and magneto-optic rotation), which were made at temperatures from 13–17°, to 15°, they are tabulated in Table III. The curves for V against concentration are given in Fig. 3, where that for carbon disulfide–benzene is plotted for comparison.

Inasmuch as the molecular rotation of benzene is slightly larger than that for carbon disulfide, while that of the other substances is smaller, the curves are not strictly analogous. They have, however, certain features in common. Over the region from about 15% component B to pure B, the points lie on a smooth curve which for all the substances (except isobutyl alcohol) is practically a straight line within the experimental error. The alcohol curve is straight also in the middle region.

But, for every curve, if these straight lines are produced to the A axis, they do not meet it at the value for pure carbon disulfide. While the lines do not meet exactly at a point, they cross at values nearer to each other than to the true value. The value for isobutyl alcohol is also slightly higher than a line extrapolated in the other direction. Schwers made no measurements in the dilute region and, as we have pointed out, our density measurements make the exact shape of the curve uncertain. But we can state definitely that the magneto-optic rotation of carbon disulfide is greater per molecular group in the pure state or dilute solution than it is in the concentrated solutions.

As a first hypothesis, it is possible that the carbon disulfide has an intermolecular structure which in itself produces an additional rotation in dilute solution. Therefore its molecular rotation is higher than that which would be expected on a simpler basis. This structure is disturbed by the presence of the B component producing a distortion of the curve in dilute solutions. If this is true, it may be possible to obtain some information as to the intermolecular stucture of various substances both in the pure state and in solutions.

Summary

The Verdet constants of different solutions of carbon disulfide and benzene were determined together with the partial Verdet constants. A correlation is shown with similar data in the literature. The possibility of the determination of intermolecular structure from Verdet constants is suggested.

BROOKLYN, NEW YORK RECEIVED JUNE 30, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD AND SYRACUSE UNIVERSITIES]

Reactions of Nitriles and Related Compounds with Sulfur in the Presence of Amines; Synthesis of Quaternary Ammonium Thiocyanates[1]

BY C. R. McCROSKY, F. W. BERGSTROM AND G. WAITKINS[2]

The cyanide, cyanate, thiocyanate, and selenocyanate groups in many inorganic compounds often simulate the behavior of the halogens in the common inorganic halides and for this reason have been called halogenoids. Analogies between organic halides and organic compounds containing halogenoid groups do not appear to have been stressed; however, it has been shown that methyl thiocyanate reacts with trimethylamine at ordinary temperatures to form tetramethylammonium thiocyanate,[3,4] just as aliphatic halides produce quaternary ammonium halides when they combine with tertiary amines. Reactions of this type between nitriles and tertiary amines have never been demonstrated but such reactions would not be expected to take place at ordinary temperatures because of the greater bond energy of the C–C linkage as compared to the C–S and C-halogen bondings. It was therefore of interest to see whether nitriles would undergo quaternary salt formation at elevated temperature and determine whether this reaction was influenced by removing the ionizable cyanide as produced either as an iron cyanide complex or as thiocyanate.

Experiments showed that tetramethylammonium cyanide, on being heated at 200° with methyl alcohol as a solvent in a sealed tube, decomposed to form trimethylamine and acetonitrile. The reverse of this reaction could not be demonstrated by the formation of the quaternary cyanide when

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[1] Constructed from a thesis submitted by G. Waitkins to the Faculty of the Graduate School of Syracuse University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address, Battelle Memorial Institute, Columbus, O.

[3] Walden, *Z. Elektrochem.*, **27**, 36 (1921).

[4] Lecher and Heydweiller, *Ann.*, **445**, 77 (1925).

trimethylamine and acetonitrile were heated together in varying proportions, nor was Prussian blue formed when a mixture of the amine, nitrile, and ferric and ferrous salts was heated in various solvents. However, in reactions where acetonitrile, trimethylamine, and sulfur were heated at 200–210° with methyl alcohol in sealed tubes, about 25% of the sulfur was found as water-soluble thiocyanate and a part of this was isolated as tetramethylammonium thiocyanate. Selenium did not form selenocyanate under the same conditions.

Water-soluble thiocyanate was produced in amounts ranging from 10–25% when other alkyl and aryl nitriles, amides and ammonium salts of organic acids were substituted for acetonitrile. Tetramethylammonium thiocyanate was also isolated from these reaction mixtures and its formation postulated by assuming the dissociation of the unsymmetrically substituted quaternary thiocyanate first formed and subsequent recombination according to the mechanism which has been advanced to explain analogous rearrangements of certain quaternary ammonium iodides[5] and sulfonium salts.[6] This assumption was substantiated in part by observing that tetramethylammonium thiocyanate was produced when pure solutions of either ethyltrimethyl- or benzyltrimethyl-ammonium thiocyanates were heated in various solvents.

With ammonia as a reactant in place of trimethylamine, 10–22% of the sulfur formed water-soluble thiocyanate. Individual thiocyanates were not isolated in these cases. (It is interesting to note in this connection that dogs and rabbits which were fed various nitriles were able to convert such compounds to ammonium thiocyanate which was excreted in the urine in one or two days after ingestion.[7] The formation of thiocyanate was explained by assuming that the C–C bond of the nitriles was split and that the resulting CN group reacted with SH to form thiocyanic acid.)

Methyl thiol and methyl sulfide were found in the volatile products of all reactions. It was not possible, however, to account for a large part of the sulfur which entered reaction and it was assumed that this sulfur formed thioacids, thioamides, and perhaps other more complex sulfur compounds for whose analysis no provision was made.

A number of quaternary thiocyanates were prepared by reactions analogous to the interaction of methyl thiocyanate with trimethylamine. This type of reaction appeared to be general and even included the formation of water-soluble thiocyanate from phenyl thiocyanate and trimethylamine. This latter observation was interesting for it was remembered that phenyl halides showed no tendency toward quaternary halide formation with tertiary amines. As expected, tetramethylammonium selenocyanate was found to be formed readily by the combination of methyl selenocyanate and trimethylamine.

Experimental Part

Dissociation of Tetramethylammonium Cyanide.—This salt was prepared by neutralizing a solution of tetramethylammonium hydroxide in anhydrous methyl alcohol with hydrogen cyanide while excluding carbon dioxide.[8] The dry salt, 0.1 g. in 5 ml. of methyl alcohol, was heated in a sealed tube for five hours at 200–210°. Analysis of the resulting solution indicated that the quaternary cyanide was dissociated completely to form trimethylamine and acetonitrile.

Varying proportions of trimethylamine and acetonitrile or phenylacetonitrile were heated in sealed tubes at 180–210° for one to five hours, but the reaction products failed to produce a precipitate of silver cyanide with aqueous silver nitrate after acidification with nitric acid. Prussian blue did not result when mixtures of ferric and ferrous salts were heated with these nitrile and trimethylamine solutions under the same conditions nor when water and methyl alcohol were used as solvents for these mixtures.

Reactions of Nitriles and Related Compounds with Sulfur in the Presence of Amines.—Acetonitrile, 1.5 ml., sulfur, 0.9 g., these in equimolar proportions, and methyl alcohol, 5 ml., were placed in a soft glass tube, 45 × 1.6 cm., and cooled in a freezing mixture. Trimethylamine in slight excess, obtained from trimethylammonium chloride, 6 g., was bubbled into the cooled mixture in the tube. The sealed tube was heated for five hours at 200–210°; the reaction mixture yielded an almost colorless solution under these conditions.

The cooled tube was opened with proper precautions because of gases under pressure. The solution was evaporated to dryness and the crystalline residue washed with cold acetone. The acetone washings were saved for determination of the acetone-soluble thiocyanate and isolation of amides which were produced from aromatic nitriles used in subsequent runs. The residue insoluble in cold acetone was recrystallized from hot acetone to give colorless needles, m. p. 296–297° (uncor.), yield approx. 0.6 g. A mixed m. p. with tetramethylammonium thiocyanate was the same. *Anal.* Calcd. for $(CH_3)_4N{\cdot}SCN$: SCN^-, 43.94. Found: SCN^-, 43.92.

Small amounts of tetramethylammonium thiocyanate, with m. p. ranging from 292–297°, were also isolated in reactions which were carried out employing in place of acetonitrile, propio-, *n*-capro-, phenylaceto-, benzo-, and

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[5] Jones and Hill, *J. Chem. Soc.*, **91**, 2083 (1907).

[6] Ray and Levine, *J. Org. Chem.*, **2**, 267 (1937).

[7] Lang, *Arch. exptl. Path. Pharm.*, **34**, 247 (1894).

[8] Thompson, *Ber.*, **16**, 2338 (1883).

p-tolunitriles, and acetamide, ammonium acetate, benzamide, and ammonium benzoate.

Ethyltrimethylammonium thiocyanate, m. p. 132°, and benzyltrimethylammonium thiocyanate, m. p. 117°, were used in 1–2 g. amounts to make separate pure solutions in methyl alcohol, ethyl alcohol, and benzene. These individual solutions were heated in sealed tubes for five hours at 200–210°. The quaternary thiocyanate isolated after this treatment was found to have melting points ranging from 262 to 296°. These experiments indicated that tetramethylammonium thiocyanate was produced by the dissociation of the substituted trimethylammonium salt and explained the method by which the tetramethyl salt was formed when nitriles other than acetonitrile reacted with trimethylamine and sulfur.

In a second series of runs the total water-soluble thiocyanate, resulting after five hours of heating at 200–210° of an equimolar mixture of sulfur–trimethylamine–nitrile or related compound and using methyl alcohol as solvent, was determined by titration. The following results were obtained with the numbers denoting the percentage of thiocyanate found: acetonitrile 23.2, propionitrile 19.8, *n*-capronitrile 10.9, benzonitrile 13.5, *p*-tolunitrile 17.0, phenylacetonitrile 24.9 (temp. 180–190°), acetamide 21.8, ammonium acetate 14.2, benzamide 21.1, and ammonium benzoate 12.6. An equimolar mixture of acetonitrile, sulfur, and triethylamine produced 11.8% thiocyanate; however, a similar mixture with tri-*n*-butylamine in place of triethylamine failed to give any thiocyanate.

A number of reactions also were carried out using ammonia in place of tertiary amines. While no individual thiocyanate was isolated in these runs, analysis of the chloroplatinate of the amine associated with the thiocyanate indicated that the product was largely ammonium thiocyanate. The total water-soluble thiocyanate was found to be as follows in equimolar mixtures heated in sealed tubes for five hours at 200–210°: acetonitrile 22.0, propionitrile 18.3, acetamide 22.2, ammonium acetate 17.7, benzonitrile 10.4, benzamide 16.1, and ammonium benzoate 15.1. Mixtures of sulfur with acetamide, ammonium acetate, benzamide, and ammonium benzoate, with methyl alcohol as solvent but containing no ammonia, produced 15.5, 11.5, 0.4, and 5.0% thiocyanate, respectively.

Analysis of Gaseous Products and the Sulfur Balance.—Reaction tubes were prepared and treated as described previously. Each tube was cooled in a freezing mixture and the tip was opened while immersed in methyl alcohol so as to absorb the more volatile vapors completely. The contents was washed with cold methyl alcohol into an Erlenmeyer flask, then the alcoholic reaction mixture was heated on a water-bath and the evolved gases led first through 50% potassium hydroxide where methane thiol and hydrogen sulfide were absorbed and, after removal of volatile amines by sulfuric acid, the remaining gases were led into a glass tube cooled to −80° where methyl sulfide was condensed. The hydrogen sulfide was determined as lead sulfide and the methane thiol as mercuric thiomethane. The condensed methyl sulfide was treated with excess methyl iodide so as to form trimethylsulfonium iodide, the iodide determined by weighing as silver iodide, and the methyl sulfide calculated from these data. Free sulfur and polysulfide sulfur was determined roughly by weighing the residue remaining after distillation and insoluble in hot water. Results for a few typical reactions are shown in Table I.

TABLE I

ANALYSIS OF VOLATILE SULFUR COMPOUNDS AND THE SULFUR BALANCE

Temperature, 200–210°; time, five hours

	Percentages found				
Reactants[a]	SCN^-	CH_3SH	$(CH_3)_2S$	H_2S	Free S or poly-sulfide
CH_3CN, $(CH_3)_3N$	24.5	29.8	8.4	0.0	0.0
C_2H_5CN, $(CH_3)_3N$	19.8	12.8	7.6	.0	.0
$C_6H_5CH_2CN$, $(CH_3)_3N$[b]	24.7	31.1	...	.0	.0
C_6H_5CN, $(CH_3)_3N$	13.5	Trace	9.0	.0	.0
CH_3CN, NH_3	22.0	...	7.1	3.4	Trace
$(CH_3)_3N$[c]	0.0	0.0	0.1	38.0	51.0
$(CH_3)_3N$[d]	0.0	0.0	Trace	39.0	50.0

[a] Reactants in 5 ml. of methyl alcohol and in equimolar proportions based on 0.9 g. of sulfur. [b] Temperature 180–190°. [c] Trimethylamine in twice molar proportion. [d] Same as (*c*) but without methyl alcohol.

Ethyl- and Benzyl-trimethylammonium Thiocyanates.—Ethyl thiocyanate,[9] b. p. 142–143°, 7 ml., and trimethylamine, 6 g., were heated for two hours at 100–110° in a sealed tube. The crystals which formed were separated from the murky brown solution and washed with benzene; yield, 7–8 g. A portion was crystallized twice from acetone as colorless, deliquescent, soft crystals, m. p. 131–132°. *Anal.* Calcd. for $C_2H_5(CH_3)_3N{\cdot}SCN$: SCN^-, 39.7. Found: SCN^-, 39.9.

A mixture of benzyl thiocyanate,[10] m. p. 39–41°, 3 g., trimethylamine, 4.5 g., and methyl alcohol, 5 ml., was allowed to stand in a sealed tube for three days. The colorless crystals were washed with ether and recrystallized from acetone as soft, non-deliquescent flakes, m. p. 117–118°; yield, 4.5 g. *Anal.* Calcd. for $C_6H_5CH_2(CH_3)_3N{\cdot}SCN$: SCN^-, 27.9. Found: SCN^-, 27.8.

Reaction of Phenyl Thiocyanate with Trimethylamine.—Phenyl thiocyanate,[11] b. p. 230–233°, when heated in a sealed tube with excess trimethylamine for an hour at 100–110° produced a tarry dark brown liquid with some brownish crystals. These crystals were very deliquescent and could not be purified satisfactorily; a water solution gave a good test for thiocyanate ion with ferric salts. Neither phenyl isothiocyanate nor phenyl iodide showed any reaction with trimethylamine under the same conditions and at 200°.

Phenyl thiocyanate, 1.5 g., trimethylamine from trimethylammonium chloride, 4 g., and methyl alcohol, 7 ml., were heated for five hours at 200–210°. Colorless crystals, 0.15 g., m. p. 295–297°, were isolated from the dark reaction product. A mixed m. p. with tetramethylammonium thiocyanate was the same.

Tetramethylammonium Selenocyanate.—Methyl selenocyanate,[12] b. p. 159–160°, 2.5 g., and trimethylamine, 6 g., were allowed to stand for two days in a sealed tube. The glittering crystal mass was washed with ether and re-

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[9] Walden, *Ber.*, **40**, 3215 (1907).

[10] Wheeler and Merriam, THIS JOURNAL, **23**, 294 (1901).

[11] Gattermann and Hausknecht, *Ber.*, **23**, 739 (1890).

[12] Stolte, *ibid.*, **19**, 1577 (1886).

crystallized from acetone to obtain non-deliquescent colorless needles, m. p. 267–268° (decompn.). *Anal.* Calcd. for $(CH_3)_4N{\cdot}SeCN$: Se, 44.1. Found: Se, 44.15.

Summary

Water-soluble thiocyanate resulted in 10–25% amounts when alkyl and aryl nitriles, amides, or ammonium salts of organic acids, mixed with trimethylamine and sulfur and using methyl alcohol as the reaction medium, were heated at 200–210° for five hours in sealed tubes. A part of this thiocyanate was isolated as tetramethylammonium thiocyanate. On replacing trimethylamine with ammonia in these reactions 10–22% of thiocyanate was produced.

Phenyl thiocyanate was shown to react with trimethylamine to form ionizable thiocyanate.

New compounds prepared and analyzed were: ethyltrimethylammonium thiocyanate, $C_6H_{14}N_2S$; benzyltrimethylammonium thiocyanate, $C_{11}H_{16}N_2S$; and tetramethylammonium selenocyanate, $C_5H_{12}N_2Se$.

RECEIVED APRIL 15, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

Synthesis of Polyenes. II. Reactions of β-Methylallyl Chloride with Sodamide in Liquid Ammonia

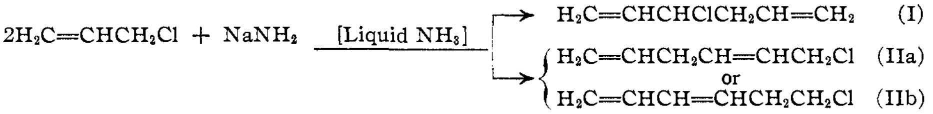
BY M. S. KHARASCH, WALTER NUDENBERG AND E. STERNFELD[1]

The reaction of allyl chloride with sodamide in liquid ammonia to form hexatriene and its polymers has been reported by Kharasch and Sternfeld.[2] This reaction has been further investigated and data bearing on the generality of the reaction

$$2RR'C{=}CR''CH_2Cl + 2NaNH_2 \xrightarrow[NH_3]]{[Liquid} RR'C{=}CR''CH{=}CHCR''{=}CRR' \quad (1)$$

have been obtained from a study of the interaction of β-methylallyl chloride with sodamide in liquid ammonia.

The probability that the conversion of allyl chloride to hexatriene proceeds through the intermediate formation of a chlorohexadiene, was



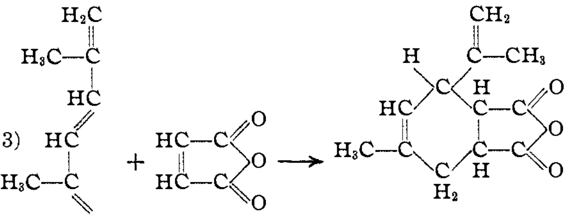
$$2H_2C{=}CHCH_2Cl + NaNH_2 \xrightarrow{[Liquid\ NH_3]} \begin{cases} H_2C{=}CHCHClCH_2CH{=}CH_2 & (I) \\ \left\{\begin{array}{ll} H_2C{=}CHCH_2CH{=}CHCH_2Cl & (IIa) \\ \text{or} & \\ H_2C{=}CHCH{=}CHCH_2CH_2Cl & (IIb) \end{array}\right. \end{cases} \quad (2)$$

investigated by treatment of two molecular equivalents of allyl chloride with one of sodamide, and careful fractionation of the lower-boiling portion of the product. An approximately 20% yield of a pure chlorohexadiene, b. p. 46–47.5° (96 mm.), $n^{20}D$ 1.4483, was obtained. Levene and Haller[3] have reported the preparation of 3-chloro-1,5-hexadiene (I) by treatment of allylvinylcarbinol, but have recorded no physical constants other than the rotations of the optically active forms. Further treatment of the purified chlorohexadiene with sodamide yielded butadienyl-2-vinylcyclohexene-3[2] instead of monomeric hexatriene.

The interaction of equimolecular quantities of β-methylallyl chloride and sodamide in liquid ammonia led to the formation of 2,5-dimethylhexatriene in yields comparable to those of hexatriene obtained from allyl chloride.[2] The product was identified by hydrogenation to 2,5-dimethylhexane, and by condensation with maleic anhydride to form 3-isopropenyl-5-methyl-1,2,3,6-tetrahydrophthalic anhydride (III)

The physical constants of 2,5-dimethylhexatriene observed in this Laboratory do not agree with those previously reported by Bourguel and Rambaud,[4] who believed they had prepared this

(3)



III

compound by treating the glycol, 2,5-dimethyl-2,5-dihydroxy-3-hexene, with dilute hydrochloric acid

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[1] Eli Lilly Fellow. The authors wish to thank the Eli Lilly Company for generous support which made this work possible.

[2] Kharasch and Sternfeld, THIS JOURNAL, **61**, 2318 (1939).

[3] Levene and Haller, *J. Biol. Chem.*, **83**, 185 (1929).

[4] Bourguel and Rambaud, *Bull. soc. chim.*, (4) **47**, 173 (1930).