Table V

Concn. KI		Concn. NaI	r	Concn. LiI	r
......	..	......	..	6×10^{-2}	0.35
......	..	1×10^{-2}	0.43	1×10^{-2}	.56
......	..	......	..	2×10^{-3}	.61
1×10^{-4}	0.52	......	..	4×10^{-4}	.62
3×10^{-5}	.53	......	..	7×10^{-5}	.62
5×10^{-6}	.58	......	..	1×10^{-5}	.61
1×10^{-6}	.69	......	..	2×10^{-6}	.61

potassium iodide, lithium iodide, with lithium iodide having the largest coefficient. This in turn means that ΔH for lithium iodide has the largest negative value, indicating either that the entropy of orientation of the solvent is greater for this ion or that the free energy of ionization is smaller. Bent and Keevil[6] point out from their somewhat meager data on ether solutions that while ΔF varies somewhat with the distance of closest approach of the ions, the entropy change is relatively constant. If this is generally true, then the variation in ΔH is due to a difference in ΔF, rather than ΔS. Since the free energy of ionization decreases with increasing ion size, that is, larger salts are more easily ionized, it follows that the lithium ion has the largest ionic radius with the potassium ion next, as deduced previously. This again probably means that the lithium ion is solvated.

In a recent article,[14] Kelso and Felsing have reported finding negative partial molal volumes for lithium chloride in methylamine solutions. This probably indicates some solvation of this salt, while sodium nitrate has a positive partial molal volume, and probably is not solvated. These findings are in accord with the results of this research in a very similar solvent, and throw some light on the mechanism of the ionization process in solution. Since only an extremely small fraction of the lithium salt present is in the form of single ions in a solution of ordinary concentration such as those measured by Kelso and Felsing, the large negative partial molal volume observed must be caused by the ions in combination, rather than those existing as single ions. If these negative partial molal volumes are to be interpreted as indicating solvation, then the ions in the ion pairs are solvated and the greater dissociation of the lithium salt is due to the greater separation of the ions in the ion-pairs, resulting in a weakening of the coulombic force between them.

The author wishes to thank Professors H. E. Bent and Grinnell Jones for many suggestions and helpful criticisms.

Summary

1. The conductances of dilute solutions of sodium, potassium and lithium iodides in dimethylamine have been measured.

2. The results are qualitatively in accord with the Kraus and Fuoss theory.

3. It was found that the lithium ion is probably solvated by dimethylamine.

Knox College
Galesburg, Ill.

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[14] E. A. Kelso with W. A. Felsing, This Journal, **60**, 1949 (1938).

[Contribution from the Chemical Laboratories of the State University of Iowa]

Stable Sulfur Dithiocyanate

By P. A. Bond and G. A. Weaver, Jr.

In 1926, while investigating the solubilities of inorganic salts in sulfur monochloride, Baker[1] found that the thiocyanates of barium and potassium formed orange-red precipitates which were amorphous, insoluble in the strongest alkali, and stable in all except the most powerful oxidizing acids. Since the determination of the exact nature of this product did not come within the scope of the thesis, the reaction was not investigated further at that time. It seemed probable, however, that the orange-red powder belonged to the general class of "pseudo thiocyanates," upon which considerable research has been carried out.

In 1922, Lecher and Goebel[2] prepared the compound sulfur monothiocyanate, $S_2(SCN)_2$, by treating a mercuric thiocyanate in carbon disulfide with sulfur monochloride. The entire experiment was carried out at low temperatures in an apparatus described as being "practically completely protected from air."

Also, Lecher and Whittwer[3] prepared sulfur dithiocyanate, $S(SCN)_2$, by treating the free

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[1] Baker, "Solubilities of Inorganic Salts in S_2Cl_2," Thesis, State University of Iowa, 1926.

[2] Lecher and Goebel, *Ber.*, **55**, 1483–1495 (1922).

[3] Lecher and Whittwer, *ibid.*, **55**, 1481–1482 (1922).

thiocyanate, $(SCN)_2$, formed by the action of bromine on thiocyanates, with diethyl ether and dry hydrogen sulfide. Sulfur dithiocyanate was described as pearly yellow crystals which darkened upon standing, decomposed into an orange-red smoke at the temperature of the water-bath, and decomposed less rapidly in water or in alcohol.

Since Baker's product was prepared at reasonably high temperatures, it did not seem possible that the product could be sulfur monothiocyanate, which has a melting point of $-3.3°$; neither did the appearance of it correspond to the sulfur dithiocyanate of Lecher and Whittwer—although, as will be seen, its formula shows it to be sulfur dithiocyanate, $S(SCN)_2$, or some isomer.

Baker's work was repeated and somewhat extended to include the thiocyanates of mercury and ammonium. (Pure salts dried at 110° and purified sulfur monochloride were used.) The product formed by the reaction of each of these, as well as by the thiocyanates of potassium and barium, upon sulfur monochloride was identical in each case. The orange-red precipitate was purified by extracting three times with carbon disulfide, then by boiling with distilled water until the filtrate gave no tests for either the chloride or the metallic ions, and finally by extracting once again with carbon disulfide. Qualitative tests established the presence of only sulfur, nitrogen, and carbon.

Sulfur was determined by oxidation with nitric acid and precipitation as barium sulfate. Kjeldahl determinations were made for the nitrogen content. Carbon was determined as carbon dioxide by combustion in the presence of copper oxide, lead chromate, and potassium dichromate. From these analyses, as shown in Table I, the purified reaction product was found to be sulfur dithiocyanate, $S(SCN)_2$, or some polymerized form. On account of its insolubility, the molecular weight was not determined.

Table I

Element	% found in prepared samples		% calcd. for $S(SCN)_2$
S	64.81	64.88	64.91
N	18.98	19.01	18.90
C	16.22	16.29	16.19

The fundamental reaction between any metallic thiocyanate and sulfur monochloride, at high temperatures, appears to be

$$2MeSCN + S_2Cl_2 \longrightarrow 2MeCl + S(SCN)_2 + S$$

During the reaction, however, there was a considerable quantity of gas evolved which is not accounted for in the reaction as written. The gas, collected over mercury, is colorless and hydrolyzes in the air or in water, in which it is very soluble. It does not condense at room temperatures as would be expected were it a vaporized sulfur chloride, nor is it cyanogen.

Because the product differed in physical aspects from the sulfur dithiocyanate of Lecher and Whittwer, their preparation was repeated and the occurrence of pearly yellow crystals was verified. This crystalline form was found to change completely in approximately forty-eight hours to the orange-red form. When this was purified and analyzed, the results (as shown in Table II) were identical with those obtained by our reaction. Since Lecher and Whittwer found the crystalline form to have this composition also, it would appear that the change is a molecular rearrangement rather than a decomposition.

Table II

Element	% found in the purified product after rearrangement		% calcd. for $S(SCN)_2$
S	64.73	64.77	64.91
N	19.08	19.00	18.90
C	16.17	16.30	16.19

The stability of the final product, with respect to the high temperatures required for its decomposition, 500–600°, and its general insolubility taken in connection with its intense color, indicate the possibility of its use as a pigment.

Summary

1. Sulfur dithiocyanate, $S(SCN)_2$, has been prepared, at moderately high temperatures, by the action of pure sulfur monochloride upon metallic thiocyanates.

2. This compound is identical with the *final* product which Lecher and Whittwer obtained by the action of bromine and hydrogen sulfide upon thiocyanates.

3. It does not correspond to the sulfur monothiocyanate, $S_2(SCN)_2$, prepared by Lecher and Goebel by the action of sulfur monochloride upon thiocyanates in carbon disulfide solution at low temperatures.

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