal									
Symbol	Na	Li	Li	Li	Na	Li	Na	Li	Na
Moles	0.424	0.424	0.424	0.424	0.424	0.342	0.342	0.200	0.200
Ammonium Salt									
Anion	$SO_4^=$	Cl^-	$SO_4^=$	—	—	$SO_4^=$	$SO_4^=$	$SO_4^=$	$SO_4^=$
Moles	0.212	0.424	0.212	—	—	0.171	0.171	0.100	0.100
Recovery									
Gas[a]									
Liters (STP)	4.88	4.48	3.52	2.09	—	3.62	3.80	1.86	2.16
% Theo. Vol.	100+	95	74	44	—	95	100+	83	97
R-S-R, Moles	0.190	0.180	0.161	0.114	0.121	0.133	0.152	0.083	0.091
R-S-H, Moles	0.0	0.005	0.025	0.063	0.053	0.003	0.0	0.005	0.0
Mole-%	90	87	88	84	82	80	89	88	91
R-S-H[b], %	0	3	13	35	31	2	0	6	0

[a] Hydrogen. [b] These values are based on 100% recovery of organic material.

TABLE IV

REDUCTION OF ALLYL SULFIDE

Number	1	2	3	4	5	6[a]	7	8
Reagents								
Sulfide, Moles	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Metal								
Symbol	Na	Na	Li	Li	Na	Li	Be	Be
Moles	0.40	0.40	0.40	0.40	0.40	0.40	0.20	0.20
Ammonium Salt								
Anion	$SO_4^=$	Cl^-	$SO_4^=$	Cl^-	Br^-	$SO_4^=$	Cl^-	$SO_4^=$
Moles	0.200	0.400	0.200	0.400	0.400	0.200	0.400	0.200
Recovery								
Gas								
Liters (STP)	4.60	4.70	4.25	4.42	—	—	3.26	0.69
% Theo	100+	100+	95	99	—	—	73	1.5
Sulfide, Moles	0.0	0.096	0.0	0.0	0.138	—	0.186	0.168
Mercaptan, Moles	0.148	0.06	0.138	0.42	0.030	0.049	0.0	0.0
H_2S, Moles	0.012	0.003	0.024	0.020	0.001	0.120	0.0	0.0
Mole-%	80	80	81	81	85	85	93	84
%[b]								
$(CH_2{=}CH{-}CH_2)_2S$	0	60	0	0	81	—	100	100
$CH_2{=}CH{-}CH_2{-}SH$	93	38	85	88	18	29	0	0
H_2S	7	2	15	12	1	71	0	0

[a] Allyl mercaptan was employed in this experiment.

[b] This summary is based on 100% recovery of organic material.

The residual organic phase (principally allyl sulfide), if any, was fractionated. (f) Potassium hydroxide extractions of (e) were slowly acidified at 25° and the aqueous and resultant organic phase (allyl mercaptan) was poured into a standard iodine solution. This solution was titrated with standardized sodium thiosulfate solution for the determination of mercaptan. In the allyl mercaptan run, only steps (a) to (d) inclusive, were necessary. The data are summarized in Table IV.

THIOPHENE

General information. Hydrogen sulfide was detected by the lead acetate test in the products of a preliminary sodium-ammonium sulfate run carried out in the same manner as in the case of the other sulfur compounds investigated. It was therefore postulated that unsaturated compounds were also by-products of the reductive cleavage of the carbon-sulfur bond in the thiophene molecule.

All runs were carried out as previously indicated for allyl sulfide. The reaction here was also more violent than that observed in the alkyl sulfide experiments.

Recovery of products from thiophene runs. The following procedure was found to give satisfactory recoveries. Two hundred milliliters of dry ether were added to the reduction products immediately after a run, the ammonia being subsequently allowed to weather off through a drying tube. The ether phase remaining in the reactor was decanted and the

TABLE V

REDUCTION OF THIOPHENE

Number	1	2	3	4	5	6
Reagents						
Thiophene, Moles	0.200	0.200	0.200	0.200	0.200	0.200
Metal						
Symbol	Li	Li	Li	Na	Na	Na
Moles	0.40	0.40	0.40	0.40	0.40	0.40
Ammonium Salt						
Anion	$SO_4^=$	Cl^-	Br^-	$SO_4^=$	Cl^-	Br^-
Moles	0.200	0.400	0.400	0.200	0.400	0.400
Recovery						
Gas						
Liters (STP)	1.59	1.86	3.89	2.57	1.39	4.15
% Theo. Vol.	36	42	87	57	31	93
Thiophene, Moles	0.0	0.0	0.081	0.0	0.0	0.090
Dihydrothiophene, Moles	0.0	0.0	0.0	0.0	0.0	0.058
H_2S, Moles	0.042	0.041	0.0	0.012	0.009	0.0
Other[a], Moles	0.13	0.12	0.09	0.17	0.17	0.01
Mole %	86	81	86	91	90	79
%[b]						
Thiophene	0	0	47	0	0	57
Dihydrothiophene	0	0	0	0	0	37
H_2S	25	26	0	6	5	0
Other[a]	75	74	53	94	95	6

[a] This item represents a product which is principally a sulfur-containing polymer (calculated as C_4H_4S) and a very small amount of substance believed to be crotyl mercaptan (1).

[b] This summary is based on 100% recovery or organic material.

residual solid material was extracted with dry ether. The solid material was acidified and the evolved hydrogen sulfide was passed through a standardized iodine-potassium iodide solution. The combined organic phases were fractionated at 34° into the iodine solution and the hydrogen sulfide thus determined iodometrically after titration with sodium thiosulfate solution. An examination of the residual material in the still pot at this point showed that if a viscous material were present, it could not be fractionated without complete decomposition. The material in the still pot was weighed and oxidized with a known iodine-potassium iodide solution for the determination of what was believed to be crotyl mercaptan (1). If the material in the still pot were non-viscous, distillation was carried out from a 50-ml. flask, the fractions being identified by their refractive indices and boiling points.

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SUMMARY

A study of the reduction of some organic sulfur compounds by different metal-ammonium salt systems in liquid ammonia is reported for the first time. A metal with a high half-cell potential favors a greater reduction of the organic compound than one of lower potential. The greater the concentration of ammonium ion as a proton donor the greater is the evolution of hydrogen, and the reduction of the organic compound decreases.

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