*plex salts in homogeneous single phase systems* will be of much smaller magnitude than those found for two phase systems. It would be hoped that studies of such effects would be accompanied by concurrent examination of the precision of the measurements, the effect of the size of the added electrolyte and an examination of the systems over a range of concentrations of the added asymmetric electrolyte.

This work was supported by a grant from the U. S. Atomic Energy Commission for which we wish to express our thanks.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIFORNIA]

# Spectrophotometric Study of a Thiocyanate Complex of Iodine[1,2]

BY CARL LEWIS AND D. A. SKOOG

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Iodine and thiocyanic acid were found to give a 1:1 complex in both aqueous and ether solutions which absorbs strongly in the ultraviolet region. In ether, 2 moles of water are consumed in forming the complex. The thermodynamic properties of the species have been determined in aqueous solution over a temperature range of 7.6 to 16.5°. The formation constant at 25° in solution of ionic strengths of 1 to 5 is estimated to be 85; the $\Delta H^0$ for the reaction is −8.1 kcal./mole.

There is a good deal of indirect evidence for the existence in aqueous solution of one or more iodine–thiocyanate complexes. For example, it is found that rather large quantities of iodine will dissolve rapidly in aqueous potassium thiocyanate to give solutions which are yellow or orange in color; these are not very stable as a consequence of slow oxidation of the thiocyanate to sulfate. Nevertheless the rate of oxidation is not sufficiently great to account for the speed with which iodine dissolves, and the presence of appreciable concentrations of a somewhat stable intermediate species must be postulated. Furthermore, addition of concentrated potassium thiocyanate to a dilute solution of the triiodide-starch complex causes rapid decolorization of the characteristic blue color. If not too much thiocyanate has been added, however, the color can be restored by addition of iodide ion; this suggests existence of a reversible equilibrium between the triiodide ion and an iodine–thiocyanate complex.

The reaction between iodine and thiocyanate ion to produce sulfate and iodine cyanide has been known for many years.[3] In neutral or somewhat basic solutions it can be made to proceed quantitatively although several hours are required for completion of the oxidation. Griffith and McKeown[4] have studied the kinetics of this reaction and have proposed the existence of the intermediates $I_2SCN^-$ and ISCN. In their paper mention is made of brief studies on the distribution of iodine between carbon tetrachloride and aqueous potassium thiocyanate which confirms the existence of the first of these species; a value of 0.009 at 25° is given for the equilibrium constant, $K = [CNS^-][I_2]/[CNS \cdot I_2^-]$.

Evidence for an iodine thiocyanate adduct also arises from investigations of the thiocyanate catalysis of the reaction between iodine and azide ion.[5] Here again, the existence of the intermediate species $I_2SCN^-$ or ISCN has been postulated.

We have found that the reaction between iodine and thiocyanate ions in aqueous as well as several other solvent media yields a product which absorbs strongly in the ultraviolet region of the spectrum. Spectrophotometric studies have shown that under some conditions this substance is relatively stable, decomposing only slowly to give sulfate ions. We have concluded that the most probable composition of the product is $I_2SCN^-$ and have evaluated the thermodynamic properties of this complex.

## Experimental

**Reagents and Solutions.**—Standard NaSCN solutions were prepared from weighed quantities of the analytical reagent grade salt which had been recrystallized twice from methanol, washed with ether and dried at 130°. This treatment was necessary in order to remove iodine-consuming impurities. The recrystallization reduced the consumption of triiodide solution to less than 0.02 ml. of 0.01 *N* reagent by 5 g. of the solid when the standard ACS test was followed.[6]

Aqueous iodine solutions were prepared by shaking finely divided reagent grade $I_2$ with distilled water until nearly saturated solutions were obtained. These were standardized frequently against analytical reagent grade $As_2O_3$.

Sodium perchlorate solutions (about 9 *F*) were prepared by dissolving NaOH pellets in a minimum quantity of water, chilling and carefully neutralizing with 60% $HClO_4$ to litmus. Small amounts of hydrous ferric and aluminum oxides were removed by filtration and the solutions concentrated by boiling. Analyses of the solutions were made by evaporation of measured quantities and weighing of the anhydrous sodium perchlorate.

Perchloric acid solutions were prepared by dilution of the 60% reagent grade substance and standardization against sodium carbonate.

For the studies in ether solution, freshly opened cans of analytical reagent grade anhydrous ether were used for all preparations. Standard iodine solutions in this solvent were prepared just prior to their use by direct weighing of the reagent and dilution in a volumetric flask. Standard water solutions in ether were also prepared by direct weighing of deionized water and dilution. Anhydrous ether solutions of thiocyanic acid were prepared by extraction of an aqueous solution which was approximately 0.35 *N* in $H_2SO_4$ and 0.3 *N* in KSCN or NaSCN with an equal volume of freshly opened ether. After shaking for 2–3 minutes, the phases were allowed to separate and the

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(1) Support of this work by the National Science Foundation (Research Grant G-6277) is gratefully acknowledged.

(2) This paper is based upon portions of a thesis by Carl Lewis which has been submitted to the Graduate School of Stanford University in partial fulfillment of the requirements for the Ph.D. degree.

(3) E. Rupp and A. Schied, *Ber.*, **35**, 2191 (1902); A. Thiel, *ibid.*, 2766 (1902).

(4) R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **31**, 875 (1935).

(5) F. Feigl, *J. Chem. Ed.*, **20**, 137 (1943); P. Senise, *J. Phys. and Colloid Chem.*, **55**, 1151 (1951).

(6) "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, D. C., 1950, p. 296.

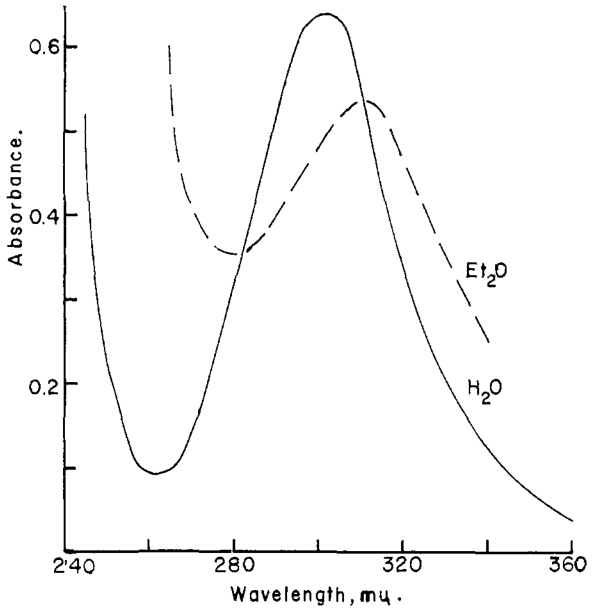

Fig. 1.—Ultraviolet absorption spectra for the iodine–thiocyanate complex in water and ether.

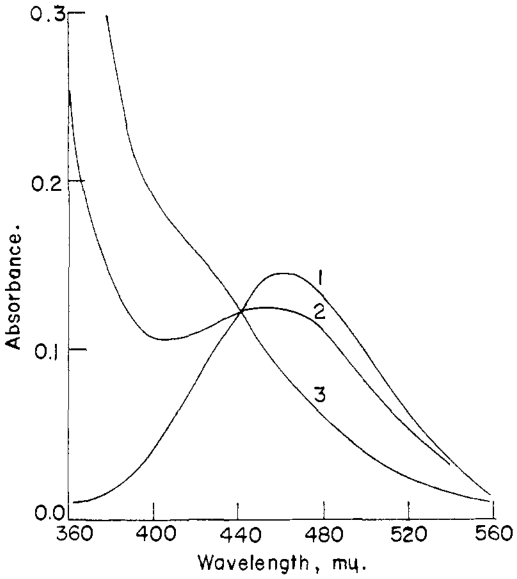

Fig. 2.—Visible absorption spectra for the iodine–thiocyanate complex in water. Iodine concentration 2.1 × $10^{-4}$; thiocyanate concentration: (1) 0.00, (2) 0.0010, (3) 0.010; measurements with 1.00 cm. cells.

ether solution run into a chilled flask containing $P_2O_5$. After shaking and cooling for 5–10 minutes, the solution was decanted into a second flask containing $P_2O_5$ and the process repeated. Finally the ether solution was decanted into a dry, clean glass-stoppered container for storage. Such preparations were approximately 0.1 *F* in HSCN and was stable for 3–4 days at room temperature. The HSCN preparations were analyzed by a modification of the Volhard procedure in which a 10–15 ml. aliquot of the solution were run into a measured excess of standard $AgNO_3$ containing a little $HNO_3$ and ferric alum indicator. The excess $AgNO_3$ was then back-titrated with a standard aqueous KSCN solution. For accurate results it was necessary that the final volume of the aqueous layer be at least 3–4 times greater than that of the ether. Large errors were encountered when attempts were made to titrate the HSCN solutions directly with $AgNO_3$ after addition of $HNO_3$ and the indicator.

The titer of a typical HSCN solution against standard alkali was found to be exactly equivalent to the $AgNO_3$ titer, and evaporation and ignition of the solution revealed the absence of any residue. A total sulfur analysis by oxidation to sulfate agreed with the data obtained by titration with alkali and $AgNO_3$. Thus, it was concluded that the preparations were essentially pure HSCN in ether.

**Spectrophotometric Measurements.**—Most of the spectrophotometric work was carried out with a Beckman Model DU Spectrophotometer; a Cary recording instrument was also employed. Standard, 1 cm., rectangular quartz cells equipped with quartz spacers to give a 1 mm. light path were used for most of the measurements in aqueous solutions. Glass-stoppered 1 cm. cells were used for the studies in ether.

To avoid problems arising from instability of the complex, the majority of the data was collected in the temperature region of 5 to 15°. This required refrigeration of the spectrophotometer cell compartment by circulation of a cooling liquid through hollow blocks fitted on either side of the compartment (standard Beckman attachment). The cooling liquid was maintained at the desired temperature in a thermostat adjoining the instrument. Temperature measurements within the cell compartment were made by means of a small copper–constantan thermocouple located in a water-filled cell immediately adjacent to the absorption cells. Temperature control to ±0.1° was achieved.

In most of the work, the various standard solutions were precooled in an ice bath. These were then mixed in appropriate amounts and transferred rapidly to the absorption cells which had been maintained at low temperature by storage in the cell compartment of the instrument. Temperature equilibrium in the cells was reached rather rapidly particularly when measurements were made in which the large quartz spacers were used in the cells. By working in this way, the problem of fogging of the windows was also largely avoided.

## Results

Upon mixing aqueous solutions of iodine and sodium thiocyanate, there is rapidly produced a soluble product which absorbs strongly in the ultraviolet region. The spectrum for this species is shown in Fig. 1; the absorption peak which occurs at 303 mμ appears to be that of a typical charge-transfer band. As is shown in Fig. 2 there is also a shift in the visible iodine band to shorter wave lengths as a consequence of complex formation; attempts to measure the wave length of the maximum in the shifted peak were not successful, however, because of the overlap of the shoulder of the strong charge-transfer band. From the position of the inflection of curve 3, it seems probable that the peak lies below 440 mμ but above 400 mμ.

Under some conditions the absorbing product decomposes rapidly, sulfate ion being the product. The rate of this decomposition is appreciably reduced by increases in the thiocyanate ion concentration and the acidity. Low temperatures also favor stabilization of the product. The effects of these variables are illustrated by the data in Table I. The decomposition reaction is also markedly retarded when the ionic strength of the solution is maintained in the region of 1 to 5. Thus at an ionic strength of 5, solutions more acidic than 0.1 *F* show no appreciable decrease in absorbance for several hours when held at 5°; even at room temperature these solutions decrease by only a few tenths to 1% in 1 hr.

At acid concentrations greater than 1 a second kind of instability involving $SCN^-$ ion was observed. In this case, a yellow product identified as isoperthiocyanic acid[7] was slowly formed.

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[7] H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, **29**, 443 (1907).

TABLE I

EFFECT OF CERTAIN VARIABLES ON THE RATE OF DECOMPOSITION OF THE IODINE–THIOCYANATE REACTION PRODUCT

| Concn. $HClO_4$, *F* | Concn. NaSCN, *F* | Temp., °C. | Decrease in absorbance in 10 minutes, % |
|---|---|---|---|
| $10^{-7}$–$10^{-3}$ | 0.1 | 25 | 60 |
| 0.1 | .1 | 25 | 40 |
| 1.0 | .1 | 25 | 20 |
| $10^{-7}$–$10^{-3}$ | .01 | 25 | 90 |
| 0.1 | 1.0 | 25 | 10 |
| 1.0 | 0.1 | 40–50 | 50–100 |
| 1.0 | 0.1 | 0–5 | 0–2 |

The effect of variation of $SCN^-$ and $I_2$ concentration on the absorbance of solutions at 303 mμ is shown in Figs. 3 and 4. In these studies, the $SCN^-$ concentration is considerably in excess of that of the $I_2$; this was made necessary by the aforementioned decomposition reaction which takes place rapidly at low concentration of the former. From the shape of the curve in Fig. 3, it is clear that essentially all of the $I_2$ present is complexed at higher concentrations of thiocyanate ion. Thus the concentration of the complex can be assumed to be that of the starting concentration of iodine and its molar absorptivity readily calculated.

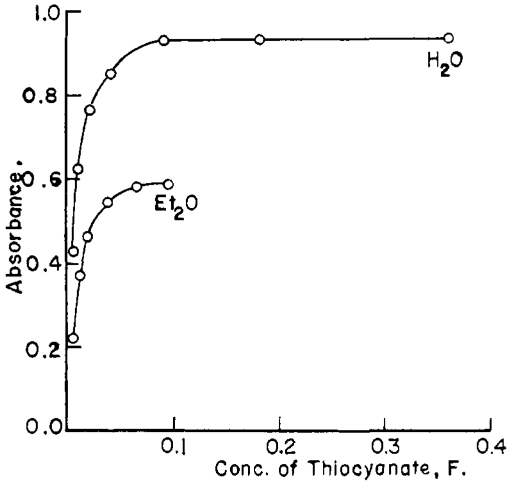

Fig. 3.—Effect of thiocyanate concentration on absorbance at 303 mu. For aqueous solutions, $F_{I_2} = 2.2 \times 10^{-4}$ and measurements made with 0.1 cm. cells. For ether solutions, $F_{I_2} = 2.00 \times 10^{-5}$ and $F_{H_2O} = 0.333$; measurements with 1.00 cm. cells.

In Fig. 4 it is seen that the absorbance of iodine–thiocyanate solutions bears a linear relationship to iodine concentration. The slopes of these curves increase with increasing $SCN^-$ concentration and become constant when sufficient $SCN^-$ is present to force the reaction nearly to completion. Under these circumstances the slope corresponds to the molar absorptivity of the complex. The best value for the constant obtained in this way is 42,900 ± 200 $cm.^{-1}$ $mole^{-1}$ liter. A value identical to this within the experimental error was obtained by plotting the same data according to the method of Benesi and Hildebrand.[8] This method requires no assumption as to the completeness of the complexing of the iodine.

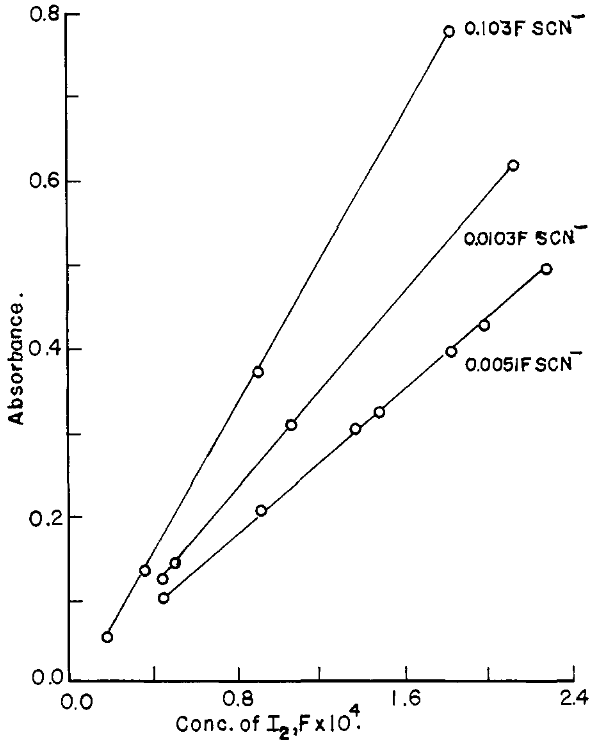

Fig. 4.—Effect of iodine concentration on absorbance at 303 mμ in aqueous solutions. Measurements made with 0.1 cm. cells.

It will be noted that the straight line in Fig. 4 at the highest $SCN^-$ concentration does not pass through the origin. This appears to be due to the presence of an unknown iodine-consuming impurity in the thiocyanate. The magnitude of the displacement could be reduced, but never completely eliminated, by recrystallization of the sodium thiocyanate. In the calculations which are described later, a correction for this iodine consumption was applied whenever low iodine and high thiocyanate concentrations were involved.

Spectrophotometric measurements were made on a series of solutions in which the initial concentrations of iodine and thiocyanate were varied over a ten- to twentyfold range. These were carried out at a temperature of 7.6° and with the ionic strength fixed at 1 or 5.5. A formation constant, $K = [I_2(SCN)^-]/[I_2][SCN^-]$, was calculated assuming the equilibrium to be

$$I_2 + SCN^- \rightleftarrows I_2(SCN)^-$$

Equilibrium concentrations of each of the species were determined by correction of the initial concentrations of the reactants for the amount consumed in forming the complex. The data from these experiments and calculations are presented in Table II. The constancy of the experimental value of *K* is strong evidence that the assumed stoichiometry is correct.

It will be noted from the data in Table II that the average formation constant at an ionic strength of 5.5 is slightly higher than that at 1 (198 as compared with 192). This difference probably rises

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(8) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

TABLE II

EQUILIBRIUM CONSTANT FOR THE IODINE–THIOCYANATE REACTION AT 7.6°

| $I_2$, $F \times 10^4$ | $SCN^-$, $F \times 10^3$ | Ionic strength | No. of measurements | Av. value for $K$ | Std. deviation of results |
|---|---|---|---|---|---|
| 0.4–3.2 | 10 | 0.99 | 11 | 198 | 10 |
| 1.06–2.09 | 5 | 0.99 | 5 | 193 | 4 |
| 1.37–2.28 | 5 | 5.5 | 8 | 199 | 3 |
| 2.45 | 2–20 | 1.0 | 27 | 190 | 10 |
| 2.24 | 2–20 | 5.5 | 20 | 198 | 5 |

from the more rapid decomposition of the complex at the lower ionic strengths. The instability under these conditions is reflected in the larger standard deviation of the data and would tend to lead to lower values of $K$. One series of data in which the ionic strength was varied over a range of 1 to 5 and where the effects of the decomposition were minimized by rapid preparation and measurement led to a value of $K$ (199) which was constant within the precision of the measurements. Thus it is concluded that the position of the equilibrium is little effected by ionic strength within the range studied.

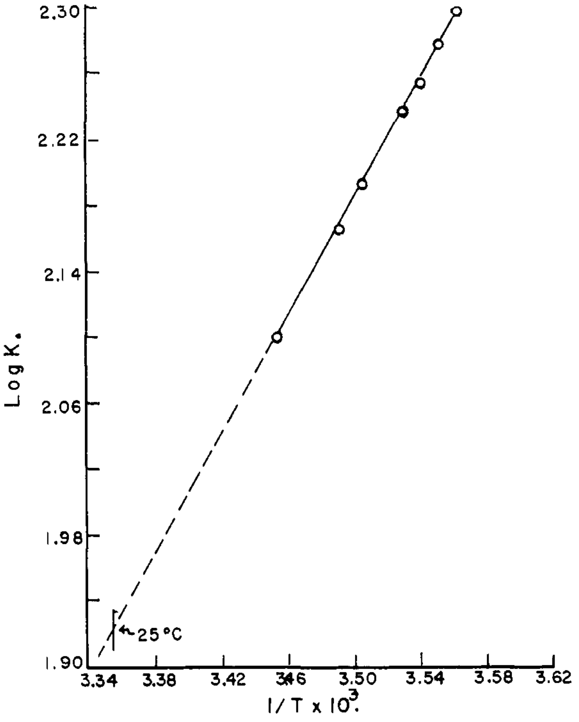

Fig. 5.—Effect of temperature on $K$ in aqueous solutions. Extrapolated value at 25° is 85.

The experimental value for $K$ was also found to be quite independent of the hydrogen ion concentration over a range of perchloric acid concentrations of 0.4 to 1.2 formal.

Variation in the formation constant as a function of temperature is shown in Table III. Calculated values for $\Delta F^0$ are also presented. A plot of log $K$ *vs.* $1/T$ is a straight line as shown in Fig. 5, and from the slope of this curve $\Delta H^0$ for the reaction was found to be −8.1 kcal./mol. A value of −18.4 e.u. was found for $\Delta S^0$.

TABLE III

VARIATION OF $K$ AND $\Delta F^0$ AS A FUNCTION OF TEMPERATURE

| Temp., °C. | $K$ | $\Delta F^0$ |
|---|---|---|
| 7.6 | 198 | −2.94 |
| 8.4 | 189 | −2.93 |
| 9.4 | 179 | −2.91 |
| 10.3 | 172 | −2.90 |
| 12.1 | 156 | −2.87 |
| 13.3 | 146 | −2.84 |
| 16.5 | 126 | −2.79 |
| 25.0 | (85) | −2.65 |

The data in Fig. 5 have been extrapolated from 16.5 to 25° to give a value of $K$ of 85 at room temperature. Attempts also were made to experimentally evaluate the constant at this temperature; these yielded values which decreased from 115 to 30 as the $SCN^-$ concentration was varied from $1 \times 10^{-3}$ to 0.1 $F$; this suggests that at room temperature the single equilibrium postulated above is not adequate for completely describing the system and other reactions are becoming significant. Because of these uncertainties and those arising from decomposition of the solution at the higher temperatures, the extrapolated value of 85 is considered to be a better value for $K$ at room temperature than any experimentally determined constant.

Polar organic solvents such as ethyl acetate, diethyl ether, aliphatic alcohols, etc., found to extract the iodine–thiocyanate complex readily from acidic aqueous solutions, two or three extractions being sufficient for quantitative transfer. Nonpolar solvents such as carbon tetrachloride, benzene and aliphatic hydrocarbons, on the other hand, removed none of the complex under similar conditions. Absorption spectra of the extracted species were found to be similar to those found in water, with a strong absorption maximum occurring at 305 to 310 mμ (305 mμ for ethyl acetate and 308 mμ for diethyl ether; see Fig. 1). A shift in the visible iodine peak toward shorter wave lengths also accompanied the reaction; here again the magnitude of the shift could not be determined because of the overlap of the charge-transfer peak.

It was found possible to form the absorbing species directly by mixing organic solutions of thiocyanic acid with solutions of iodine in the same solvent. It was discovered, however, that water was essential to the appearance of the absorption peak. Thus, when anhydrous solutions of thiocyanic acid and iodine in either ethyl acetate or ether were combined no peak was formed unless a trace of water was added. Furthermore, the extent of the reaction was found to be directly dependent upon the water concentration.

The species responsible for the absorption in ether solutions had many of the characteristics of the iodine–thiocyanate complex in water. It formed rapidly but had only limited stability at room temperature, being decomposed irreversibly and completely after a few hours. At 5 to 10°, however, decomposition was slowed to less than 1 % per hour; furthermore reduction in temperature led to the formation of greater concentration of the absorbing species.

Attempts were made to determine the molar absorptivity of the iodine–thiocyanate complex in ether by the same technique as was used for aqueous solutions, *i.e.*, by employing large enough concentrations of thiocyanic acid and water so that essentially all of the iodine present was in the form of the absorbing species. Because of solubility limitations, however, sufficient concentrations of the two reagents could not be attained to force the reaction to the point where the absorption measurements were completely independent of these concentrations (see Fig. 3). With very small amounts of iodine and maximum water and thiocyanic acid concentrations, the reaction did appear to approach completion and from measurements of these solutions, an approximate value of 30,000 for the molar absorptivity was estimated.

In order to study the stoichiometry of the reaction in ether solutions, and particularly to determine the role of water, spectrophotometric studies were undertaken in which the reagent concentrations were low enough so that the reaction was quite incomplete. Under these circumstances, it was possible to assume that the equilibrium reactant concentrations were not appreciably different from their initial concentrations. The data obtained were treated as follows: the reaction producing the absorbing species was assumed to be

$$m\mathrm{I_2} + n\mathrm{HSCN} + p\mathrm{H_2O} = X$$

where $X$ represents 1 mol of product or products. The equilibrium constant for this reaction can be expressed in terms of the molar absorptivity $\epsilon_x$ of $X$, the absorbance $A$ of solution of $X$ and the cell length $b$.

$$K = \frac{A/\epsilon_x b}{[\mathrm{I_2}]^m[\mathrm{HSCN}]^n[\mathrm{H_2O}]^p} \qquad (1)$$

If conditions are now chosen so that the reaction does not proceed very far to the right, the initial formal concentration of the reactants, $C_{\mathrm{I_2}}$, $C_{\mathrm{HSCN}}$ and $C_{\mathrm{H_2O}}$ can be substituted for the equilibrium concentration. Thus

$$K = \frac{A/\epsilon_x b}{C_{\mathrm{I_2}}{}^m C_{\mathrm{HSCN}}{}^n C_{\mathrm{H_2O}}{}^p} \qquad (2)$$

which may be written as

$$\log A = m \log C_{\mathrm{I_2}} + n \log C_{\mathrm{HSCN}} + p \log \mathrm{H_2O} + \log K\epsilon_x b \quad (3)$$

If $C_{\mathrm{HSCN}}$ and $C_{\mathrm{H_2O}}$ are held constant, a plot of log $A$ *vs.* log $C_{\mathrm{I_2}}$ should yield a straight line of slope $m$. When the experimental data were treated in this way, a very good straight line of slope $1.00 \pm 0.01$ was obtained. Analogous plots gave a value for the combining ratio for $\mathrm{H_2O}$, $p$, of $1.97 \pm 0.07$ and for the combining ratio of HSCN, $n$, of $0.84 \pm 0.02$.

Values for the formation constant in ether solution were calculated with the aid of (2); in these computations, $\epsilon_x$ was assumed to have a value of 30,000. While $K$ was found to remain perfectly constant with respect to wide variation in $C_{\mathrm{H_2O}}$ and $C_{\mathrm{I_2}}$, it decreased appreciably with increases in $C_{\mathrm{HSCN}}$. This is shown by the data in Fig. 6. It will be noted that at high thiocyanic acid concentrations, $K$ appears to be approaching a constant value. From this variation in $K$ and the non-integer value of $n$, it seems clear that the single postulated equilibrium reaction does not completely describe the iodine–thiocyanic acid system in ether solution. This was also indicated by the lack of linearity of a Benesi–Hildebrand plot of the data.

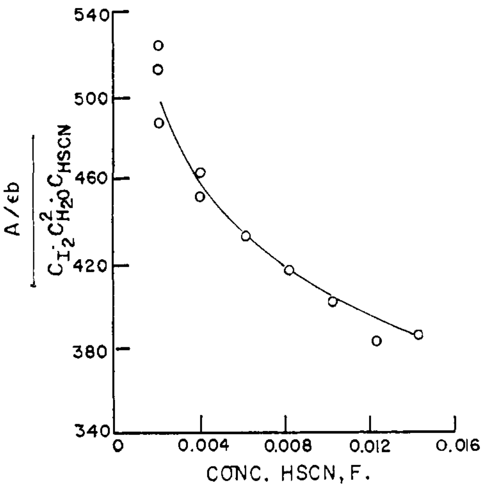

Fig. 6.—Variation in assumed equilibrium constant expression for ether solutions as a function of thiocyanic acid concentration.

Both aqueous and ether solutions containing iodine and thiocyanate were found to undergo a photochemical oxidation in the presence of direct sunlight and dissolved oxygen. The effect of this was to somewhat more than double the absorbance of the solutions when an excess of thiocyanate was present. Solutions freed of oxygen exhibited no absorbance change upon similar treatment. The position of the absorption maximum was unaffected by the oxidation process. Studies by Mr. Calvin Long in these laboratories have demonstrated that other oxidizing agents such as hydrogen peroxide and potassium iodate will cause a similar change in the solutions. These preliminary studies suggest that the stoichiometry of the oxidation in aqueous solutions is

$$\mathrm{I_2(SCN)^-} + 3\mathrm{SCN^-} \rightleftharpoons 2\mathrm{I(SCN)_2^-} + 2\mathrm{e}$$

The absorption spectrum of $\mathrm{I(SCN)_2^-}$ is apparently very similar to that of $\mathrm{I_2(SCN)^-}$. Details of the study of this reaction will be reported in a later publication.

## Discussion

It is clear from this work that in aqueous solutions iodine and thiocyanate ion form a complex having the composition $\mathrm{I_2SCN^-}$. At low temperatures this species is stable and appears to be the predominant one in such solutions. At room temperature other iodine–thiocyanate complexes may exist in appreciable concentrations. It is of interest that our value of 85 for the formation constant at 25° is in reasonable agreement with the 110 obtained by Griffith and McKeown by rather limited distribution studies.[4]

The close similarity between the spectra and the behavior of aqueous and ether solutions suggest strongly that iodine and thiocyanic acid complex in a one to one ratio to give an absorbing product in the latter solvent also. Water is also a participant in the reaction and the stoichiometry appears to be

$$I_2 + HSCN + 2H_2O \rightleftarrows HI_2SCN \cdot 2H_2O$$

It is notable, however, that the plot of log $A$ *vs.* log $C_{HSCN}$ has a slope which is somewhat less than unity and that the experimentally determined equilibrium constant in ether is not entirely independent of the thiocyanic acid concentration. Enough careful measurements were made in determining the slope to convince us that the value obtained 0.84 was not the consequence of a systematic error in the measurement or of impurities in the reagents employed but rather was due to some other equilibrium operating in the solution. One possible reaction which would lead to the observed slopes would involve dimerization of the HSCN. Distribution studies of thiocyanic acid between water and ether eliminated this, however. In the HSCN concentration range studied such a system was found to closely obey the relationship

$$K_D = \frac{(HSCN)_{ether}}{(a_{H^+})_{H_2O}(a_{SCN^-})_{H_2O}}$$

Here the quantity in the numerator is the analytical concentration of HSCN in the ether and the quantities in the denominator are the activities of the two ions in the aqueous solvent.

A possible competing equilibrium which could lead to the experimentally observed slopes for water and iodine and which would also give a HSCN slope of less than unity is

$$HSCN + 2I_2 + 4H_2O \rightleftarrows ISCN \cdot 2H_2O + HI_3 \cdot 2H_2O$$

Here the ratio of the concentration of $ISCN \cdot 2H_2O$ to $HI_2SCN \cdot 2H_2O$ would be independent of the concentration of $I_2$ and $H_2O$ but dependent upon that for HSCN. High concentration of HSCN would favor formation of the $HI_2SCN \cdot 2H_2O$ and a more constant value for the experimentally determined $K$.

The similarity between the absorption spectrum of the iodine–thiocyanic acid complex and those of the 1:1 complexes of iodine and organic sulfides, disulfides and N,N-dimethylaniline derivatives is striking.[9] In various organic solvents, these exhibit strong charge transfer bands with maxima in the region of 300–310 mμ; they also show a similar shift in the visible iodine absorption peak toward shorter wave lengths. It should perhaps be mentioned that because of interaction of the solvent with iodine the values for $K$ and $\Delta H^0$ reported in this paper are not directly comparable with those for the sulfide, and N,N-dimethylaniline with those for the sulfide, disulfide and N,N-dimethylaniline complexes which have all been measured in non-polar solvents.

In contrast to the behavior of thiocyanic acid, *n*-butyl sulfide was found to complex with iodine in the absence of water to give a strong absorption peak. It is also of interest that neither ethyl thiocyanate nor ethyl isothiocyanate form an absorbing product regardless of whether or not moisture is present. These observations suggest that the role of water in the thiocyanic acid–iodine reaction may, in part, involve the formation of an ion pair in which form the thiocyanate is a better electron donor.

**Acknowledgment.**—The authors wish to thank Mr. Calvin Long for his assistance in making some of the spectral measurements reported in this paper.

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[9] S. H. Hastings, *Anal. Chem.*, **25**, 420 (1953); H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961); H. Tsubomura, *ibid.*, **82**, 40 (1960).

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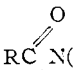
[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, URBANA, ILLINOIS]

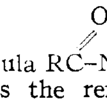
# Thermodynamic Data for Iodine Adducts with a Series of Substituted N,N-Dimethylamides

BY RUSSELL S. DRAGO, DONALD A. WENZ[1] AND ROBERT L. CARLSON[1]

RECEIVED SEPTEMBER 13, 1961

Thermodynamic data for the formation of adducts of iodine with a series of amides of the type  $RC(=O)N(CH_3)_2$ are reported. Compounds investigated include those in which R is either a $-H$, $-C_2H_5$, $-CH_2Cl$ or $-CCl_3$ group. The enthalpies of formation agree well with those expected from the inductive effect of the R group as measured by the $\sigma^*$ values. Deviations are encountered when the equilibrium constants are compared with the $\sigma^*$ values. These deviations are explained by considering the entropy effects that can arise from the rotational isomers that probably exist for some of these amides.

## Introduction

In a recent publication[2] the thermodynamic data for the formation of the adduct between N,N-dimethylacetamide (DMA) and iodine are reported. In conjunction with our program of evaluating basicity of non-aqueous solvents, a systematic study of the basicity of a series of amides of general formula  $RC(=O)-N(CH_3)_2$ was undertaken using iodine as the reference acid. The amides in which R is $-CH_3$, $-H$, $-C_2H_5$, $-CH_2Cl$ and $-CCl_3$ have now been investigated. This series of compounds provides a set of solvents of varying basicity. N,N-Dimethyl propionamide (DMP) and DMA are more basic toward iodine than N,N-dimethylformamide (DMF); while N,N-

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[1] Abstracted in part from the Ph.D. theses of Donald A. Wenz, University of Illinois (1961) and Robert L. Carlson, University of Illinois (1962).

[2] R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).