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Electrochemical Studies on Sulfur and Sulfides in $AlCl_3$–NaCl Melts

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Abstract: Liquid sulfur has been reduced coulometrically in $AlCl_3$–NaCl melts at 175 °C. The reduction is a two-electron process yielding S^{2-}. The current efficiency for the process is 100%. Copper and silver electrodes have been used for coulometric titrations of the sulfide content of the melt. By following the potential of the metal/metal ion during these titrations, the solubility product of cuprous and silver sulfide in the basic melt at 175 °C has been determined. The solubility of metal sulfides was found to increase markedly as the melt was made more acid, i.e., as $AlCl_3$ was added. Nernst plots for the sulfur–sulfide redox couple have a slope corresponding to a four-electron reaction, which may be represented as $S_2 + 4e^- = 2S^{2-}$. From the variation of the S_2/S^{2-} redox potential with melt acidity, it is deduced that the acid–base equilibrium involving sulfide and the solvent may be $AlCl_4^- + S^{2-} = AlSCl + 3Cl^-$. The oxidation of sulfur yields cations of oxidation state +1 or higher.

Electrochemical studies of sulfur and sulfides in molten salts have received considerable attention in recent years.[1-9,14,16-19]

Delarue[1,2] investigated redox reactions involving sulfur and sulfides in lithium chloride–potassium chloride melts. He quantitatively studied the solubility of a series of sulfides in the eutectic melt. The sulfides of manganese(II), thallium(I), and of the alkaline and earth alkaline metals were soluble, whereas sulfides of Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Ag^+, Sn^{2+}, Sb^{3+}, Bi^{3+}, Pd^{2+}, Pt^{2+}, Cu^+, Fe^{2+}, Ce^{3+}, and Pb^{2+} were insoluble. Sulfides of copper(II), iron(III), gold(I) and mercury(II) reacted in the melt; the metal ions were reduced and sulfide oxidized to sulfur.

Bodewig and Plambeck[3,4] studied sulfur–sulfide solutions in LiCl–KCl eutectic by potentiometric, voltammetric, chronopotentiometric, and spectrophotometric techniques. The sulfur–sulfide couple showed Nernstian behavior with a value of 1.86 for the number of electrons taking part in the reaction. Their Nernst plots were made by coulometrically reducing sulfur from a saturated solution, thus maintaining the sulfur activity constant. Coulometric titrations of anodically generated Fe^{2+}, Ni^{2+}, Co^{2+}, and Ag^+ by reduction of a sulfur pool electrode produced potentiometric titration curves with breaks of 160–400 mV. These breaks were reported to occur a considerable, but not a reproducible, distance before the theoretical equivalence point. Solutions containing both sulfur and sulfide had a blue color. Since it disappeared when either sulfur or sulfide was absent, they postulated that the color was due to a polysulfide ion formed by sulfur and sulfide; i.e., $S^{2-} + xS \rightleftarrows S_{x+1}{}^{2-}$.

Gruen et al.[5] carried out spectrophotometric measurements on the sulfur–sulfide system in LiCl–KCl. The spectrum of dissolved sulfur had its maximum at 36 000 cm^{-1}, close to the absorption peak of gaseous S_2 molecules. On the basis of the absorption spectra for sulfur–sulfide solutions, they propose the two equilibria between sulfur and sulfide:

$$2S^{2-} + 3S_2 = 4S_2^-$$

$$2S^{2-} + 5S_2 = 4S_3^-$$

The S_3^- ion is attributed to the ultramarine blue color and the S_2^- ion to ultramarine green.

Giggenbach[18] concluded from his spectrophotometric measurements in LiCl–KCl that S_2^- is responsible for the blue color. The blue melt loses its color on cooling to temperatures below 400 °C, which is ascribed to the dimerization of S_2^- ions to form $S_4{}^{2-}$ ions.

Bernard et al.[19] carried out chronopotentiometric and spectrophotometric measurements on sulfide in LiCl–KCl eutectic. Calcium sulfide was dissolved in the melt and the sulfide was said to be oxidized in three steps. The ultimate products of oxidation and reduction were said to be S^+ and S^{2-}, respectively. The three sulfide species S^{2-}, $S_x{}^{2-}$, and $S_y{}^-$ were attributed to absorption bands at 320, 390, and 590 nm. The most probable values for y were 2 or 3 and for x, 5.

Cleaver et al.[17] found that Na_2S was practically insoluble in the LiCl/KCl eutectic at 420 °C and no cyclic voltammetric waves could be observed. Addition of $Na_2S_{2.2}$ gave lime green solutions which lost sulfur gradually. Cyclic voltammograms using a gold electrode showed two redox couples. The waves at the most negative potentials were attributed to a one-electron process: $S_2{}^{2-} \rightarrow S_2^- + e$. The other waves were deposition and stripping of sulfur. Sulfur was found to be the final oxidation product.

Liu et al.[6] determined the solubility product for NiS and Li_2S in the LiCl/KCl eutectic. They developed a NiS/Ni electrode which gave very large potential breaks at the end point when sulfide was titrated with coulometrically generated Ni(II).

King and Welch[16] studied electrolysis of metal sulfide in chloride melts. They showed that, for production of lead, dissolution of sulfur was the major contributor to the lowering of cathodic current efficiency. When the limiting current density for sulfur evolution was reached, the anode potential increased rapidly to that of the next process, evolution of sulfur monochloride,

$$2S + 2Cl^- = S_2Cl_2\uparrow + 2e \qquad (1)$$

Two papers deal with the behavior of sulfur in a low-tem-

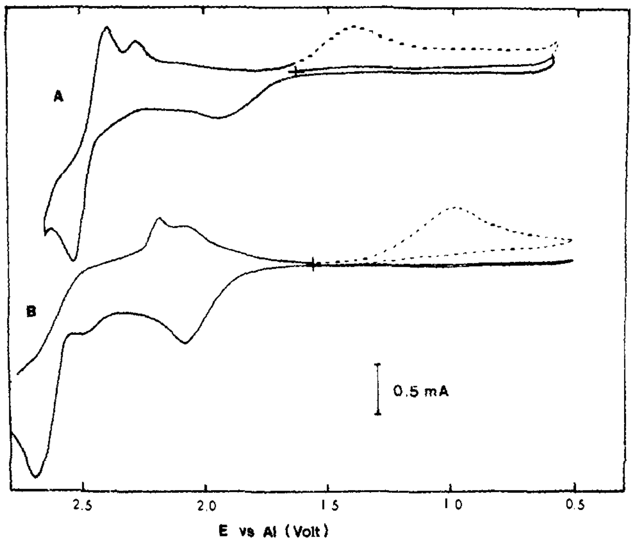

Figure 1. All potentials vs. Al in a NaCl saturated melt in Figures 1-13. Cyclic voltammograms of sulfide in acid melt. (A) Vitreous carbon electrode (newly made) 0.07 cm^2; Melt; 53.5 mol % $AlCl_3$-46.5 mol % NaCl, 20.3 mM Na_2S (B) Vitreous carbon; 51 mol % $AlCl_3$-49% NaCl; 19 mM Na_2S.

perature melt containing $AlCl_3$. Marassi et al.[8] briefly examined the cyclic voltammetry of elemental sulfur in an $AlCl_3$-NaCl melt. Redey et al.[9] investigated an aluminum sulfur battery in an $AlCl_3$-NaCl-KCl melt.

In this paper, we report on the electrochemical behavior of sulfur in acid and basic $AlCl_3$-NaCl melts at 175 °C. The acidity of the melt has been adjusted and measured as described previously.[12]

The concentrations of the basic and acid species in the melt are interrelated by the following equilibria:

$$2AlCl_3(l) = Al_2Cl_6(l) \qquad k_0 = 2.86 \times 10^7 \qquad (2)$$

$$AlCl_4^- + AlCl_3 = Al_2Cl_7^- \qquad k_2 = 2.4 \times 10^4 \qquad (3)$$

$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \qquad K_m = 1.06 \times 10^{-7} \qquad (4)$$

k_0, k_2, and K_m are mole fraction equilibrium constants at 175 °C.[10] Equation 4 is the dominant acid-base equilibrium. The sodium tetrachloroaluminate melt can be considered as a Lewis acid-base system by equilibrium 4:

$$K_m = [Al_2Cl_7^-][Cl^-]/[AlCl_4^-]^2 \qquad (5)$$

The heptachloroaluminate ion and the chloride ion are the dominant Lewis acid and base species, respectively.

Experimental Section

Electrochemical Instrumentation. A multipurpose instrument similar to one described previously was used for the cyclic voltammetric studies.[11] Pulse voltammetric measurements were performed with a PAR Model 174 Polarographic Analyzer. The instrument had been externally modified to permit parametric studies as described below.[15] A Wenking potentiostat was used for the constant potential coulometric experiments. A Sargent Coulometric Current Source Model IV was used for melt acidity adjustments and for coulometric titrations of sulfide in the melt.

Melt Preparation and Purification. Fluka (A.G. anhydrous iron free) aluminum chloride and Fisher (certified A.C.S.) sodium chloride were used to prepare the melts. Preelectrolysis was carried out between two aluminum electrodes in a cell similar to that previously described.[12] The purification and all electrochemical measurements were made under a purified argon atmosphere in a Vacuum Atmospheres Co. drybox operated as previously described.[13]

Electrodes. For the pulse voltammetric and cyclic voltammetric studies, three planar working electrodes sealed into Pyrex were used: (i) a ⅛ in. diameter tungsten rod (Alfa Inorganics, M3N8), (ii) a 3 mm diameter vitreous carbon rod electrode (Atomergic Chemetals, V25), and (iii) a ⅛ in. diameter molybdenum rod (Alfa Inorganics, m 3N7). For tungsten and molybdenum a bead of uranium glass was used to obtain a good seal. The electrodes were ground flat on an emery wheel and polished to a mirrorlike finish using Type B alumina powder (Fisher). During the exhaustive constant potential coulometric experiments, a tungsten crucible (Research Organic/Inorganic Chemical Corp., W120) or a vitreous carbon crucible (Atomergic Chemetals Co., V25-16) were used as cells and working electrodes. During these experiments, a Pyrex glass covered stirring bar was used to facilitate mass transfer. The reference electrode was a coiled aluminum wire in the sodium tetrachloroaluminate melt saturated with sodium chloride at 175 °C. This electrode was isolated from the bulk of the melt with a fine glass frit. The auxiliary electrode was a coiled aluminum wire, which was isolated from the working electrode compartment with a glass frit.

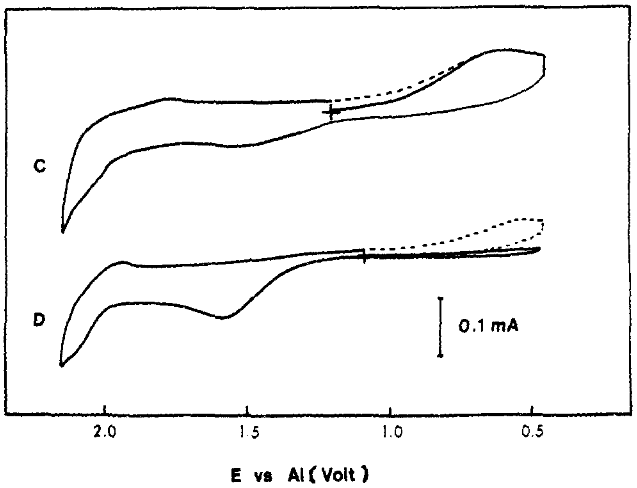

Figure 2. Cyclic voltammograms of sulfur and sulfide in basic melt: (C) 4.45 mM sulfur (considered monomeric), vitreous carbon electrode (0.07 cm^2); (D) 4.45 mM Na_2S, vitreous carbon electrode (0.07 cm^2).

Results and Discussion

The cyclic voltammetric behavior of sulfur and sulfide in basic and acidic melts at 175 °C is shown in Figures 1 and 2. Addition of sulfur to the melt yields a clear, light-yellow homogeneous solution; solubility equilibrium is slow but was achieved in all cases (see Figure 4 below). The cathodic wave at ~1.5 V (A) and 1.0 V (B) corresponds to the reduction of S formed at the electrode surface during the initial anodic scan. The oxidation waves at ~2.2 V correspond to the oxidation of S^{2-} to S (see below). The potentials for the corresponding waves in Figure 2, the basic melt, are shifted to less positive potentials. All sweeps were started from the rest potential. For the sulfur-sulfide couple, both the anodic and cathodic peaks are drawn out and irreversible. The peak separation depends on the electrode material used, being up to 900-1000 mV for vitreous carbon. The electrode surfaces are easily poisoned by products of electrode reactions. Figure 1A shows the behavior of sulfide on a new vitreous carbon electrode. The vitreous carbon electrode used for curve B probably was partly covered by a surface layer. The temperature used, 175 °C, corresponds to the peak of the curve for chain length of polymer sulfur vs. temperature.[20] If the sulfur produced on the anodic sweep polymerizes on the surface instead of diffusing out into the solution, an insulating sulfur layer would be formed.

Marassi et al.[8] observed a second reduction peak 4-500 mV cathodic to the sulfur reduction peak on their cyclic voltammograms of sulfur on a platinum electrode. This peak was not found in our measurements on molybdenum, carbon, and tungsten electrodes.

Figure 3 shows pulse voltammograms for the first wave of sodium sulfide oxidation in an acid melt. By using a modified

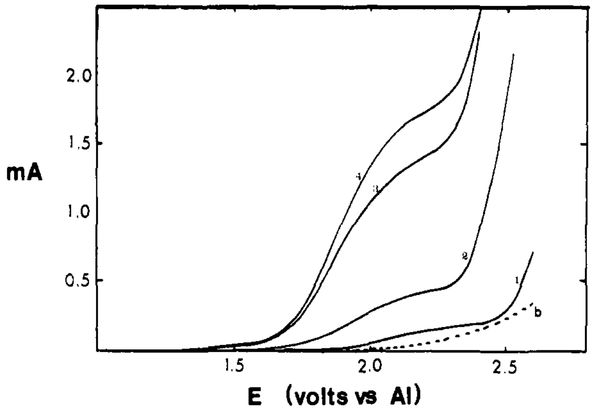

Figure 3. Pulse voltammograms on molybdenum (0.07 cm^2); pulse width 48.5 ms; scan rate 2 mV/s; acid melt (53.5 mol % $AlCl_3$-46.5 mol % NaCl) 175 °C; current is anodic: (1) 2.65 mM Na_2S, (2) 6.82 mM Na_2S, (3) 20.3 mM Na_2S, (4) 28.03 mM Na_2S, (b) background.

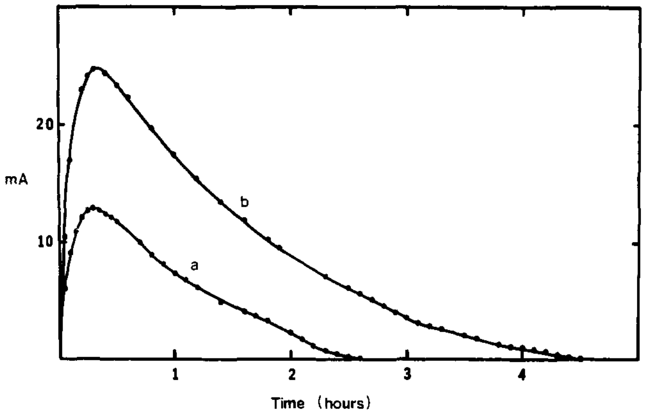

Figure 4. Reduction of sulfur in a tungsten crucible at 175 °C; melt 34 ml $AlCl_3$-NaCl (54-46 mol %): (a) 9 mg of sulfur added; (b) 25.3 mg of sulfur added. (Total added sulfur, 2.139 mequiv for a two-electron reaction. Total coulombs passed = 2.145 mequiv.) Background current was determined over 11 h prior to sulfur addition and was 0.555 μequiv/h. The reduction was done at 400 mV vs. Al (in NaCl saturated melt).

PAR 174[15] the pulse width could be varied. Plots of the limiting current for the oxidation of sulfide to sulfur vs. the inverse square root of the pulse width were linear, indicating a diffusion controlled process. Plots of the current vs. sulfide concentration also were linear. The pulse voltammograms had poorly defined limiting currents for sulfide concentrations above 10 mM (Figure 3) and for pulse widths below 80-90 ms. The diffusion plateau was better defined in acid than in the basic melt. A plot of log $(i_d - i)/i$ vs. potential obtained from a pulse voltammogram of 3.82 mM sulfide in the basic melt was linear with a slope of 146 mV/decade. For a reversible one- or two-electron reaction at 175 °C, the theoretical slopes are 89 and 44.5 mV, respectively. On the time scale of the pulse voltammograms, the oxidation of sulfide to sulfur shows irreversible behavior. Similar treatment of a voltammogram for the reduction of sulfur to sulfide in the basic melt yielded a linear plot of log $(i_d - i)/i$ and a slope of 95 mV/decade, which for an irreversible reaction corresponds to an αn of unity.

To establish the stoichiometry involved, constant potential exhaustive coulometry was performed for the reduction and oxidation of sulfur and sulfide. Typical current-time behavior for the sulfur reduction in a tungsten crucible is shown in Figure 4. Weighed amounts of sublimed sulfur were added to the crucible whose potential previously had been adjusted to a value 100 mV more negative than the sulfur reduction peak. In this way, loss of sulfur due to evaporation during the coulometric experiment was minimized. Reduction of 10-20 mg of sulfur in a 50-60 g melt could be completed in 3-4 h. Both in acid and basic melt, the number of electrons per mole of sulfur (considered to be monomeric) was found to be 2.00 ± 0.01 from the coulombs passed. A coulometric experiment was carried out by holding the potential at the desired value for several hours before sulfur was added. The average background current found was then calculated as coulombs/hour and subtracted from the total number of coulombs passed. Table I summarizes the data from several coulometric experiments. The amount of sulfide produced was measured in two ways. In the first instance, the melt was dissolved in 1 N sodium hydroxide and titrated with sodium plumbate solution using a sulfide sensitive indicator electrode.[21] The amount of sulfide was also determined in situ by making the melt basic and carrying out a potentiometric titration with coulometrically generated Cu(I). The generation of Cu(I) in the melt has previously been studied and found to take place at 100% current efficiency.[12] A typical titration curve is shown in Figure 5. The solubility product for Cu_2S in the basic melt was calculated from the titration curve and by taking into account that Cu(I) is complexed by chloride ions in the basic melt.[12] The solubility product was found to be $6.8 \times 10^{-15} \pm 0.4 \times 10^{-15}$ M^3 at 175 °C. The calculation made use of the Nernst expression for the copper electrode potential, the solubility product expression, mass balance equations for copper and sulfide, and the complex equilibrium for copper(I) and chloride,

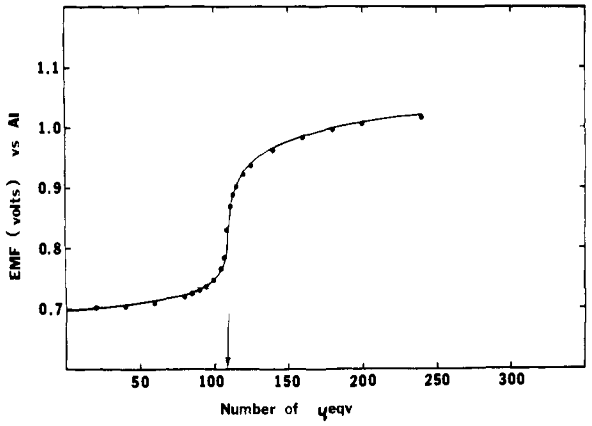

Figure 5. Potentiometric titration of 0.010 71 M Na_2S in $NaAlCl_4$ with coulometrically generated Cu^+ at 175 °C. Amount of melt = 8.665 g. Theoretical titration curve calculated from the experimental points. Arrow indicates theoretical equivalence point based on added sulfide.

Table I. Coulometric Reduction of Sulfur in $AlCl_3$-NaCl

Melt	Theor sulfide content, μequiv	Potentiometric Cu^+ titration, μequiv	Potentiometric aqueous titration, μequiv
Acid (54:46, $AlCl_3$:NaCl)	194	197 ± 3	
Basic (NaCl saturated)	198	194 ± 3	
	200	190	190

$$Cu^+ + 2Cl^- \rightleftharpoons CuCl_2^-$$

$$K = 6.5 \times 10^4[\text{mole fraction}]^{-2} \quad (6)$$

The expressions for pairs of points on both sides of the titration end point were compared and from that the solubility product and standard potential for the Cu^+/Cu couple were calculated. The potential of the point prior to the end point is determined by K_{sp} and $E°_{Cu^+/Cu}$, while the potential of the end point is

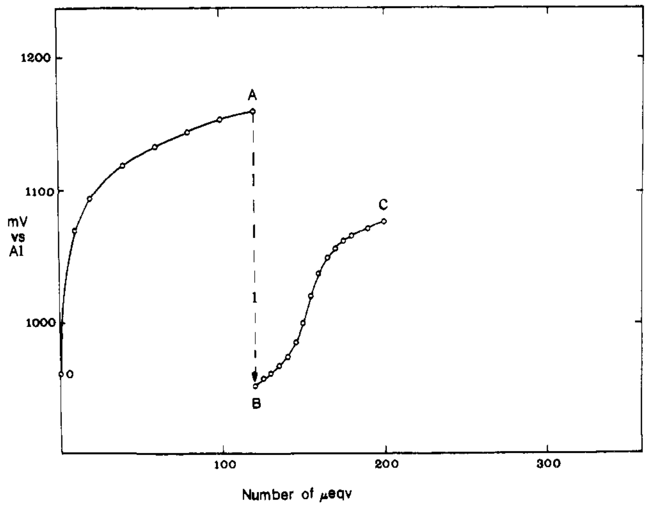

Figure 6. Potentiometric titration of sulfide formed from coulometric reduction of S, 31.6 mM, with coulometrically generated Cu^+: (0-A) acid melt (54-46 mol % $AlCl_3$-NaCl); (B-C) basic melt (NaCl saturated). 5.175 g melt with theoretical end point 194 μequiv.

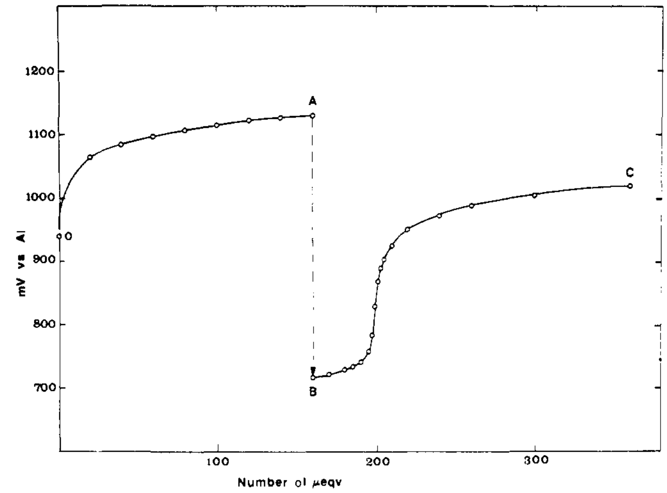

Figure 7. Potentiometric titration of sulfide formed from constant potential coulometric reduction of S, 31.6 mM, with coulometrically generated Ag^+: (0-A) acid melt (54-46 mol % $AlCl_3$-NaCl); (B-C) basic melt. 4.561 g melt with theoretical end point 170 μequiv.

determined by $E°_{Cu^+/Cu}$. The average value of the standard potential was found to be 1240 ± 5 mV vs. Al reference in a NaCl saturated melt. Since Al in a NaCl saturated melt is 170-175 mV more negative than Al in a 50:50 melt, 1240 mV is in good agreement with 1073 mV reoorted earlier.[12] The copper sulfide precipitate x-ray diffraction powder pattern showed that stoichiometric Cu_2S was formed.

When the coulometric reduction of sulfur had been carried out in an acid melt for the first time, an attempt was made to titrate the sulfide with coulometrically generated copper(I). The copper wire electrode was stirred continuously during anodization. The curve obtained is shown in Figure 6 (0-A). It was observed that no precipitation of Cu_2S occurred. At point A sodium chloride was added to make the melt basic. Copper sulfide precipitated and the electrode potential moved to point B. A Nernst plot for Cu^+ for the curve from 0 to A was made and was linear with the correct $2.3RT/1F$ slope. Extrapolation to log $(Cu^+) = 0$ gives $E°_{Cu^+/Cu}$ = 1240-1245 mV in agreement with earlier results. These results show that the sulfide activity is markedly lower in acid melts, presumably as a result of the sulfide species being complexed in the acid melt.

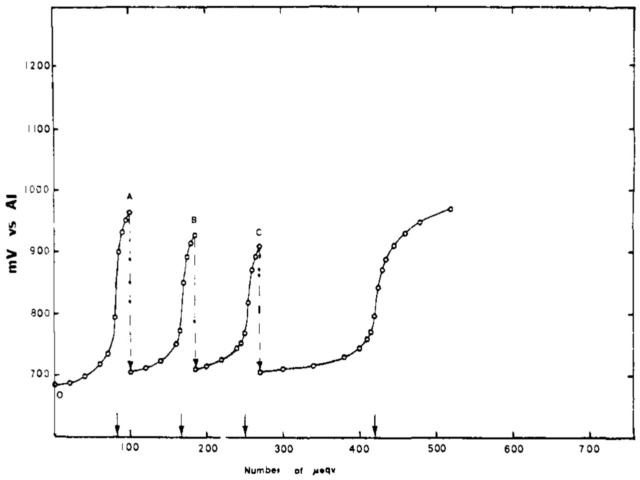

Figure 8. Successive titrations of 21.5 mM sulfide meet with coulometrically generated Cu^+; basic melt 175 °C; (0) 6.661 g of melt, theoretical end point 84 μequiv; (A) 6.695 g of melt added, theoretical end point 168.4 μequiv; (B) 6.685 g of melt added, theoretical end point 252.7 μequiv; (C) 13.385 g of melt added, theoretical end point 421.5 μequiv. Arrows show theoretical end points.

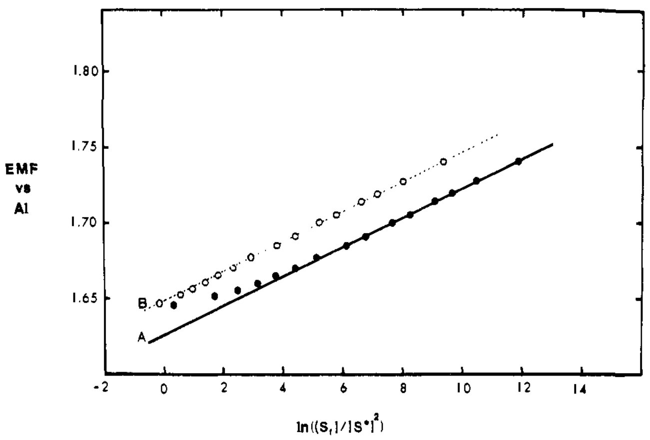

Figure 9. Nernst plot for sulfur-sulfide in $AlCl_3$-NaCl (53.5-46.5 mol %). Curve A: reduction of 1.172 mequiv of sulfur to sulfide in the tungsten crucible. Curve B: same as A, but the equilibrium $S_8 = 4S_2$ with $K = 2 \times 10^{-10}$ (M^3) was included when $[S_2]$ was calculated.

The potentiometric titration was also carried out by anodization of a silver wire to generate Ag(I). In an acid melt behavior similar to that of copper was observed. On curve 0-A in Figure 7 no precipitate formed. Upon addition of sodium chloride at point A, black Ag_2S precipitated and the potential moved to point B. The titration curve then continued as shown. From the titration curve (B to C) the solubility product for silver sulfide in the basic melt was calculated as 10^{-9} M^3.

Successive additions of sulfide could be titrated using the copper electrode. The end points were all sharp and accurate (Figure 8). The silver wire, however, became coated with a black silver-silver sulfide layer, and after the first titration curve, no sharp potential change occurred at the end point.

The sulfur-sulfide reaction was studied by measuring the electrode potential as a function of the ratio of sulfur and sulfide concentrations. Nernst plots obtained in acid (Figure 9) and basic melts (Figure 10) are shown. The solid straight lines drawn have a slope of $RT/4F$. These experiments were carried out in the tungsten crucible. A weighed amount of sublimed sulfur was added to a known amount of melt with the counter and reference electrodes isolated from the main body of the melt by glass frits. The sulfur was quantitatively reduced to sulfide by using the crucible as the working electrode as described previously. The sulfide of known concentration was

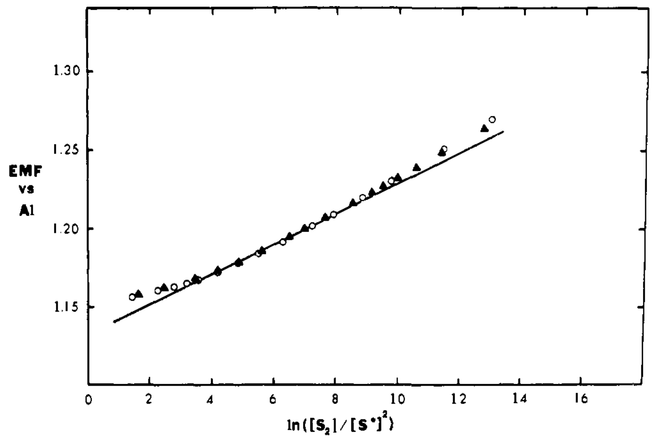

Figure 10. Nernst plot for sulfur-sulfide in basic melt; 175 °C. (▲) Going in cathodic direction, reduction of sulfur (6.41 mM as monomeric sulfur). (●) Going in anodic direction, oxidation of sulfide (7.09 mM).

Table II. Nernst Experiments

Sulfur added: 9.5 mg to basic melt	Loss
Coulombs on first reduction corresponds to: 9.5 mg of sulfur	0
Coulombs on succeeding oxidation corresponds to: 9.33 mg	0.17 mg = 1.8%
Coulombs on succeeding reduction corresponds to: 8.45 mg	1.05 mg = 11%
n, Nernst plot	4 ± 0.05
n, exhaustive coulometry	2 ± 0.01
$E^0_{S_2/S}$ = in basic melt (NaCl saturated)[a]	1.132 ± 0.010

[a] Potential in volts vs. Al in NaCl saturated melt determined by extrapolation of the line in Figure 10 to ln $([S_2]/[S^{2-}]^2) = 0$.

then oxidized stepwise back to sulfur. After each step the sulfur-sulfide rest potential was measured with a vitreous carbon or tungsten indicator electrode. The number of coulombs passed was measured with an Integrator-Totalizer from Acromag Incorporated; a high impedance voltmeter was employed for the potential measurements. In the basic melt, when all sulfide had been oxidized to sulfur, the same stepwise procedure was followed for the reduction back to sulfide (Figure 10). When plotting the experimental points, different sulfur and sulfide species were fitted to the expression for the electrode reaction, but only when S_2 and S^{2-} were used was a straight line obtained. The Nernst plots shown were calculated at fixed pCl^- using the equations:

$$S_2 + 4e = 2S^{2-} \tag{7}$$

$$[S_{total}] = 2[S_2] + [S^{2-}] \tag{8}$$

The total amount of sulfur and sulfide was calculated from the coulombs passed during the reduction or oxidation. The initial reduction of added sulfur was quantitative, as was the oxidation of the sulfide back to sulfur. The second reduction, however, gave 5–15% less sulfide due to evaporation of sulfur. A summary of the Nernst plot data is given in Table II. For low sulfur concentrations the experimental points are above the lines with slope $RT/4F$. A possible explanation for this might be that S_2 is in equilibrium with sulfur molecules containing more than two atoms. By postulating the reaction:

$$S_8 = 4S_2 \quad K_1 = [S_2]^4/[S_8] \tag{9}$$

line B in Figure 9 is obtained for $K_1 = 2 \times 10^{-10}$ M^3.

The potential for the sulfur-sulfide couple depends on the acidity of the melt. Figure 11 shows the sulfur-sulfide electrode potential in the chloroaluminate melt at 175 °C as a function of pCl^- in the melt. The experiment was carried out in the tungsten crucible which initially contained 60.55 g of sodium chloride saturated melt. Sulfur (5 mg) was added and quantitatively reduced to sulfide. Two percent of the sulfide was then reoxidized to sulfur, giving a solution 4.4×10^{-5} M S_2 and 4.3×10^{-3} M S^{2-}. Weighed amounts of acid melt (58 mol % $AlCl_3$-42 mol % NaCl) were then added to this solution. For each addition, the total composition of the melt and the pCl^- was calculated.[10]

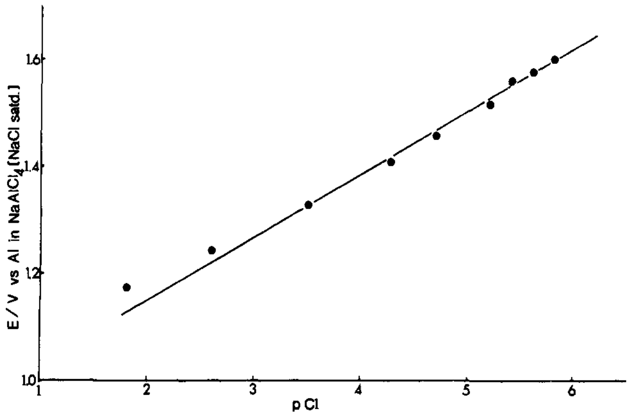

Figure 11. Sulfur-sulfide electrode potential in the chloroaluminate melt at 175 °C as a function of pCl^-. Line has $3RT/2F$ slope. Sulfur concentration 4.4×10^{-5} M S_2; sulfide concentration 4.3×10^{-3} M Na_2S.

From the Nernst plot for the sulfur-sulfide reaction (Figures 9 and 10) showing a four-electron reaction and the pCl^- plot showing a slope close to $3RT/2F$ (Figure 11), the following electrode reaction is postulated:

$$S_2 + 2AlCl_4^- + 4e = 2AlSCl + 6Cl^- \tag{10}$$

The Nernst expression for the electrode potential is:

$$E = E_{10}^0 - \frac{RT}{4F} \ln \frac{[AlSCl]^2 \cdot [Cl^-]^6}{[S_2][AlCl_4^-]^2} \tag{11}$$

where

$$E_{10}^0 = E_7^0 - \frac{RT}{4F} \ln K_2^2 \tag{11'}$$

If it is assumed that except for a small dilution effect the concentrations of S_2, AlSCl, and $AlCl_4^-$ are constant, which is reasonable for $pCl^- > 3$ (see below), eq 11 can be simplified to:

$$E = E_{10}^{0\prime} - \frac{RT}{4F} \ln [Cl^-]^6 = E_{10}^{0\prime} - \frac{3RT}{2F} \ln [Cl^-] \tag{12}$$

Formation of AlSCl from aluminum chloride and sodium sulfide in the dry state is reported to occur at 330 °C with a 20% yield.[22]

Because of the observed change in solubility of copper sulfide and silver sulfide with acidity, the free sulfide ion concentration must be a function of the melt acidity. If the following equilibrium is assumed:

$$\begin{gathered} AlSCl + 3Cl^- = S^{2-} + AlCl_4^- \\ K_2 = [S^{2-}][AlCl_4^-]/[AlSCl][Cl^-]^3 \end{gathered} \tag{13}$$

then eq 11 can be written:

$$E = E_{10}^0 - \frac{RT}{4F} \times \ln \frac{[S^{2-}{}_{total}]^2[Cl^-]^6}{[S_2][(1 + K_2[Cl^-]^3)/[AlCl_4^-]]^2 \cdot [AlCl_4^-]^2} \tag{14}$$

Here $[S^{2-}{}_{total}] = [AlSCl] + [S^{2-}]$. By including constant

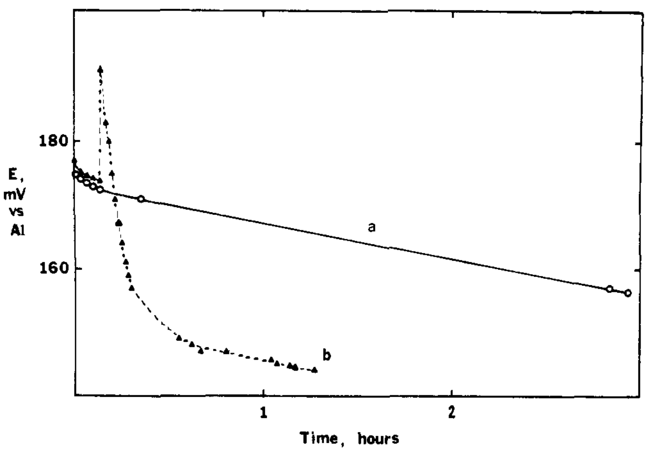

Figure 12. Change of potential of Al electrode as Na_2S added to $NaAlCl_4$ melt. (a) Change in potential of Al electrode with time; open cell. Potential decrease is probably a result of $AlCl_3$ volatilization. (b) Al electrode potential after addition of 7 mg of Na_2S to 59 g of $NaAlCl_4$ at 175 °C.

terms in E_{10}^0 eq 14 at fixed total concentration of S_2^{2-} and S^{2-} is transformed to

$$E = E_{10}^{0\prime\prime} - \frac{RT}{4F} \ln \frac{[Cl^-]^6}{\{[AlCl_4^-] + K_2[Cl^-]^3\}^2} \qquad (15)$$

When $K_2[Cl^-]^3 \ll [AlCl_4^-]$, the slope of Figure 11 will be $3RT/2F$, and when $[AlCl_4^-] \ll K_2[Cl^-]^3$, the slope will approach zero. In Figure 11 the two points for the basic melt composition log, $[Cl^-] = -2$ and -2.5, are above the line with slope $3RT/2F$, which is as expected if the assumed equilibria are correct.

K_2 could be calculated from the deviation from the straight line, but due to the uncertainty in the calculated Cl^- concentrations, a reliable value cannot be obtained by this method. However, from Figure 11 K_2 can be estimated to be of the order of 10^7–10^9 [mole fraction]$^{-2}$.

From the copper deposition peak of a cyclic voltammogram of a saturated solution of cuprous sulfide in an acid melt, the copper concentration in solution can be calculated to be in the order of 0.1 M. In order to fit the solubility product of $10^{-14.17}$, the concentration of free sulfide cannot be higher than 10^{-12}, which should give an $[AlSCl]/[S^{2-}]$ ratio of 10^{11}. If this is introduced into eq 13 together with $[Cl^-] = 10^{-6.7}$ and $[AlCl_4^-] = 10^{-0.5}$, K_2 is calculated to be $10^{8.6}$ [mole fraction]$^{-2}$, roughly the same order of magnitude as estimated from Figure 11. The effect of adding sodium sulfide to a 50:50 $AlCl_3$-$NaCl$ melt is shown in Figure 12. This is the most unbuffered composition of the melt, and if equilibrium 13 is shifted to the left at this pCl^-, a marked change of the potential of an aluminum electrode can be expected. The aluminum electrode potential in the melt is given by

$$E = E_0 - \frac{RT}{3F} \ln \frac{[Cl^-]^3}{[AlCl_4^-]} \qquad (16)$$

Curve A in Figure 12 shows the change of the aluminum electrode potential with time most probably due to evaporation of $AlCl_3$ and diffusion of Cl^- from the reference electrode compartment. Curve B shows the observed potential when 7 mg of Na_2S (CERAC/PURE, Inc., typically 99.9%) had been added to 59 g of $NaAlCl_4$. From the difference in potential between a and b after all the Na_2S had dissolved, a K_2 value of 10^{10} [mole fraction]$^{-2}$ was calculated. From the increase in potential just after addition of sodium sulfide, however, it is suspected that this salt contains reducible impurities, which by oxidation of the aluminum electrode make the melt more acid. The K_2 value of 10^{10} is therefore probably too high. Further work is now in progress to determine the solubility of sulfides as a function of acidity, from which K_2 can be calculated.

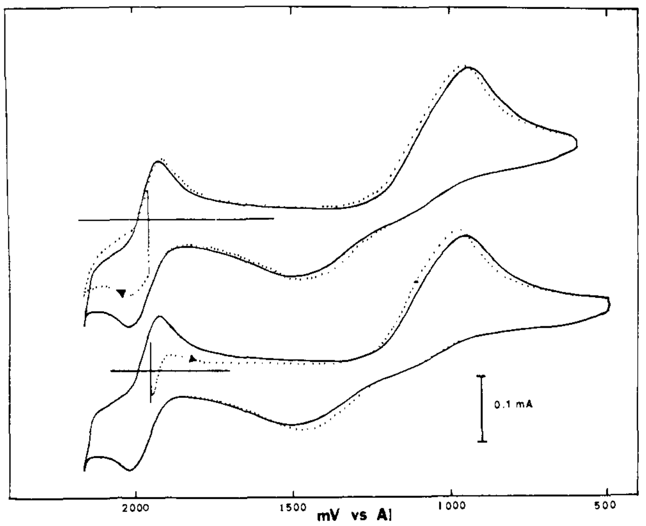

Figure 13. S_2Cl_2 in basic melt. Tungsten electrode (0.07 cm^2). Concentration approximately 0.05 ml S_2Cl_2 in 10 ml of melt (50–60 mM).

In connection with our observations on metal sulfide solubility, chalcopyrite was observed to possess appreciable solubility in the melt, although part of the sulfide was found to have been oxidized to sulfur by the Cu(II). Cyclic voltammograms indicated both metallic copper and iron could be deposited from the melt. Additional work will be carried out on this material as the ore's high solubility suggests that the solvent system might be useful for metal production.

The oxidation of sulfur has been briefly investigated in the basic melt. Cyclic voltammograms of S_2Cl_2 are shown in Figure 13. S_2Cl_2 boils at 135.6 °C and after a few hours disappears from the melt. Coulometric oxidation of sulfur was attempted by holding the electrode potential for oxidation at 2.01 V vs. Al.

An n value of 1.15 was obtained without correcting for background. Since the oxidation takes place close to the chlorine evolution potential, the background was high and very sensitive to small changes in acidity. The cyclic voltammograms obtained after the oxidation resembled those of Figure 13. Because of the volatility of S_2Cl_2, most of what was produced probably evaporated from the solution during the oxidation. At more anodic potentials than 2.01 V sulfur was apparently oxidized with an n indication 3–4 electron reaction. However, accurate values could not be obtained due to the high background bordering on Cl_2 evolution.

The experimental results obtained for the sulfur-sulfide system show that sulfide ion acts as a strong base in the $AlCl_3$-$NaCl$ melt. The change of solubility of metal sulfides shows that sulfide ion activity is several orders of magnitude smaller in acid than in basic melt, and experimental evidence indicates the formation of AlSCl. The reduction of sulfur showed no evidence of formation of polysulfide ions. Sulfur can be oxidized to S_2^{2+} and perhaps higher oxidation states. Further work on stoichiometry of sulfide systems in these melts is in progress.

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Electrochemical and Electron Paramagnetic Resonance Studies of a Series of Ammonium and Phosphonium Compounds

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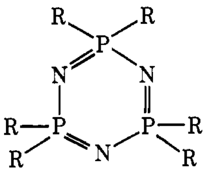
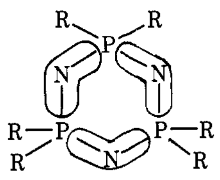
Abstract: Electrochemical studies were conducted on a variety of ammonium and phosphonium derivatives of nitrobenzene. The stable one-electron reduction products were also studied by electron paramagnetic resonance. Hückel as well as CNDO molecular orbital calculations were carried out on these molecules. Evidence for significant conjugative interaction of the phosphonium substituents is presented. Finally, several phosphonium and ammonium compounds were prepared which gave stable one-electron reduction products.

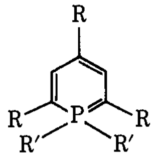
The significance of conjugative interaction involving tetravalent phosphorus has been the subject of a large number of investigations over the past 15 years and the problem is still not clearly resolved.[2] Most of the work has been directed toward the phosphazenes (I), which have at various times been proposed to be stabilized by dπ-pπ bonding in a cyclic manner[3] or an "island" manner[4] (II) or by no dπ-pπ bonding at all.[5,6] Other systems that have received attention are the phosphorines (III) and ylides (IV). Theories similar to those mentioned above have also been proposed in these cases,[7-15] but there appears to be no unequivocal proof of any of the models of dπ-pπ bonding.[2,6,11,12]



I



II



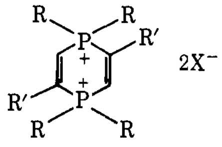
III

$R_3P{=}CR'R''$

IV

The present work extends the study of phosphorus conjugative interaction to phosphonium salts by application of electrochemistry (EC), electron paramagnetic resonance (EPR) and molecular orbital (MO) calculations.

In general the initial reduction products of phosphonium salts are unstable,[18-25] but it has recently been demonstrated that radical cations produced by the reduction of diphosphonium salts (V) are very stable.[16,17] Stabilization of the radical cation by d-orbital participation was proposed.[16] The present work describes new stable radicals from reduction of phosphonium and ammonium salts.



V

Results

Electrochemistry. Five onium derivatives of nitrobenzene (4-nitrophenyltriphenylphosphonium iodide (VI), 3-nitrophenyltriphenylphosphonium iodide (VII), 4-nitrophenyltrimethylammonium chloride (VIII), 3-nitrophenyltrimethylammonium chloride (IX), and 3-nitrophenyltrimethylammonium iodide (X)) were studied by dc polarography and cyclic voltammetry (CV) in acetonitrile (AN).

In each case, these nitrobenzenes were observed to have their first reduction wave positive of −1.0 V. Polarographic results for VI-X are given in Table I. Table II gives CV data at 50 mV/s for the first wave of these compounds. The value of unity for i_{pa}/i_{pc} indicates that the reduction product is stable.[26] The