Table V

Freezing Points and Conductivities of H_2O–1:3 I_2–$S_2O_6F_2$ Solutions at −78.5°

10^2m		$10^1\kappa$,	10^2m		Fp,
I_2	H_2O	$ohm^{-1} cm^{-1}$	I_2	H_2O	°C
0.00	0.00	0.392	0.00	0.00	−89.000
1.00	0.00	0.909	2.82	0.00	−89.213
1.00	1.13	4.306	2.82	1.79	−89.199
1.00	2.35	8.101	2.82	3.64	−89.190
1.00	3.59	23.83	2.82	5.43	−89.248
1.00	4.77	48.54	3.82	7.20	−89.335
1.00	5.88	70.56			

Experimental Section

The techniques used for the purification of fluorosulfuric acid and for cryoscopic and conductometric measurements in this solvent have been described elsewhere.[6,7] Peroxydisulfuryl difluoride was prepared by the method of Cady and Shreeve.[8] Shawinigan reagent grade iodine was used directly. The nmr spectra were obtained with a Varian HR 60 spectrometer.

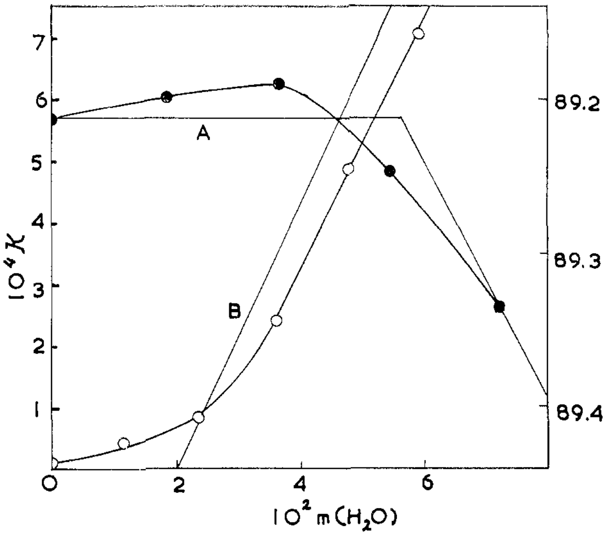

Figure 2.—Conductivities and freezing points of $I(SO_3F)_3$–H_2O solutions (Table V): ○, conductivities; ●, freezing points; A, predicted freezing point curve; B, predicted conductivity curve.

Acknowledgment.—We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research and the National Research Council of Canada for generous financial aid. J. B. M. also thanks the National Research Council of Canada for the award of a studentship.

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Contribution from Avery Laboratory of Chemistry
of the University of Nebraska, Lincoln, Nebraska

Thiocyanogen: Its Spectra and Heat of Formation in Relation to Structure[1]

By CECIL E. VANDERZEE and ARVIN S. QUIST[2]

Received August 11, 1965

By means of solution calorimetry, $\Delta H_f°[(SCN)_2(l)]$ has been found to be 74.3 ± 1 kcal/mole at 25°. This is about 4 kcal/mole less than the value estimated from bond energies for the structure N≡C—S—S—C≡N. Spectroscopic data obtained in this study support those of other investigators and are fully in accord with the above structure.

Introduction

The only thermodynamic datum pertaining to thiocyanogen is the standard electrode potential, *viz.*

$$2SCN^- \rightleftharpoons (SCN)_2 + 2e^- \qquad E° = -0.77 \text{ v} \qquad (1)$$

reported by Bjerrum and Kirschner,[3] who postulated the presence of $(SCN)_2$ in the decomposition of aqueous auric thiocyanate. The first successful isolation of $(SCN)_2$ was reported by Söderbäck[4] in an extensive study of the properties of thiocyanogen. These two extensive studies[3,4] showed that the compound was stable only in the absence of water and in the pure state only at temperatures well below room temperature. Since Söderbäck's initial isolation of solid $(SCN)_2$, the only other report of its isolation is that of Seel and coworkers.[5,6] Söderbäck's preparation, isolated from ether, melted between −2 and −3°. Seel and Wesemann[5] obtained a product melting at 15 to 16° from the decomposition of nitrosyl thiocyanate in liquid SO_2 as solvent. Later Seel and Müller[6] reported that the preparation of $(SCN)_2$ from AgSCN and Br_2 in liquid SO_2 was much easier, but they did not report the melting point of their product obtained by this method.

In this study, several preparations of solid $(SCN)_2$ by the method of Seel and Müller[6] failed to yield a product melting above 0°. In every case, the liquid form was unstable, as reported by other workers.[4–6] Since there appeared to be no practical route to the heat of formation by way of a condensed phase, attention was turned to solution calorimetry.

The most clean-cut and quantitative reaction of thiocyanogen in solution appears to be the oxidation of iodide in acid solution, which is given by eq 2.

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(1) From the Ph.D. Thesis of Arvin S. Quist, July 1959.

(2) Minnesota Mining and Manufacturing Company Fellow, 1956–1957; DuPont Teaching Fellow, 1957–1958; National Science Foundation Fellow, 1958–1959.

(3) N. Bjerrum and A. Kirschner, *Kgl. Danske Videnskab. Selskabs, Skrifter, Naturvidenskab Math. Afdel.*, [8] **5**, 1 (1918).

(4) E. Söderbäck, *Ann. Chem., Liebigs*, **419**, 217 (1919).

(5) F. Seel and D. Wesemann, *Chem. Ber.*, **86**, 1107 (1953).

(6) F. Seel and E. Müller, *ibid.*, **88**, 1747 (1955).

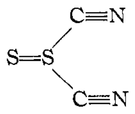
$$(SCN)_2 + 3I^- \longrightarrow 2SCN^- + I_3^- \qquad (2)$$

It is essential to have at least a 50% excess of iodide ion to compete adequately against the hydrolysis of thiocyanogen,[7-9] and the solution of thiocyanogen *must be added to* the iodide solution. This reaction, commonly used for the quantitative determination of thiocyanogen, should also serve as a basis for calorimetric determination of its heat of formation. From the numerous studies of the stability of thiocyanogen solutions,[8,10-18] it was apparent that anhydrous acetic acid was the optimum solvent in which to prepare thiocyanogen solutions for use in calorimetric studies of reaction 2, serving to combine ease of preparation, stability and purity of the solutions, and moderate, well-characterized thermal effects when mixed with water. The first part of this investigation concerns such a calorimetric study and a comparison of the resulting heat of formation against values obtained from bond energies for various structures.

Kaufmann[8] proposed that thiocyanogen in solution existed in two forms, *viz.*

$N\equiv C—S—S—C\equiv N$

I



II

Most of the chemical and physical evidence strongly supports form I as the proper structure.[4,15,19-24] In particular, the Raman spectra by Feher and Weber[23] show a strong line at 489 cm^{-1} characteristic of the –S–S– linkage, and Nelson and Pullin[24] observed a weak band at 491 cm^{-1} in the infrared. Our own infrared studies, completed before the article by Nelson and Pullin[24] appeared, are reported in this paper together with ultraviolet spectra and are compared with previously reported data (see Discussion).

Experimental Section

Preparation of Thiocyanate Salts.—Lead and silver thiocyanates were precipitated by treating potassium thiocyanate solutions with those of the appropriate metal nitrate. The precipitates were washed numerous times by decantation and after filtration were dried *in vacuo* over phosphorus pentoxide. They were normally dried and stored in the dark.[18]

Preparation of Anhydrous Acetic Acid.—In this work, all studies in acetic acid were made with the purified anhydrous acid. This solvent was prepared by refluxing glacial acetic acid 10 hr with chromium trioxide;[25] the distillate was then collected and refluxed 8 to 10 hr with anhydrous ferrous sulfate to remove traces of oxidizing agents. The distillate from this process was then refluxed with an excess of tetraacetyl diborate[26,27] to remove remaining traces of water. The middle fraction of distillate from this source was collected as the solvent for preparations of thiocyanogen. All refluxing and distillation in each step were carried out under dry nitrogen. Spectroscopic study of the solvent showed the presence of a slight amount of acetic anhydride, characterized by a sharp absorption peak at 252 $m\mu$.[28] When the refluxing over anhydrous ferrous sulfate was omitted, sufficient oxidizing agent was present in the acetic acid to oxidize iodide ion to iodine rapidly and to produce yellow thiocyanate solutions, presumably containing trithiocyanate ion.

The anhydrous ferrous sulfate was prepared by adding ferrous sulfate heptahydrate slowly, with stirring, to an excess of reagent grade acetic anhydride at 100°. The exothermal nature of the reaction enabled one to maintain the temperature between 100 and 120° by controlling the rate of addition of the ferrous sulfate heptahydrate. The solution was filtered, and the gray residue was added to a second portion of hot (90–100°) acetic anhydride; no reaction was observed during this addition. The solution was again cooled and filtered; the gray powdery product was stored *in vacuo* over solid KOH.

Preliminary Studies.—Following the procedure of Gardner, Pribyl, and Weinberger,[17] solutions of thiocyanogen, 0.05 to 0.12 *N*, were prepared by allowing lead thiocyanate to react with bromine, using as solvents acetic acid–acetic anhydride–carbon tetrachloride, acetic acid–acetic anhydride, and acetic acid. These solutions were very pale yellow, becoming faintly cloudy in a few hours, and within a few days a yellow amorphous material separated out, even when the solutions were stored at 2 to 4°. Solutions prepared in chloroform and acetonitrile (Spectro Grade) were intensely yellow and much more unstable than those in acetic acid.

Solutions in acetic acid prepared in a similar manner from silver thiocyanate were less colored than those obtained from the lead salt and were somewhat more stable. We attribute these differences to the smaller solubility of the silver salt in acetic acid and the effect of the resulting thiocyanate ions in catalyzing the polymerization of thiocyanogen. It was found that addition of a small amount of potassium thiocyanate to the thiocyanogen solutions in acetic acid produced a brilliant yellow solution, initially clear but turning cloudy in a few minutes, which yielded a voluminous burnt-orange precipitate in a few hours. Supporting evidence for the effect of thiocyanate ion was found in the work of Kerstein and Hoffmann[7] and of Söderbäck.[29]

Accordingly, all further solutions prepared and used in this work utilized silver thiocyanate as the starting material. About 100% excess of silver thiocyanate was placed in the reaction flask with the appropriate amount of solvent, and the bromine, dissolved in an equal volume of solvent, was added dropwise to the stirred slurry. With acetic acid as solvent, the reaction mixture was kept near 16°, while with carbon tetrachloride it was cooled to near 0°. About 0.5 hr after completing the addition of the bromine, the thiocyanogen solution was filtered and transported to the storage flask, using a filter stick with a fine-fritted disk. All glassware was oven dried before use; solutions were protected under dry nitrogen at all times and were protected somewhat from light during preparation and storage. Teflon stopcocks and glands were used to eliminate the need for lubrication of ground-glass surfaces.

Spectroscopic Studies.—Using a Beckman Model DU

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(7) H. Kerstein and R. Hoffmann, *Ber.*, **57**, 491 (1924).

(8) H. P. Kaufmann, *Arch. Pharm.*, **263**, 675 (1925).

(9) H. P. Kaufmann and P. Gaertner, *Ber.*, **57**, 928 (1924).

(10) E. Söderbäck, *Ann. Chem., Liebigs*, **419**, 217 (1919); **443**, 142 (1925); *Acta Chem. Scand.*, **8**, 1851 (1954).

(11) H. P. Kaufmann, *Ber. Deut. Pharm. Ges.*, **33**, 139 (1923); U. S. Patent 1,790,097 (Jan 27, 1931); *Chem. Abstr.*, **25**, 1258 (1931).

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(13) H. P. Kaufmann and H. Grosse-Oetringhaus, *Fette u. Seifen*, **49**, 194 (1942).

(14) P. Mesnard and A. Liermain, *Bull. Soc. Pharm. Bordeaux*, **90**, 87 (1952).

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(16) A. B. Angus and R. G. R. Bacon, *ibid.*, 774 (1958).

(17) W. H. Gardner, G. Pribyl, and H. Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **6**, 259 (1934).

(18) W. H. Gardner and H. Wienberger, *Inorg. Syn.*, **1**, 84 (1939).

(19) E. Söderbäck, *Ann. Chem., Liebigs*, **465**, 184 (1928).

(20) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947.

(21) H. Lecher and A. Gobel, *Ber.*, **54**, 2223 (1921); **55**, 1483 (1922).

(22) A. Gutmann, *ibid.*, **56**, 2365 (1923); *Z. Anal. Chem.*, **66**, 224 (1925).

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(25) W. Eichelberger and V. K. LaMer, *J. Am. Chem. Soc.*, **55**, 3633 (1933).

(26) A. Pictet and A. Geleznoff, *Ber.*, **36**, 2219 (1903).

(27) R. Hayter, A. Laubengayer, and P. Thompson, *J. Am. Chem. Soc.*, **79**, 4243 (1957).

(28) S. Bruckenstein, *Anal. Chem.*, **28**, 1920 (1956).

(29) E. Söderbäck, *Acta Chem. Scand.*, **8**, 1851 (1954).

spectrophotometer with matched quartz cells, visible and ultraviolet spectra of thiocyanogen were examined in carbon tetrachloride and in acetic acid. In neither case was there significant absorption in the visible region (above 400 mμ), although the solutions in acetic acid were a very light yellow or salmon color and those in carbon tetrachloride were a very faint yellow.

In carbon tetrachloride, a broad symmetric peak appeared at 296 mμ (ϵ 170). Bacon and Irwin[15] reported a peak at 295 mμ (ϵ 140) in this solvent.

Freshly prepared solutions in acetic acid showed a similar symmetric peak at 288 mμ (ϵ 120), with a sharp spike rising from it at 249 to 250 mμ. The relative height of the peaks varied somewhat from one preparation to another, those prepared from silver thiocyanate having smaller spikes than those prepared from lead thiocyanate. With aging, the spike at 250 mμ increased in height, becoming higher than the peak at 288 mμ.

Freshly prepared solutions of KSCN and HSCN in acetic acid showed sharp, narrow peaks at 250 to 251 mμ (ϵ 220 and 190, respectively). Based on these data, saturated solutions of Pb(SCN)_2 and AgSCN in acetic acid contain about 1.5×10^{-3} and 1.8×10^{-4} mole of salt per liter, respectively. From solubility considerations alone, the spike observed at 250 mμ in the thiocyanogen solutions could not be entirely due to dissolved salts. Addition of a small amount of KSCN to the thiocyanogen solutions greatly intensified the peak at 250 mμ and also intensified the broad peak (considerably less) but displaced it to about 300 mμ. Such solutions were bright yellow, were not stable, and soon became cloudy. These observations suggest that the spike at 250 mμ is due to the trithiocyanate ion, $(\text{SCN})_3^-$, or to some other condensed species with a large extinction coefficient.

Infrared absorption spectra of approximately 0.12 *M* thiocyanogen in Matheson Coleman and Bell Spectroquality carbon tetrachloride were measured in the region 3500 to 350 cm^{-1}. The thiocyanogen solutions, prepared from AgSCN, were studied immediately after preparation. The sample was contained in a 1-mm cell using KBr windows with a Teflon ring for a spacer. The cell was cemented together by means of a glyptal[30] cement.

The absorption in the region 3500 to 650 cm^{-1} was determined with a Perkin-Elmer Model 21 double-beam spectrophotometer using the NaCl prism. In the region 720 to 350 cm^{-1} a Perkin-Elmer Model 112 single-beam spectrophotometer equipped with a CsBr prism was used. This instrument was calibrated by using the peaks of water vapor and carbon dioxide as standards in this region, according to the method of Downie, Magoon, Purcell, and Crawford.[31] With this instrument, a slit width of 0.200 mm was used in the range 720 to 445 cm^{-1} and a slit width of 0.600 mm was used in the range 445 to 350 cm^{-1}.

An intense, sharp peak was found at 668 cm^{-1} in the region covered by both instruments. At approximately 368 cm^{-1} a very weak, broad peak was found. Sharp peaks of about equal intensity were found at 2175 and 1990 cm^{-1} and broad, weak peaks appeared at 1735 and 1350 cm^{-1}. No others could be found. A summary of the infrared data is presented in Table I, together with pertinent data from the literature.[15,23,24]

Preparation of Solid Thiocyanogen.—Following the procedure of Seel and Müller,[6] thiocyanogen was prepared in liquid SO_2 by allowing bromine to react with silver thiocyanate. After filtering off the silver bromide, the SO_2 was evaporated off under reduced pressure at −50°, leaving white crystals of $(\text{SCN})_2$, with a few having a light yellow color. The system was held under vacuum at −50° for 2 hr to remove the last traces of sulfur dioxide. Upon warming, the crystals became yellow and melted at about −7° to give an orange suspension. Cooling to −70° yielded white crystals and the color disappeared. If the freezing-melting process was repeated several times, the melting point was successively lowered, indicating that melting was accompanied by decomposition. In no case, among the several times the preparation was repeated, could a melting point above 0° be obtained. Seel and Weseman[5] reported a melting point of 15 to 16°, which is so far above our values and those of Söderbäck (−2 to −3°) as to suggest the possibility of different crystalline forms of the substance. (Seel and Müller[6] did not report a melting point for their material.) If, on the other hand, decomposition occurs in the solid state as well, then the rate of warming would be a factor in producing different melting points.

TABLE I

SUMMARY OF SPECTRAL DATA FOR THIOCYANOGEN[a]

Raman	Infrared			
F and W[23]	B and I[15]	N and P[24]	Q and V	Assignment
	3050			
2160 s	2175 s	2171 s	2175 s	C≡N asym str
			1990 m	C≡N sym str
			1735 vw, b	
			1350 vw, b	
668 w		673 s	668 s	C—S str
		667 s		
489 s		491 vw		S—S str
399 w		359 vw	368 w	S—C≡N def
205				
163				

[a] Tabular values are in units of cm^{-1}.

The liquid form was never observed to be stable for any length of time; it progressively darkened and ultimately fulminated to an orange-red powder in every case.

Colorimetric Studies.—The solution calorimeter described by Vanderzee and Myers[32] was used to measure the heats of the following processes at 25°

$$[n_2\text{KI in } n_1\text{H}_2\text{O}] + [(\text{SCN})_2 \text{ in } n_3\text{HOAc}] \longrightarrow [\text{KI}_3 + (n_2 - 3)\ \text{KI} + 2\text{KSCN}] \text{ in } [n_1\text{H}_2\text{O} + n_3\text{HOAc}] \quad (3)$$

$$[n_2\text{KI in } n_1\text{H}_2\text{O}] + [n_3\text{HOAc}] \longrightarrow [n_2\text{KI in } (n_1\text{H}_2\text{O} + n_3\text{HOAc})] \quad (4)$$

By properly matching the amounts of anhydrous acetic acid and potassium iodide solutions, reaction 4 could almost exactly compensate for the dilution effects in reaction 3.

In the absence of other information, the heat of solution of liquid thiocyanogen in anhydrous acetic acid was assigned the value of zero (that of an ideal solution). The choice of the liquid state as the standard state for thiocyanogen is consistent with the reported melting points; it may not be realizable experimentally because of the tendency of $(\text{SCN})_2$ to fulminate after melting. For the final solutions formed in reactions 3 and 4, the heats of dilution to infinite dilution can be assumed to be equal, since the total molality of 1–1 electrolyte would be the same in each case, with a common cation and quite similar anions. With these considerations, the heat of reaction for the standard-state process

$$(\text{SCN})_2(\text{l}) + 3\text{I}^-(\text{aq}) \longrightarrow 2\text{SCN}^-(\text{aq}) + \text{I}_3^-(\text{aq}) \quad (5)$$

is given by

$$\Delta H_5^\circ = \Delta H_3 - \Delta H_4 \quad (6)$$

In calorimetric studies of reaction 3, the thiocyanogen solution was weighed in a specially designed all-glass delivery pipet, which after weighing could be mounted in the thermostat with its delivery tip passing through a port in the calorimeter lid. With this arrangement, the calorimeter could be assembled and equilibrated with the thermostat during the last stages of preparation of the thiocyanogen solution. In this way the thiocyanogen solution could react almost immediately after its preparation. A differential thermometer measured the temperature difference between the calorimeter and the thermostat to 0.001°; 0.5 hr was allowed for equilibration, during which time the foreperiod of the calorimetric process was determined. By gentle pressure of dry nitrogen, the thiocyanogen solution could be transferred to the calorimeter within 10 sec. The reaction appeared to be instantaneous, with no indication of any secondary thermal processes. The afterperiod and electrical determination of the

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(30) General Electric Glyptal Cement No. 1276.

(31) A. Downie, M. Magoon, T. Purcell, and B. Crawford, Jr., *J. Opt. Soc. Am.*, **43**, 941 (1953).

(32) C. E. Vanderzee and R. A. Myers, *J. Phys. Chem.*, **65**, 153 (1961).

energy equivalent were carried out by standard procedures.[32] The calorimeter was then carefully opened, and the liberated iodine was titrated with thiosulfate directly within the calorimeter dewar vessel. The delivery pipet was carefully wiped dry and reweighed to determine the amount of solution delivered. In computing the correction for energy transported during delivery of the sample, the specific heat of the solution was taken equal to that of acetic acid.

Calorimetric studies of reaction 4 were carried out in the same manner as those for reaction 3, using the same relative values for n_1, n_2, and n_3. It was expected, and found, that the heats of solution of anhydrous acetic acid in salt solutions would be slightly different from those in the literature for mixing with water; the results of two runs of reaction 4 differed from the literature by the same amount, making it simple to set up an interpolation curve for use in correcting for reaction 4 at various ratios of n_1/n_3.

The results of the calorimetric studies are given in Table II. The term Q_{cor} includes the correction for energy transported during the delivery of the sample and includes -0.1 cal for the kinetic energy correction in delivery. The heats of solution of anhydrous acetic acid in potassium iodide solutions (runs 1 and 3) were made using portions of the same batch of solvent used for the runs 2 and 4. All runs were made at 25°.

TABLE II

SUMMARY OF CALORIMETRIC DATA

	Run no.[a,b]			
	1	2	3	4
Q_{obsd}, cal	224.8	289.4	251.3	278.0
Q_{cor}, cal	224.8	289.6	251.8	278.0
ΔH_{soln}, HOAc, cal/mole				
Exptl	280.7		275.5	
Calcd		278.0		281.7
n_1/n_3	70.0	66.12	62.5	71.38
Q_{soln}, cal		235.0		223.0
Q_{nx}, cal		54.6		55.0
n_r, moles of $(SCN)_2$		0.00515		0.00526
$\Delta H_r° = \Delta H_5°$, cal/mole		$-10{,}600$		$-10{,}450$

Mean $\Delta H_5° = -10.5$ kcal/mole, at 25°

[a] In all runs, the concentration of KI was close to 0.18 mole/l. Q_{soln} is the heat attributable to dissolution of the HOAc, and Q_{nx} is that attributed to reaction 5. [b] Reaction temperature was 25° in all runs, which were initiated at 25°, and the energy equivalent was run on the final solution. n_r is the number of moles of $(SCN)_2$ which liberated Q_{nx} on reaction.

Discussion

The spectroscopic data assembled in Table I are in accord with structure I for thiocyanogen, and we agree with the other sources[15, 23, 24] on the assignment of frequencies. The behavior of the band near 490 cm^{-1} is to be expected of the –S—S– linkage[33, 34] and rather conclusively rules out an isothiocyanate structure with the two radicals linked through nitrogen, when considered together with the distinct C≡N frequency near 2175 cm^{-1}. We attribute the peak at 1990 cm^{-1} to the symmetric stretching mode associated with the two C≡N groups. The two very weak bands at 1735 and 1380 cm^{-1} do not correspond to any reasonable assignment for thiocyanogen and may be due to traces of impurity or decomposition product. However, the same solutions when examined in the ultraviolet region showed only the simple broad peak at 296 mμ. Neither we nor Nelson and Pullin observed the 3050-cm^{-1} peak reported by Bacon and Irwin,[15] and it, too, cannot be readily attributed to thiocyanogen.

In the ultraviolet spectra observed for thiocyanogen in acetic acid, the main peak is shifted to 288 mμ. This shift from 296 mμ in carbon tetrachloride is consistent with the response of an R-type band to the difference in dielectric constant of the solvent, and there is little question that this peak is an R-type band.[35] This band quite likely is due to the –S—S– linkage, although it is some 40 mμ greater than the usual aliphatic disulfide bands near 250 mμ.[36, 37] The shift to longer wavelengths may be due to interaction of the cyanide groups with the disulfide linkage in the excited state.

The appearance of the sharp spike at 250 mμ in the acetic acid solutions of thiocyanogen is most reasonably attributed to traces of the trithiocyanate ion, $(SCN)_3^-$, which would not be expected in carbon tetrachloride (see Experimental Section). The compelling factor leading to this assignment was the ease and extent of enhancement of this peak when traces of KSCN were added to the thiocyanogen solutions in acetic acid. This behavior explains the relatively smaller spikes observed when the less soluble AgSCN was used as a preparative material instead of $Pb(SCN)_2$. Since the peak or spike appears due to a species with a large extinction coefficient, as might be expected for $(SCN)_3^-$ or a subsequent condensed species, we conclude that only a very small amount of such material is present in the freshly prepared solutions in acetic acid.

As a consequence, we have considerable assurance that the calorimetric process is reliably described by reaction 3, especially since the procedure of basing the heat of reaction upon the amount of iodine released should best measure the amount of thiocyanogen reacting. The effects of possible side reactions should be quite small.

The agreement between the experimental heats of reaction, $\Delta H_5°$, is about what was anticipated, considering the large correction for the heat of dilution of acetic acid, reaction 4. We estimate an uncertainty of ±0.15 kcal/mole in $\Delta H_5°$, associated with experimental errors, and the error in the estimated heat of solution of liquid thiocyanogen in acetic acid should be less than 1 kcal/mole.

To calculate the heat of formation of thiocyanogen from $\Delta H_5°$, we used supplemental data on the heats of formation of $I^-(aq)$, $I_3^-(aq)$, and $SCN^-(aq)$ recently compiled in NBS Technical Note 270-1.[38] Their data lead to $\Delta H_f°[(SCN)_2(l)] = +74.3$ kcal/mole at 25°. From this we estimate $\Delta H_f°[(SCN)_2(g)] = +82.3$ kcal/mole by estimating 8.0 kcal/mole for the heat of

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(33) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 352.

(34) D. W. Scott and J. P. McCullough, *J. Am. Chem. Soc.*, **80**, 3554 (1958).

(35) A. Gillam and E. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," E. Arnold, Ltd., London, 1958, pp 126–128.

(36) See ref 35, p 69.

(37) J. Baer and M. Cormack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

(38) D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965.

vaporization of thiocyanogen, assuming a normal Trouton constant and a boiling point near 100°. We observed the solid thiocyanogen to be only slightly volatile; this behavior was also reported by Kerstein and Hoffmann[7] and by Seel and Wesemann.[5] These large positive heats of formation are expected from the instability of thiocyanogen. Its entropy of formation will be small for the gaseous state, and consequently the free energy of formation will not differ greatly from the heat of formation.

It is of interest to compare the experimentally determined heat of formation for thiocyanogen with that available from bond energy considerations. An internally consistent set of bond energies was assembled based on heats of formation of gaseous cyanogen,[39] alkanes,[39] and the corresponding alkane disulfides.[40] This procedure avoids some of the problems of assigning bond energies to the –C—S– and –S—S– linkages and uses a –C≡N bond energy characteristic of that in cyanogen and hydrogen cyanide, rather than a value characteristic of nitriles.[41] We obtain from these considerations an expected value of +86.5 kcal/mole for the heat of formation of gaseous thiocyanogen, in contrast to the experimental value of +82.3 kcal/mole.

The bond energy value will carry an uncertainty of about 1 kcal/mole associated with the heats of formation of the cyanogen, alkanes, and alkane disulfides from which it was derived, and the scatter among the results from several sets of alkanes and disulfides was close to that value.

The uncertainties in the experimental heats of formation arise from estimated errors of ±0.15 kcal/mole in $\Delta H_5°$, 1 kcal/mole in the estimated zero heat of solution of liquid thiocyanogen in acetic acid, 1 kcal/mole in the estimated heat of vaporization of thiocyanogen, and possibly 1 kcal/mole associated with the supplemental data from the literature.[38,39] These lead to estimated uncertainties of ±1.5 and ±1.8 kcal/mole in the experimental heats of formation of liquid and gaseous thiocyanogen, respectively.

The difference, 4.2 kcal/mole, between the bond energy value and the experimental value is just outside the range of random combination of individual uncertainties but within the range of a possible combination. Consequently, the difference is probably not significant, although it is in the proper direction for a slight internal stabilization of the molecule by interaction of the –S—S– linkage with the –C≡N groups, or a –C≡N bond energy 1 or 2 kcal/mole higher than that characteristic of cyanogen or hydrogen cyanide.

It is worth noting that structures in which the SCN groups are linked through nitrogen rather than sulfur lead to even higher values (>100 kcal) for the expected heat of formation. Such structures could almost be ruled out from energy considerations alone, were it not for the spectroscopic evidence for linkage through sulfur. While the alternate structure II proposed by Kaufmann cannot be ruled out on the basis of bond energies, it has rather clearly been eliminated through chemical evidence by Gutmann.[22] The existing evidence, spectroscopic and thermochemical, quite cleary supports structure I for thiocyanogen.

Acknowledgments.—We wish to express our appreciation to the sources listed in ref 2 for fellowships supporting A. S. Q. We are indebted to Dr. G. A. Gallup for his aid in obtaining and interpreting the infrared spectra.

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