

Kinetic Studies of the Reactions of Sodium with Simple Alkyl Sulfides in Liquid Ammonia

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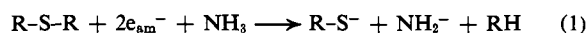
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Abstract: The reactions of sodium with dimethyl sulfide, diethyl sulfide, di-*n*-propyl sulfide, and methyl ethyl sulfide studied in liquid ammonia were found to be second order, first order with respect to both the alkyl sulfide and the ammoniated electron. Second-order rate constants at -33.9° were calculated to be 5.54 ± 0.08 , $8.50 \pm 1.3 \times 10^{-2}$, $2.95 \pm 0.05 \times 10^{-2}$, and $2.26 M^{-1} \text{ sec}^{-1}$ for dimethyl sulfide, diethyl sulfide, di-*n*-propyl sulfide, and methyl ethyl sulfide, respectively. Activation energies were found to be 3.8 ± 0.6 , 9.3 ± 0.7 , 11.6 ± 1.0 , and 3.1 ± 0.4 kcal/mol for dimethyl sulfide, diethyl sulfide, di-*n*-propyl sulfide, and methyl ethyl sulfide, respectively.

The solvated electron is now widely accepted as a fundamental species occurring in a wide variety of solvent systems.¹⁻⁵ These reactive species have been shown to occur as intermediates in a number of chemical phenomena such as radiolysis and photolysis and in electrolytic processes in both aqueous and nonaqueous media.⁶⁻⁸ The hydrated electron has been the subject of a great deal of scientific expenditure. Its physical properties and chemical reactivity have been examined by a large number of investigators.⁴ Kinetic investigations involving the hydrated electron have resulted in the determination of over 700 rate constants for its reaction with a variety of both organic and inorganic substrates.^{4,9}

In comparison, research involving the solvated electron in ammonia and in various amines has been concerned mainly with the characterization of the species present in these metal solutions and in the development of models for the solvated electron.¹⁻³ This is due, in part, to the exceptional stability of the solvated electron in ammonia and in some amines.^{3,10} However, in contrast with the extensive kinetic data available for the hydrated electron, few homogeneous kinetic studies have been carried out involving the ammoniated electron.^{11,12}

The reactions of the ammoniated electron with simple straight chain alkyl sulfides occur with cleavage of the sulfur-carbon bond according to the following general scheme¹³⁻¹⁵



where R is an alkyl group and e_{am}^- is the ammoniated electron generated by the dissolution of an alkali metal in liquid ammonia. In view of the paucity of available kinetic data involving the ammoniated electron, this simple reaction of e_{am}^- with alkyl sulfides appears to present a unique opportunity to investigate the factors governing the rates of cleavage reactions involving the ammoniated electron.

Experimental Section

Ammonia (Matheson, 99.99%) was purified under vacuum in about 500-ml quantities by an established repeated freezing-degassing-thawing process in contact with sodium metal.^{16,17} The purified ammonia was stored in a stainless steel storage tank (Matheson, Model 804) equipped with a Nupro (SS-4H-SW) metal valve at room temperature. Sodium (United Mineral and Chemical Co.) was obtained in the highest purity commercially available. Sodium samples were prepared by distilling the metal twice under high vacuum into sealed capillary tubes.^{16,17} Quantities of sodium, estimated from the size of the capillary tubes, were distilled into the reaction apparatus as needed. The purification and preparation of samples of dimethyl sulfide (Fischer certified), diethyl sulfide (Eastman, 957), di-*n*-propyl sulfide (K & K Laboratories), and methyl ethyl sulfide (K & K Laboratories, 22350) was accomplished by repeated freezing-degassing-thawing cycles^{18,19} followed by high vacuum fractional distillation of the sulfide to tared fragile glass ampoules or break-seal tubes.

The reported mole ratio of 2 mol of sodium per mole of alkyl sulfide¹⁸⁻¹⁵ was substantiated for the reaction of sodium with dimethyl sulfide in liquid ammonia at -33.9° by a high vacuum conductometric titrator. The design and operation of this titrator have been described elsewhere.²⁰ Products of the reactions of sodium with the alkyl sulfides studied were also collected to substantiate the reported stoichiometry¹⁸⁻¹⁵ and to verify that reduction was occurring. In the cases of dimethyl sulfide and diethyl sulfide, the hydrocarbons produced in the reactions with sodium in liquid ammonia were collected and identified. Both gases were collected in a calibrated gas buret using a procedure and apparatus similar to that described elsewhere.^{18,17} After the gases were collected and the amount of gas determined, they were identified from their characteristic mass spectra. A similar procedure²¹ and apparatus was used to quantitatively collect and identify methyl mercaptan produced in the reaction of sodium with dimethyl sulfide in liquid ammonia as its sodium salt. In addition, the products and stoichiometry of the reaction of sodium with di-*n*-propyl sulfide were investigated. In this case, the excess sulfide was

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Table I. Results of Product Analyses on Some Alkyl Sulfides

| Expt no. | Sulfide | Initial sodium, mmol | Product collected | Theoretical amount of product | Actual amount collected | % recovery |
|----------|---|------------------------|-----------------------------|-------------------------------|---------------------------|------------|
| 78-1 | Dimethyl sulfide | 2.38×10^{-5} | Methane | 1.19×10^{-5} mol | 1.20×10^{-5} mol | 101 |
| 78-1 | Dimethyl sulfide | 2.38×10^{-5} | Methyl mercaptan | 1.19×10^{-5} mol | 1.29×10^{-5} mol | 108 |
| 81-1 | Dimethyl sulfide | 5.61×10^{-5} | Methane | 2.80×10^{-5} mol | 2.77×10^{-5} mol | 99 |
| 81-1 | Dimethyl sulfide | 5.61×10^{-5} | Methyl mercaptan | 2.80×10^{-5} mol | 2.91×10^{-5} mol | 103 |
| 37-3 | Diethyl sulfide | 3.53×10^{-4} | Ethane | 1.76×10^{-4} mol | 1.70×10^{-4} mol | 97 |
| 40-3 | Methyl ethyl sulfide | 3.61×10^{-4} | Methane (no ethane present) | 1.80×10^{-4} mol | 1.56×10^{-4} mol | 87 |
| 45-3 | Di- <i>n</i> -propyl sulfide (3.8537 g) | 31.79×10^{-3} | Excess sulfide | 1.9754 g | 2.1477 g | 108 |
| 48-3 | Di- <i>n</i> -propyl sulfide (4.0300 g) | 31.50×10^{-3} | Excess sulfide | 2.1673 g | 2.1502 g | 99 |
| 60-3 | Di- <i>n</i> -propyl sulfide (4.8321 g) | 19.64×10^{-3} | Excess sulfide | 3.6711 g | 3.6506 g | 99 |
| 60-3 | Di- <i>n</i> -propyl sulfide (4.8321 g) | 19.64×10^{-3} | <i>n</i> -Propyl mercaptan | 0.7479 g | 0.7370 g | 99 |

collected to determine the mole ratio by separation of the unreacted sulfide from all other products by high vacuum fractional distillation. The procedure and apparatus used both to prepare the weighed sodium samples and to separate and collect the unreacted sulfide have been described elsewhere.²¹ Propyl mercaptan was also quantitatively collected and identified after hydrolysis of the thoroughly evacuated salts of the reaction of sodium with di-*n*-propyl sulfide in liquid ammonia using a procedure previously described.²¹ In several experiments, the presence of sodium amide in the thoroughly evacuated salts of the reactions of sodium with the alkyl sulfides studied was qualitatively determined by the use of Nessler's Reagent (Fischer certified) on the aqueous solution of the hydrolyzed salts. The amount of ammonia present in these aqueous solutions can be estimated from the amount of precipitate formed upon addition of Nessler's reagent in comparison to a standard ammonium hydroxide solution.

Since it was necessary to ensure completely homogeneous solutions in this work, the concentrations of the alkyl sulfides studied were chosen so that solubility was never exceeded. Since all other alkyl sulfides employed in this study are more soluble than di-*n*-propyl sulfide,¹⁴ the limits of solubility over the temperature range of -65 to -33.9° were determined for this alkyl sulfide.

Reactions with half-times greater than 150 sec were studied utilizing conventional conductometric or spectrophotometric methods. The reaction cell used when monitoring the progress of reactions conductometrically was designed to permit independent preparation of the sodium-ammonia and the reactant ammonia solutions. Both the apparatus and procedure used have been described in detail elsewhere and only a brief description will be given herein.^{12,18} A break-seal tube containing a weighed amount of reactant was sealed to the apparatus or a fragile glass ampoule containing a weighed quantity of reactant was introduced into the apparatus and the entire apparatus was thoroughly cleaned using an established procedure.²² After the reaction cell was evacuated to less than 5×10^{-6} Torr for a minimum of 2 hr with intermittent flaming, sodium was distilled into the sodium make-up vessel *via* a side arm. The side arm was subsequently sealed off and the apparatus was treated twice with ammonia. Ammonia was then condensed into the reactant make-up vessel and the constriction joining the two make-up vessels was sealed. Next, ammonia was distilled into the sodium make-up vessel and the reaction cell was removed from the vacuum manifold and placed into a thermostated silicone fluid bath (Harris Mfg. Co.) capable of maintaining temperatures (within the range -80 to 25°) to within 0.1° at the selected temperature. After the reaction cell had equilibrated with the bath temperature, the resistance of the sodium-ammonia solution was measured and the initial sodium concentration was determined from reported conductance data.¹⁶ The fragile glass ampoule or break seal was then broken with a glass encased magnet and the reactant solution mixed thoroughly. Next, the break seal connecting the two make-up vessels was broken. The solutions

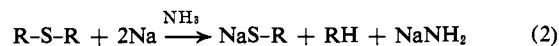
were then mixed thoroughly and the resistance of the reacting system was measured as a function of time. The reaction was taken to be complete when the resistance of the bleached solution remained constant. The apparatus and procedure employed when monitoring the progress of slow reactions spectrophotometrically is quite similar to that described above. A detailed description of the apparatus and procedure has been provided elsewhere.²¹

The rates of reactions which had half-times greater than 5 msec (in the range of 5 msec to 15 sec) were determined using a thermostated all-glass stopped-flow system. This thermostated stopped-flow system was used in studying the rates of some of the reactions (second-order rate constant greater than $2.0 M^{-1} \text{sec}^{-1}$ at -34°) reported herein at -34° . Both the apparatus and the procedure have been described elsewhere.^{23,24}

Resistance *vs.* time data were translated to ammoniated electron concentration as a function of time according to an established procedure.²⁵ Optical data, collected as a function of time, were analyzed to yield ammoniated electron concentration *vs.* time data by assuming Beer's law to be valid under these conditions.^{6,26} The analysis of the data collected by monitoring the progress of the reactions spectrophotometrically by both the stopped-flow technique²⁴ and the conventional method²¹ has been described elsewhere.

Results

The reactions of simple alkyl sulfides with sodium in liquid ammonia have been reported to proceed according to the following general scheme^{13,14}



where R is an alkyl group. This reported stoichiometry was duplicated for the case of dimethyl sulfide by conductometric titrations described elsewhere.²⁰ Quantitative and qualitative analyses were carried out on the products of the reactions of selected alkyl sulfides with sodium in liquid ammonia to verify that reduction was taking place and to substantiate the reported stoichiometry.^{13,14} Table I summarizes the sulfides investigated and the products of these reactions that were collected. A ratio of two moles of sodium per mole of sulfide was assumed in all cases and the per cent recovery listed is based on the theoretical amount of product assuming that mole ratio. The quantity of products in every case agrees well with the expected

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amount which supports the two to one stoichiometry. Since the autodecomposition of sodium-ammonia solutions to sodium amide and hydrogen was a possibility,^{27,28} the quantitative determination of the amount of sodium amide as a product of the alkyl sulfide reactions did not appear to be infallible as a tool for investigating the stoichiometry of these reactions in liquid ammonia. The presence of sodium amide in experiments 78-1, 81-1, 37-3, 40-3, 45-3, 68-1, 20-3, and 31-3 was determined in approximately the amounts expected by the use of Nessler's reagent on the hydrolyzed salts of the reactions. In the case of experiment 60-3 (see Table I), a portion of the salts of the reaction (in the form of $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4) was sent to Galbraith Laboratories, Knoxville, Tenn., for per cent nitrogen analysis. Their results (although they were not self-consistent) indicate sodium amide as a reaction product in the amount expected.

Reasonable estimates of the minimum solubilities of di-*n*-propyl sulfide in liquid ammonia were found to be $6.4 \times 10^{-2} M$ at -65° , $1.1 \times 10^{-1} M$ at -45° , and $1.7 \times 10^{-1} M$ at -33.9° from data obtained by a method described elsewhere.²¹ Since experiments involving di-*n*-propyl sulfide never employed concentrations of the sulfide greater than $3 \times 10^{-2} M$ at any temperature (see Table V), homogeneous solutions were assured. In addition, the highest concentration of any other sulfide studied (see Tables II-V) at any of

Table II. Kinetic Data for Reactions of Sodium with Dimethyl Sulfide in Liquid Ammonia

| Expt no. | Sodium concn, $10^4 M$ | Sulfide concn, $10^3 M$ | Temp, $^\circ\text{C}$ | $k, M^{-1} \text{sec}^{-1}$ |
|----------|------------------------|-------------------------|------------------------|-----------------------------|
| 53-1 | 9.30 | 1.68 | -65 | 1.9 |
| 56-1 | 6.87 | 2.27 | -65 | 1.6 |
| 64-1 | 2.23 | 2.96 | -65 | 1.6 |
| 65-1 | 3.04 | 2.73 | -65 | 1.7 |
| 68-1 | 4.18 | 4.75 | -65 | 1.6 |
| 78-1 | 4.45 | 6.31 | -65 | 1.6 |
| 81-1 | 10.10 | 10.09 | -65 | 1.4 |
| 92-1 | 5.90 | 7.16 | -65 | 1.7 |
| 96-1 | 6.96 | 4.44 | -65 | 1.6 |
| 23-1 | 10.35 | 12.35 | -34 | 5.47 |
| 55-3 | 10.10 | 21.54 | -34 | 5.62 |
| 92-3 | 7.15 | 16.74 | -75 | 0.81 |
| 87-3 | 5.79 | 11.90 | -75 | 0.91 |

Table III. Kinetic Data for Reactions of Sodium with Methyl Ethyl Sulfide in Liquid Ammonia

| Expt no. | Sodium concn, $10^4 M$ | Sulfide concn, $10^3 M$ | Temp, $^\circ\text{C}$ | $k, M^{-1} \text{sec}^{-1}$ |
|----------|------------------------|-------------------------|------------------------|-----------------------------|
| 25-3 | 12.00 | 5.59 | -65 | 0.85 |
| 28-3 | 7.70 | 6.92 | -65 | 0.92 |
| 30-3 | 5.75 | 10.90 | -65 | 1.00 |
| 54-3 | 10.25 | 30.18 | -37 | 2.26 |

the temperatures did not exceed $4.5 \times 10^{-2} M$, which is well below the estimated minimum solubility found for di-*n*-propyl sulfide in liquid ammonia. Because all

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Table IV. Kinetic Data for Reactions of Sodium with Diethyl Sulfide in Liquid Ammonia

| Expt no. | Sodium concn, $10^3 M$ | Sulfide concn, $10^3 M$ | Temp, $^\circ\text{C}$ | $10^2 k, M^{-1} \text{sec}^{-1}$ |
|----------|------------------------|-------------------------|------------------------|----------------------------------|
| 3-3 | 1.66 | 4.66 | -33.9 | 7.9 |
| 14-3 | 0.96 | 3.16 | -33.9 | 9.8 |
| 22-3 | 1.56 | 5.99 | -33.9 | 7.8 |
| 98-1 | 1.71 | 19.70 | -45 | 3.2 |
| 20-3 | 4.33 | 12.95 | -45 | 3.1 |
| 35-3 | 7.57 | 36.97 | -45 | 2.7 |
| 83-3 | 6.47 | 13.70 | -55 | 1.15 |
| 82-3 | 6.39 | 43.50 | -55 | 1.00 |
| 9-3 | 2.27 | 9.62 | -65 | 0.52 |
| 36-3 | 6.94 | 18.38 | -65 | 0.40 |
| 37-3 | 6.40 | 16.97 | -65 | 0.38 |
| 85-3 | 10.90 | 26.60 | -75 | 0.13 |
| 84-3 | 7.62 | 13.50 | -75 | 0.14 |

Table V. Kinetic Data for Reactions of Sodium with Di-*n*-propyl Sulfide in Liquid Ammonia

| Expt no. | Sodium concn, $10^3 M$ | Sulfide concn, $10^3 M$ | Temp, $^\circ\text{C}$ | $10^2 k, M^{-1} \text{sec}^{-1}$ |
|----------|------------------------|-------------------------|------------------------|----------------------------------|
| 23-3 | 5.58 | 14.67 | -33.9 | 2.9 |
| 29-3 | 5.60 | 23.37 | -33.9 | 3.0 |
| 43-3 | 1.54 | 14.11 | -33.9 | 2.9 |
| 18-3 | 2.71 | 18.52 | -45 | 1.1 |
| 31-3 | 5.45 | 15.27 | -45 | 1.0 |
| 34-3 | 6.10 | 15.75 | -45 | 1.0 |
| 24-3 | 3.48 | 12.30 | -55 | 0.37 |
| 32-3 | 5.36 | 22.94 | -55 | 0.26 |
| 33-3 | 6.52 | 18.90 | -55 | 0.35 |

other sulfides employed are more soluble than di-*n*-propyl sulfide in liquid ammonia,¹⁴ homogeneous solutions were assured in all cases.

Tables II through V give summaries of the kinetic data for each of the reactions studied of sodium with dimethyl sulfide, methyl ethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide. The second-order rate constants were obtained from the integrated second-order rate expression

$$kt = \frac{1}{[S]_t - [e_{\text{am}}^-]_t} \ln \frac{[e_{\text{am}}^-]_t [S]_i}{[e_{\text{am}}^-]_i [S]_t}$$

where the subscripts *i*, *t*, [S], and $[e_{\text{am}}^-]$ signify initial concentration, time, sulfide concentration, and ammoniated electron concentration, respectively. Values of $[S]_t$ were obtained from the stoichiometry of 2 mol of sodium per mole of alkyl sulfide.

Activation energies for the reactions of sodium with the alkyl sulfides studied were estimated from the Arrhenius equation²⁹ or from plots of $\log k$ vs. $1/T$ where data were available at more than two temperatures. Figure 1 shows such plots of $\log k$ vs. $1/T$ for the reactions of sodium with diethyl sulfide and di-*n*-propyl sulfide in liquid ammonia. Table VI summarizes the kinetic data for the reactions of the selected alkyl sulfides with sodium in liquid ammonia.

Discussion

The linearity of the second-order plots²¹ and the consistency of the second-order rate constants at each

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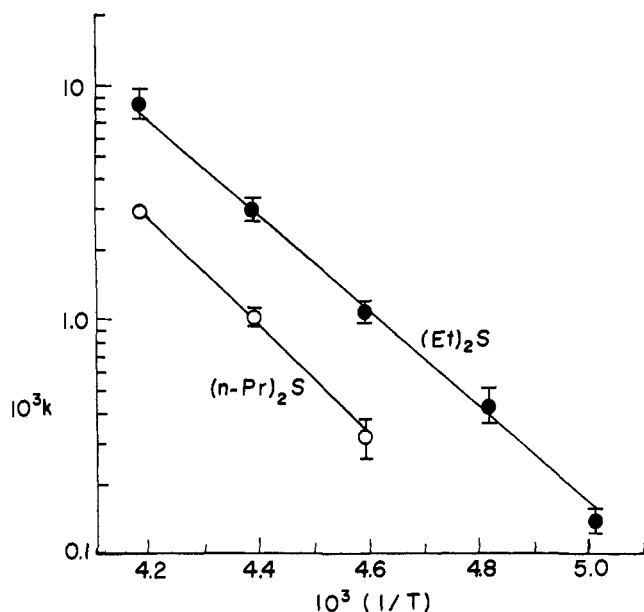


Figure 1. Semilog plots of second-order rate constants *vs.* $1/T$ for the reactions of sodium with diethyl and di-*n*-propyl sulfide in liquid ammonia.

Table VI. Summary of Kinetic Data for the Reactions of Sodium with each Alkyl Sulfide Studied in Liquid Ammonia

| Substrate | Av k , $M^{-1} \text{sec}^{-1}$ | Temp, $^{\circ}\text{C}$ | E_a , kcal/mol ^a |
|------------------------------|-----------------------------------|--------------------------|-------------------------------|
| Dimethyl sulfide | 1.65 ± 0.25^b | -65 | 3.8 ± 0.6^b |
| | 5.54 ± 0.08 | -33.9 | |
| | 0.86 ± 0.05 | -75 | |
| Methyl ethyl sulfide | 0.93 ± 0.08 | -65 | 3.1 ± 0.4 |
| | 2.26 | -37 | |
| Diethyl sulfide | $8.50 \pm 1.3 \times 10^{-2}$ | -33.9 | |
| | $3.00 \pm 0.3 \times 10^{-2}$ | -45 | 9.3 ± 0.7 |
| | $1.08 \pm 0.08 \times 10^{-2}$ | -55 | |
| | $4.33 \pm 0.8 \times 10^{-3}$ | -65 | |
| | $1.35 \pm 0.05 \times 10^{-3}$ | -75 | |
| Di- <i>n</i> -propyl sulfide | $2.95 \pm 0.05 \times 10^{-2}$ | -33.9 | |
| | $1.03 \pm 0.07 \times 10^{-2}$ | -45 | 11.6 ± 1.0 |
| | $3.10 \pm 0.06 \times 10^{-3}$ | -55 | |

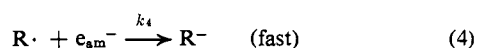
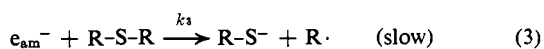
^a Estimated using the Arrhenius rate equation. ^b Average error.

temperature investigated indicate that the reactions of the ammoniated electron with simple alkyl sulfides are first order with respect to each reactant and second order over-all. The rate law corresponding to these conditions can be expressed as

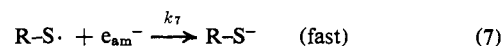
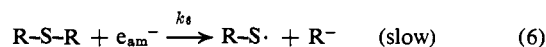
$$-d[e_{\text{am}}^-]/dt = k[e_{\text{am}}^-][\text{R-S-R}]$$

where R-S-R denotes any one of the alkyl sulfides investigated.

The simplest interpretation of these results assumes that the rate-limiting step is (3) in the following sequence of reactions.



In addition, another mechanism can be postulated in agreement with the observed rate law and the observed stoichiometry. That pathway is presented by the following reactions.



Steady-state treatment of $[\text{R}\cdot]$ in the scheme 3 \rightarrow 5 yields the rate law

$$-d[e_{\text{am}}^-]/dt = k'[e_{\text{am}}^-][\text{R-S-R}]$$

where $k' = 2k_3$ in agreement with the observed rate law assuming that k_4 and $k_5 \gg k_3$. Steady-state treatment of $[\text{RS}\cdot]$ in steps 6 \rightarrow 8 yields the same rate law assuming in this treatment that $k_7 \gg k_6$.

Evidence has been presented indicating that the position of cleavage depends upon the chain size of the alkyl groups.³⁰ That is, in the reduction of R-S-R', the cleavage of the carbon-sulfur bond proceeds preferentially reducing the R-S bond where $\text{R}' > \text{R}$ in terms of the number of carbon atoms in the chain. This is consistent with the second-order rate constants found in this study (see Table VI). In addition, the second-order rate constant for methyl ethyl sulfide is about one-half (within experimental error) of that observed for dimethyl sulfide at -65° indicating that the reactive sites on the molecule (methyl ethyl sulfide) have been reduced to one. Methane was the only hydrocarbon detected in the reduction of methyl ethyl sulfide by sodium in liquid ammonia (see Table I) at -65° . In view of the second-order rate constants at -65° for the reactions of sodium with dimethyl sulfide ($k = 1.65 M^{-1} \text{sec}^{-1}$) and diethyl sulfide ($k = 4.33 \times 10^{-3} M^{-1} \text{sec}^{-1}$), this result is not surprising.

In both suggested mechanisms, the rate-determining step is cleavage of the carbon-sulfur bond. The electron density in the carbon-sulfur bond might be expected to be one of the controlling factors which govern the rate at which the ammoniated electron attacks the carbon-sulfur bond. The large decrease in rate of reaction encountered upon going from dimethyl to diethyl sulfide (see Table VI) and the relatively small decrease between diethyl and di-*n*-propyl sulfide can be interpreted from the standpoint of an increasing inductive effect as the size of the alkyl chain is increased. The rate constants found for the reactions of sodium with dimethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide in liquid ammonia qualitatively mimic the behavior of the rate constants in nucleophilic displacement reactions involving methyl, ethyl, and *n*-propyl halides with various nucleophiles in a variety of solvents.³¹ This behavior has been interpreted broadly in terms of the inductive effects of the alkyl substituents.³¹

Figure 2 shows a plot of the log of the relative second-order rate constants for the reactions of dimethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide with sodium in liquid ammonia at -33.9° *vs.* the log of the relative second-order rate constants for the reactions of methyl, ethyl, and *n*-propyl bromide with ethoxide ion in dry ethyl alcohol at 55° .³² The agreement again indicates the correlation of the rate of the ammoniated electron attack upon the carbon-sulfur bond to the inductive effects of the alkyl groups involved. In

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(32) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).

Table VII. Values of ΔH^\ddagger and ΔS^\ddagger for Reactions of Sodium with Dimethyl Sulfide, Methyl Ethyl Sulfide, Diethyl Sulfide, and Di-*n*-propyl Sulfide in Liquid Ammonia at -33.9°

| Substrate | ΔH^\ddagger , cal mol ⁻¹ | ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹ |
|------------------------------|---|---|
| Dimethyl sulfide | 3,300 | -41 |
| Methyl ethyl sulfide | 2,600 | -44 |
| Diethyl sulfide | 8,800 | -26 |
| Di- <i>n</i> -propyl sulfide | 11,100 | -19 |

addition, the activation energies of 3.8, 9.3, and 11.6 kcal/mol for the reactions of sodium with dimethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide, respectively, in liquid ammonia also demonstrate the differences in reactivity of the ammoniated electron toward increasing inductive effects of the alkyl groups. A similar effect is encountered in nucleophilic displacement reactions of alkyl halides by various nucleophiles although the effect is not as striking.^{31,32}

Table VII gives values of ΔH^\ddagger and ΔS^\ddagger for reactions of dimethyl sulfide, methyl ethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide with the ammoniated electron at -33.9° . The values of ΔH^\ddagger and ΔS^\ddagger for dimethyl sulfide and methyl ethyl sulfide are not significantly different due to comparable activation energies and rates. The trends in ΔH^\ddagger and ΔS^\ddagger with increasing molecular weight in the alkyl chain are striking. The trend in the values of ΔH^\ddagger with increasing size of the alkyl substituent is similar to that observed in the nucleophilic displacement reactions of alkyl halides with a variety of nucleophiles.^{31,32} However, the trend for ammoniated electron reactions is more striking possibly indicating the inherent differences between the ammoniated electron and the other nucleophiles. Values of ΔH^\ddagger are essentially the same as the activation energies since the difference between them, $-RT$, is comparable to the uncertainty in the values of the activation energies. However, the large negative ΔS^\ddagger values are not as easily correlated to some characteristic feature of the system. If a direct correlation is assumed between ΔS^\ddagger and ΔV^\ddagger , then a negative ΔS^\ddagger would be expected on arguments based on the cavity size of the ammoniated electron.^{6,33} The increasing (more positive) values of ΔS^\ddagger with increasing size of the alkyl chain might be associated with an increasing dispersion of charge in the activated complex.

Based on a large body of information, Anbar and Hart⁴ have concluded to a first approximation that the rates of the solvated electron reactions are independent of the dielectric constant and the viscosity of the solvating medium. In addition, they suggest that hydrated electron reactions are in accord with an electron tunneling mechanism. Their reasoning is based on the surprisingly similar rates of reactions of aromatic compounds with solvated electrons in water and methanol,³⁴ the equality (within experimental error) of relative rates of mobile electrons in ice with different substrates at 77°K and the relative rates of the same solutes with e_{aq}^- in water at 300°K,³⁵ and the invariance of the activation energy.⁴ According to theoretical treatments, tunneling becomes relatively more impor-

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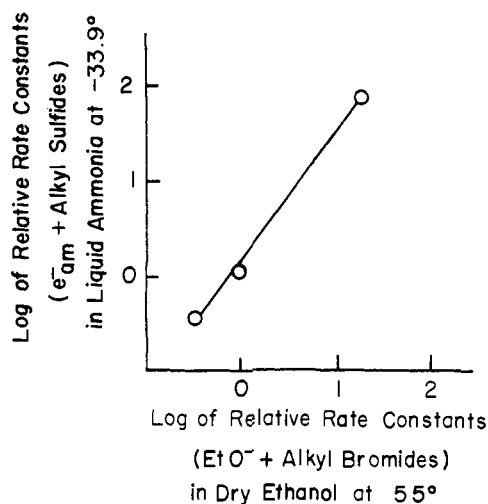


Figure 2. Log-log plot of the relative rate constants of reaction of the ammoniated electron with alkyl sulfides in liquid ammonia *vs.* the relative rate constants of the reactions of ethoxide ion with alkyl bromides in dry ethanol.

tant as the temperature is lowered.³⁶ This does not appear to be the case for reactions involving diethyl sulfide and di-*n*-propyl sulfide from an inspection of Figure 1. Unfortunately, due to the limited liquid range of ammonia, rate-temperature data are too limited to draw any firm conclusions on the above point.

The reactions of sodium with dimethyl sulfide and methyl ethyl sulfide have rate constants of 5.5 and 2.3 $M^{-1} \text{ sec}^{-1}$ at -34° , while the activation energies for these reactions have been estimated to be 3.8 and 3.1 kcal/mol, respectively. These observations are not in accord with normal Arrhenius type reactions in solution since the activation energies are exceptionally small.³⁷ Also, as a consequence of the magnitude of the rate constants and low activation energies, the frequency factors for these reactions are abnormally small. A possible explanation of these observations has been provided by Schindewolf, *et al.*,^{6,33} in that a large negative entropy of activation should be associated with the formation of the transition state due to the cavity size of the ammoniated electron. Moreover, according to these authors,³³ if a transition state is formed, then $k_{(e_{am}^-+R)}$ would be much greater than $k_{(e_{aq}^-+R)}$. The results of this study tend to support the transition-state hypothesis as shown by the large negative values of the entropy of activation given in Table VII. In addition, the second-order rate constant for the reaction of e_{aq}^- with dimethyl sulfide at 25° was reported to be $2 \times 10^7 M^{-1} \text{ sec}^{-1}$,³⁸ some six orders of magnitude greater than the reaction rate constant for e_{am}^- with dimethyl sulfide. On the other hand, it should be pointed out that the rate constants for reactions of e_{am}^- and e_{aq}^- with certain substrates do not differ greatly.³⁹

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