2. Computations using the Gronwall, La Mer and Sandved development of the Debye–Hückel theory for osmotic deviations show that for solvents of such low dielectric constant calculations based on the first approximation will yield erroneous values for the parameter "*a*," and those based on the fifth approximation are valid only when "*a*" is greater than 10 Å. due to the slow convergence of the series.

3. From our data we may conclude that: (a) in the region of 0.005 to 0.05 molal, ammonium nitrate when dissolved in anhydrous acetic acid behaves as though associated into at least binary ion pairs. (b) When the concentration of the solute is small, 100% sulfuric acid is appreciably dissociated in anhydrous acetic acid. At concentrations of about 0.1 molal it behaves as though highly associated in the Bjerrum sense.

4. As might be expected, these electrolytes, ammonium nitrate and sulfuric acid, when dissolved in anhydrous acetic acid deviate widely from the predictions of the Debye–Hückel limiting law.

NEW YORK, N. Y. RECEIVED NOVEMBER 2, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Oxidation by Oxygen of the Tellurides, Selenides, and Sulfides of Sodium in Liquid Ammonia

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The present investigation had as its object the determination of the products of the action of gaseous oxygen on the mono- and polytellurides, -selenides, and -sulfides of sodium. Although the principal products of these reactions have been determined, such information has been gathered largely as a by-product of studies not bearing directly on this topic. The studies reported here were carried out in liquid ammonia (1) because the preparation of the pure compounds in this solvent is a relatively easy matter, (2) because liquid ammonia is a good solvent for all of the salts having polyatomic anions, and (3) because liquid ammonia possesses a relatively low solvolyzing power and would thus tend to diminish complicating side reactions. This technique is not all that may be desired, however, because the monosulfides, -selenides, etc., and oxygen gas are only slightly soluble in liquid ammonia.

Experimental

The reaction cell was that of Kraus and Chiu,[1] with minor modifications. In the preparation and purification of materials, the methods of Kraus and Chiu and of Bergstrom[2] were used. It should be remembered that the colors of solutions of the polytellurides, etc., are: Na_2Te_2, purple; Na_2Te_4, dark red; Na_2S_2, red; Na_2Se_3, green; Na_2Se_4, red; Na_2Se_5, red-green; Na_2S_2, orange; Na_2S_{3-5}, red.[1,2,3]

Standard analytical methods were used throughout although certain ones are not so familiar.[4]

Oxidation of the Sodium Tellurides.—Upon treating the suspension of the monotelluride with gaseous oxygen, the solution acquired first a deep lavender color, then changed to red, and soon became water clear above the white precipitate. The products of this reaction, except for a trace of free tellurium, were water soluble and consisted of tellurite and tellurate in varying amounts. On oxidation the lavender color of the ditelluride changed to the red of the saturated compound (apparently Na_2Te_4 but possibly a mixture of Na_2Te_2 and Na_2Te_6).[1,5] At the end of the oxidation of both Na_2Te_2 and Na_2Te_4 a clear liquid and a gray precipitate remained. From substances of the following compositions: $Na_2Te_{1.10}$, $Na_2Te_{2.13}$ and $Na_2Te_{3.36}$; there were obtained 0.14, 1.02 and 2.06 atoms of free Te; 0.52, 0.71 and 1.00 atoms of Te as $TeO_3^=$; and 0.46, 0.44 and 0.34, respectively, atoms of Te as $TeO_4^=$. The substance Na_2Te_2 gave 0.93 atom of free Te and 1.06 atoms of Te as a mixture of $TeO_3^=$ and $TeO_4^=$.

Oxidation of the Sodium Selenides.—Upon treating the suspension of sodium selenide with oxygen (two to three hours) a transitory light orange coloration appeared. The reaction product (in three cases) contained no unchanged selenide and consisted approximately of 0.1 atom of free Se and 0.9 atom of Se as a mixture of $SeO_3^=$ and $SeO_4^=$. Moderately soluble diselenide (red) exhibited the following behavior when treated with oxygen. The red color soon changed to a very brilliant green which rapidly became darker and then suddenly changed to a wine red. This latter red color slowly altered to a much

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[1] C. A. Kraus and C. Y. Chiu, THIS JOURNAL, **44**, 2003 (1922).

[2] F. W. Bergstrom, *ibid.*, **48**, 147 (1926).

[3] *Cf.* W. C. Johnson and W. C. Fernelius, *J. Chem. Ed.*, **7**, 986 (1930); E. Zintl, J. Goubeau and W. Dullenkopf, *Z. physik. Chem.*, **154A**, 1–46 (1931).

[4] Separation of tellurites and tellurates: P. E. Browning and W. R. Flint, *Z. anorg. Chem.*, **64**, 104–111 (1909). Determination of selenite in the presence of selenate: E. Müller, *Z. physik. Chem.*, **100**, 347 (1922).

[5] C. A. Kraus and S. W. Glass, *J. Phys. Chem.*, **35**, 999 (1929); *cf.* E. Zintl, J. Goubeau and W. Dullenkopf, *loc. cit.*, p. 30.

darker red and finally became black. The precipitated selenium (dark gray) and oxidation products (white) settled to the bottom of the cell when stirring was discontinued, leaving the supernatant liquor clear and colorless. The triselenide (green) gave the same series of color changes except for the absence of the initial red color. The saturated solution (Na_2Se_{5-6})[2] exhibited only the final change in which the selenium and oxidation products were precipitated. From substances of the compositions Na_2Se_2, $Na_2Se_{2.96}$ and $Na_2Se_{5.62}$, there were obtained 0.76, 1.84 and 4.38 atoms of free Se; 0.98, 1.06 and 1.16 atoms of Se as $SeO_3^{=}$; and 0.26, 0.05 and 0.04 atoms of Se as $SeO_4^{=}$. The substances Na_2Se_2 and $Na_2Se_{2.06}$ gave 0.94 and 0.82, respectively, atoms of free Se and the latter 1.23 atoms of Se as a mixture of $SeO_3^{=}$ and $SeO_4^{=}$.

Oxidation of the Sodium Sulfides.—During the oxidation of sodium sulfide there were no color changes and an insoluble white precipitate remained throughout the reaction. Much sulfide remained even after long-continued reaction and only small amounts of sulfite and sulfate. The moderately soluble bright orange disulfide gradually changed to a white product. At no time were there any colorations indicative of the presence of higher polysulfides. The sole product was thiosulfate (96% yield). A solution of a material having the composition $Na_2S_{2.01}$ gave 1.82 atoms of S as $S_2O_3^{=}$ and 0.11 atom as $SO_4^{=}$. A considerable quantity of white precipitate formed gradually, although the intense red colors of the higher polysulfides persisted throughout the period of oxidation. From substances of the compositions Na_2S_3, Na_2S_4 and Na_2S_5, there were obtained 2.57, 3.43 and 3.54 atoms of S as $S_2O_3^{=}$; 0.10, 0.35 and 0.07 atom as free S, and 0.33, 0.09 and 0.46, respectively, atom as $SO_3^{=}$.

Discussion

None of the reactions above needs comment except those of the polysulfides containing more than two atoms of sulfur. With these compounds it is to be noted that a portion of the sulfur liberated in the reaction is itself oxidized to give additional thiosulfate and some sulfite.[6] Check runs made on a "solution" of sulfur and on ammonium sulfide and sulfur nitride—the materials constituting a "solution" of sulfur in liquid ammonia: $10S + 16NH_3 \rightleftharpoons 6(NH_4)_2S + S_4N_4$.[7] Both sulfur and sulfur nitride gave moderate amounts of thiosulfate (some sulfate from sulfur alone), while ammonium sulfide gave only a very small amount of sulfate.

Summary

The mono- and polytellurides, -selenides and -sulfides of sodium in liquid ammonia have been subjected to the action of molecular oxygen with the following results.

The monotellurides, -selenides and -sulfides are converted into a mixture of -ite and -ate oxygen salts.

Oxygen displaces the polytelluride tellurium and the polyselenide selenium from the respective poly-compounds, with the formation of the free elements and the -ite and -ate oxygen salts. Whenever possible the free element combines with the polytelluride or -selenide to form compounds with greater tellurium or selenium content.

The disulfide is oxidized directly to sodium thiosulfate.

The polysulfides containing more than two atoms of sulfur per molecule, when treated with oxygen give thiosulfate and a small amount of free sulfur.

Liquid ammonia solutions of sulfur and of sulfur nitride give small amounts of thiosulfate on oxidation.

COLUMBUS, OHIO RECEIVED NOVEMBER 6, 1933

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[6] *Cf.* O. Ruff and L. Hecht, *Z. anorg. Chem.*, **70**, 63 fn. (1911).

[7] O. Ruff and E. Geisel, *Ber.*, **38**, 2659–2667 (1905); F. W. Bergstrom, THIS JOURNAL, **48**, 2323 (1926).