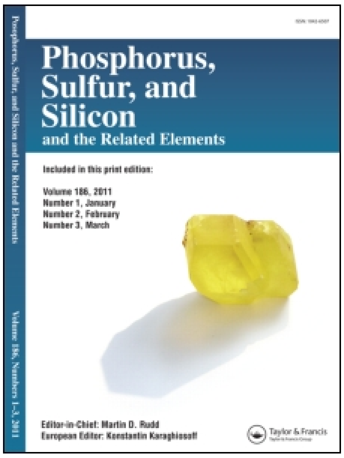

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# SOME REACTIONS OF ALIPHATIC AMIDES WITH SULFUR AND SODIUM POLYSULFIDES

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Some reactions of the aliphatic amides, $CH_3CONH_2$, $CH_3CONHCH_3$, $CH_3CON(CH_3)_2$ and $CH_3CON(C_2H_5)_2$ with elemental S and sodium sulfides, $Na_2S_n$, $n \geq 1$, have been studied. The initial reaction product with elemental sulfur appears to be a substituted polysulfane, $CH_3COS_nNR_2$, formed by the insertion of the sulfur chain into the C—N bond. This product decomposes on further heating, forming COS as the major gas product. In solutions of $Na_2S_n$ in the amides, the reactive material appears to be elemental S, present in equilibrium with $S_n^{-2}$. In the N-dialkyl substituted amides, $CH_3CON(CH_3)_2$ and $CH_3CON(C_2H_5)_2$, the tetrasulfide is uniquely stabilized by solvent coordination so that solutions of $Na_2S_4$ in these amides are stable for long periods of time at 130°C.

## INTRODUCTION

Aliphatic amides have received considerable attention over the years as non-aqueous solvents suitable for a variety of electrochemical studies.[1] We have shown recently that sodium polysulfide ($Na_2S_n$) solutions in N,N-dimethylacetamide (DMAC) possess the necessary reversible redox properties to serve as the cathode of a moderate temperature Na/S secondary battery.[2] While pursuing this investigation, we have carried out a study of the reactions of elemental S and sodium polysulfides, $Na_2S_n$, with a series of aliphatic amides, in order to assess their suitability for use in the battery cathode. It was of special interest to characterize the stability properties and hence reactivities of these solutions under conditions of prolonged heating at 130°C, the anticipated operating temperature of the Na/S battery. Specifically, we have investigated the reactions of the amides, $CH_3CONH_2$, $CH_3CONHCH_3$, $CH_3CON(CH_3)_2$ or $CH_3CON(C_2H_5)_2$, with sulfur or $Na_2S_n$ during a heating period of ~20 days at 130°C. The reaction products were analyzed spectroscopically.

## EXPERIMENTAL SECTION

All the experiments were carried out in the absence of air and moisture using standard techniques employed for the manipulation of air sensitive compounds.[3] Wherever appropriate, the handling and transfer of the reagents were also done in an argon-filled dry box (Vacuum Atmospheres Company) with a relative humidity maintained at ≤5 ppm.

*Reagents.* All the reagents were of highest purity materials available commercially. They were further purified and/or rigorously dried using the following procedures.

Acetamide (AC), $CH_3CONH_2$, obtained from Aldrich Chemical Co., was twice recrystallized from a mixture of MeOH and $(C_2H_5)_2O$[4]. The needle-like crystals were dried in vacuum ($10^{-3}$ torr) by continuously pumping for ~20 hr. at room temperature; m.p. 79–80°C.

High purity *N*-methylacetamide (NMAC), $CH_3CONHCH_3$, obtained from Aldrich Chemical Co., Milwaukee, Wisconsin was dissolved in anhydrous $Et_2O$ (100g NMAC/100 ml $Et_2O$) and the solution was dried by passing over freshly regenerated[3] Linde 4 Å molecular sieves. The ether from the sieved solution was finally removed by low temperature vacuum distillation.

*N,N*-dimethylacetamide (DMAC), $CH_3CON(CH_3)_2$, and *N,N*-diethylacetamide (DEAC), both obtained from Aldrich Chemical Co., were distilled *in vacuo* over anhydrous $Ba(OH)_2$, collecting only the middle portions of the distillate. The distilled solvents were further dried over molecular sieves.

Anhydrous $Na_2S$, $Na_2S_4$ and elemental S, all obtained from Ventron Corp., Danvers, Mass, were dried in vacuum at temperatures of 510, 215 and 110°C respectively, with continuous pumping for ~16 hr.

*Analytical Methods.* Infrared spectra were obtained on a Beckman Aculab-5 Spectrometer. Liquid (0.025 mm path length) and gas (10 cm path length) cells provided with KBr windows were used. UV-visible spectra were obtained on a Perkin-Elmer double-beam spectrometer, using 1 mm path length quartz cell. Mass spectra of the gases were obtained using a Hitachi-Perkin Elmer, RMU-6L mass spectrometer operating at an ionization voltage of 70 ev. The NMR spectra were recorded using a Varian A-60 spectrometer.

*Reaction of S with* $CH_3CON(CH_3)_2$ The reaction vessels consisted of 30 ml pyrex tubes equipped with break-seals, analogous to the ones described previously.[5] These were also equipped with ground-glass joints for attachment to the vacuum system.

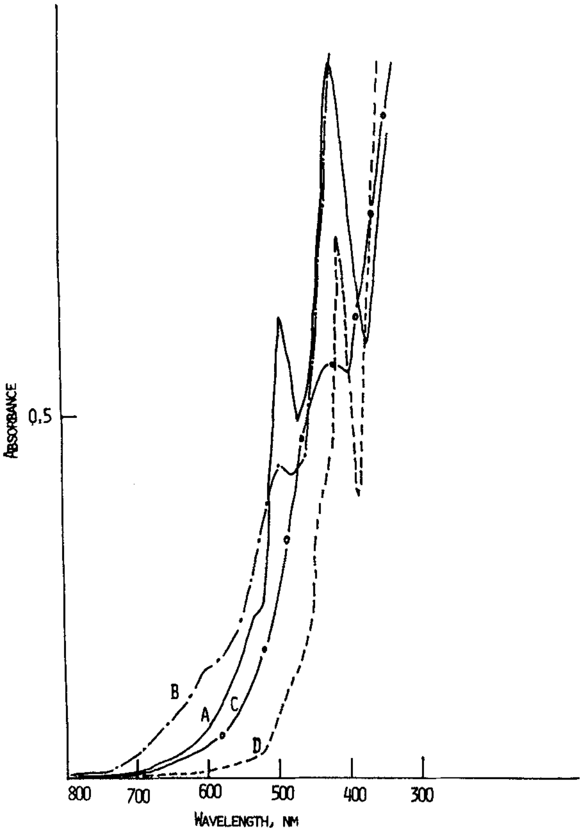

FIGURE 1 Absorption spectra of dialkylacetamide-sulfur reaction products after various stages of heating: (A) 2 ml DEAC + 0.1 g S after 16 hrs. at 130°C, (B) same solution as A after 40 days at 130°C, (C) 2 ml DMAC + 0.1 g S after 16 hrs. at 130°C, (D) same solution as C after 21 days at 130°C.

In a typical experiment, the tube was charged with 2 ml (24 mmoles) of DMAC and 0.1 g (3.1 mmoles) S. It was then evacuated to $10^{-3}$ torr and sealed off. The tube was then heated to 130°C for a period of 21 days. It was then attached to a vacuum system, opened at the break seal, and the gases were collected and measured with a Hg manometer. The amount of gas was measured to be 0.78 mmoles in this reaction.

The vapor phase infrared spectrum of the gas showed absorptions at 2910(m), 2110(m), 2060(v.s.), 1895(m), 800(m) and 528(m) characteristic of carbon oxysulfide, COS, and at 1537(v.s.) characteristic of $CS_2$. The mass spectrum exhibited the fragmentation pattern at M/e values of 76 ($CS_2^+$), 60($COS^+$), 44($CS^+$), 32($S^+$) and 28($CO^+$), indicative of a mixture of $CS_2$ and COS. The major component was COS (~75%). The solution was analyzed by means of UV-visible (Figure 1D), infrared and NMR spectral methods (see text for results).

Three other tubes were charged with essentially identical amounts of DMAC and S and heated for periods of 16 hr., 5 days and 12 days at 130°C. The sample heated for 16 hr. did not contain any gas. The solution turned orange-yellow. The UV-visible spectrum of the solution is shown in Figure 1 and shows an absorption maximum at 437 nm. The sample heated for 5 days produced 0.31 mmole of gases and the sample heated for 12 days produced 0.52 mmole of gases. In each case, the gases were a mixture of COS and $CS_2$ as evidenced by IR spectra. The UV-visible spectra of the latter two solutions were similar to that in Figure 1D.

*Reaction of* $Na_2S_4$ *with* $CH_3CON(CH_3)_2$ Three tubes, each containing 2 ml DMAC and 0.2 g $Na_2S_4$ (4.75 mmoles S), were heated for periods of 5, 12, and 21 days at 130°C. Gas pressure measurements after each heating period showed that no gases were produced. The UV-visible spectra of all the solutions were similar and identical to fresh solutions of $Na_2S_4$ in DMAC with a strong absorption at 618 nm.

*Reaction of* $Na_2S_8$ *with* $CH_3CON(CH_3)_2$ A solution of 0.30M $Na_2S_8$ in DMAC was initially prepared by stirring stoichiometric amounts of S and $Na_2S_4$.[6] The polysulfide was characterized by analysis of total S and sulfidic S and by absorption spectrum.[2] Two ml each of this solution was charged into three reaction tubes and heated for periods of 5, 12 and 21 days. Gas pressure measurements showed, 0.36, 0.47 and 1.02 mmole gases in samples heated for 5, 12 and 21 days respectively. The gases were a mixture of COS and $CS_2$ (infrared spectra). The UV-visible spectra of solutions heated for 5 and 21 days are shown in Figure 2.

*Reaction of* $Na_2S$ *with* $CH_3CONH_2$ Two gram AC and 0.33 g (4.2 mmoles) $Na_2S$ were heated in a sealed tube for 18 days at 130°C. After the heating period, the tube contained 1.01 mmoles gases, identified by vapor phase IR spectrum to be a mixture of $NH_3$ with a small amount of $H_2S$.

Reactions of S, $Na_2S$, $Na_2S_4$ and $Na_2S_8$ were also investigated in the above manner with $CH_3CONH_2$, $CH_3CONHCH_3$ and $CH_3CON(C_2H_5)_2$. In all samples of $CH_3CONHCH_3$ and $CH_3CON(C_2H_5)_2$ which produced gases (i.e., with S, $Na_2S_4$ and $Na_2S_8$), the major gas component was COS. $Na_2S$ did not show any reaction with $CH_3CON(CH_3)_2$ or $CH_3CON(C_2H_5)_2$ in 21 days at 130°C. From $CH_3CONH_2/Na_2S_n$, $n$ = 4 and 8 samples, the major gas component was $H_2S$. The latter gases contained some COS and $CS_2$ also.

## RESULTS AND DISCUSSION

*Reactions of Aliphatic Amides with* S *at* 130°C. Elemental S is insoluble in N,N-dimethylacetamide or in N,N-diethylacetamide at room temperature. However, when a mixture of S and either of these amides is heated to 130°C an orange-yellow solution is formed. No gas is formed from this reaction mixture in 16 hr. at this temperature. This visible spectra of these solutions (Figure 1), show broad absorptions with a peak at 437 nm for the DMAC-sulfur reaction product and two peaks at 500 nm and 425 nm for the DEAC-sulfur reaction product. It should be noted that the solvents alone do not show any absorptions above 300 nm after heating for the same period of time.

Further heating of these solutions produces gases, the amount of which increases with increasing

FIGURE 2 Absorption spectra of $Na_2S_n$ solutions in DMAC after various stages of heating. (A) $Na_2S_4$ (2.46 MS) solution after 21 days at 130°C, (B) $Na_2S_9$ (3.32 MS) solution after 5 days at 130°C, (C) $Na_2S_8$ (2.2 MS) solution after 21 days at 130°C. To record spectra, all the solutions were diluted to S concentrations of $\sim 0.05M$.

heating time. Some changes are also observed in the visible spectrum of the solution, although the gross features of the spectra are maintained. Vapor phase infrared and mass spectral data proved that the gases were a mixture of carbon oxysulfide (COS) and carbon disulfide ($CS_2$). About 75% of the mixture was carbon oxysulfide. It was found that the reaction of each of the four amides with S under the present reaction conditions produces a similar mixture of volatile products of COS and $CS_2$. The observation that COS and $CS_2$ are formed during continued heating of the initial reaction product of S suggests that these gases are secondary reaction products. It appears that elemental sulfur reacts initially with the amides to produce long chain sulfur-containing products which, on continued heating, decompose to give COS and $CS_2$, as shown in Eqs. 1 and 2:

$$CH_3CON(CH_3)_2 + nS \xrightarrow{130^\circ C} \underset{\textbf{I}}{CH_3COS_nN(CH_3)_2} \tag{1}$$

$$CH_3COS_nN(CH_3)_2 \xrightarrow{\Delta} \underset{\textbf{II}}{CH_3S_{n-1}N(CH_3)_2} + COS \tag{2}$$

The various physical properties of the solution products are also consistent with the formation of the polysulfides I and II. For example, the visible spectrum resembles that of alkali metal polysulfides in non-aqueous solvents.[6, 7] The infrared spectrum of the orange solution from DMAC and S exhibited an absorption at 1135 $cm^{-1}$ which is in the region of C–S stretching vibrations. The $^1H$ nmr spectrum of this solution exhibited a complex pattern. Nevertheless, the presence of new $—N(CH_3)_2$ resonances centered at 2.9 ppm and a new $—COCH_3$ or $—SCH_3$ resonance at 1.51 ppm, are also consistent with the structures **I** and **II**.

The other amides, $CH_3CONH_2$ and $CH_3CONHCH_3$, also react with elemental S in a similar manner. Semi-quantitative rate studies of gas formation indicate the trend of reactivity

$$CH_3CONH_2 > CH_3CONHCH_3 > CH_3CON(CH_3)_2 \approx CH_3CON(C_2H_5)_2.$$

*Reactions of Aliphatic Amides with Sodium Sulfides at* 130°C. A solution of $Na_2S_4$ in DMAC or DEAC (2–3MS) did not produce any gas even after heating for a period of 21 days at 130°C. The visible spectra of fresh and heated solutions were similar. The primary absorption in these solutions is the strong peak at 618 nm due to $S_3^-$.[8–11] The nmr and IR spectra also indicate no products in solution.

Longer-chain polysulfides ($S_n^{-2}$, $n > 4$), on the other hand, were found to react with the amides. The gaseous products, again, contained mostly COS with small amounts of $CS_2$. A solution of $Na_2S_8$ in DMAC, after heating for 21 days at 130°C showed major changes in the visible spectrum, as depicted in Figure 2. The absorption peak at 520 nm, characteristic of long chain polysulfide species[2] found in freshly prepared solutions, has considerably decreased in intensity. After 21 days of heating, the spectrum at wavelengths below 500 nm resembles that of DMAC-sulfur products. The spectrum above 500 nm is similar to that of the DMAC-$Na_2S_4$ solutions. It appears that when a solution of $S_n^{-2}$, $n > 4$, in DMAC, is heated.

the neutral S present in equilibrium[7,11,12] (Eq. 3), reacts with the amide to form I

$$S_n^{-2} \rightleftharpoons S_{n-x}^{-2} + xS^\circ \qquad (3)$$

This reaction shifts equilibrium 3 to the right until all the $S_n^{-2}$ is converted to $S_4^{-2}$. Further dissociation of $S_4^{-2}$ is not observed probably because of a unique stabilization of $S_4^{-2}$ in this solvent.

Solutions of $S_n^{-2}$, $n > 4$, in acetamide or N-methyl acetamide also behave in a similar manner to the N-dialkyl substituted amides, except that these solutions are less stable. Some $H_2S$ is also observed as a gas product.

The reactions of acetamide with $Na_2S_4$ or $Na_2S$ differ markedly from those of the dialkyl substituted amides with these sulfides. Thus, unlike $CH_3CONR_2$, acetamide does react with $Na_2S_4$ during prolonged heating at 130°C. The volatile products are mostly COS and some $H_2S$. It appears that the unique stability accorded to $S_4^{-2}$ in DMAC or DEAC is lessened or eliminated by the different solution properties of acetamide.

Sodium monosulfide, $Na_2S$, is only sparingly soluble either in DMAC or DEAC and no reaction is observed in saturated solutions containing excess undissolved $Na_2S$. The monosulfide is soluble to the extent of ~1M in AC at 130°C. This solution is quite unstable in prolonged heating and produces $NH_3$ as the major gas product. It is interesting to note that $NH_3$ is produced in the reaction of acetamide only with $Na_2S$ and not with $Na_2S_4$ or $Na_2S_8$. The latter two produces $H_2S$ with acetamide. These differences may be explained on the basis of dissociation equilibria involving acetamide and $S_n^{-2}$, and the relative rates of reaction of the equilibrium species. For example, equilibria such as those shown in Eqs. 4 and 5 are possible:

$$CH_3CONH_2 + S_n^{-2} \rightleftharpoons CH_3CONH^- + HS_n^- \qquad (4)$$

$$CH_3CONH_2 + HS_n^- \rightleftharpoons CH_3CONH^- + H_2S_n \qquad (5)$$

The hydrosulfanes, $HS_n^-$ and $H_2S_n$ are thermally unstable compounds[12,13] and may decompose on heating to produce $H_2S$, as shown in Eqs. 6 and 7

$$2HS_n^- \longrightarrow H_2S + S_{2n-1}^{-2} \qquad (6)$$

$$H_2S_n \longrightarrow H_2S + (n-1)S \qquad (7)$$

However, $HS^-$, the primary species that would be found in the reaction of an excess of acetamide with $Na_2S$, is relatively more stable and could react further with acetamide to produce $NH_3$ and thioacetate, as depicted in Eq. 8.

$$CH_3CONH_2 + HS^- \longrightarrow CH_3COS^- + NH_3 \qquad (8)$$

Reaction 9 is analogous to the reaction of $CH_3COOC_6H_5$ with NaSH to form $CH_3COSNa$, as shown in Eq. 9.[14]

$$CH_3COOC_6H_5 + NaSH \longrightarrow CH_3COSNa + C_6H_5OH \qquad (9)$$

In conclusion, we find that the reactions in solutions of alkali metal polysulfides in aliphatic amides are related to dissociation equilibria involving elemental sulfur and polysulfides species. The material that reacts with amides in these solutions is elemental S. The latter reacts with amides in a two-step process giving initially polysulfide I, which decomposes on further heating to form COS as the major volatile product. The rather high thermal stability of the tetrasulfide, $S_4^{-2}$, in the N-dialkyl substituted amides appears to be due to a unique solvent—polysulfide coordination. Such a coordination process seems to be minimized or absent in solutions of $S_n^{-2}$ in unsubstituted amides.

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