This temperature was not measured experimentally but since the calculated flame temperature at atmospheric pressure has been confirmed by direct measurements and in view of the precision of the calculated values, it is not unreasonable to assume that this temperature is actually obtained at 100 p.s.i. (this value accounts for the reactants being preheated to 100°).

A study of the flashback velocities at various pressures yielded the data in Fig. 5. In making these measurements the rates of each gas were set to give the stoichiometric composition and the chamber pressure was gradually increased until a flashback was obtained. The gas rates were kept constant as the chamber pressure was increased. The value at 4.4 atmospheres was not determined accurately. A flashback at this pressure was obtained at 400 cc./min. but not at 800 cc./min. From visual observations it was estimated that no flashback would be obtained at 500 cc./min. These data indicate that the linear velocity through the torch corresponding to flashback is very sensitive to pressure.

## Conclusions

The theoretical flame temperature for the combustion of cyanogen in oxygen is in good agreement with the experimental value providing the high value for the dissociation of nitrogen is used.

A technique is proposed for the operation of the cyanogen–oxygen flame (or other premixed flames) under pressure which provides for fairly safe (explosion-free) operation.

Blow-off rates for the cyanogen–oxygen mixtures at atmospheric pressure are presented and indicate velocity boundary gradients which are much lower than corresponding values for methane–oxygen mixtures. Flashback data at various pressures indicate that the linear velocity through the torch at flashback is very sensitive to pressure.

**Acknowledgments.**—The authors acknowledge the contribution of Dr. R. H. Wilson, Jr., in developing the modified line-reversal technique using the sun as the comparison radiator. The assistance of W. Smith and W. Liddell in the experimental portions of this study is also gratefully acknowledged.

PHILADELPHIA, PENNA.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

# Studies on the Chemistry of Halogens and of Polyhalides. XV. Iodine Halide Complexes with Acetonitrile[1]

BY ALEXANDER I. POPOV AND WILLIAM A. DESKIN

RECEIVED JANUARY 2, 1958

Slow chemical changes occurring in acetonitrile solutions of iodine halides have been investigated conductometrically and spectrophotometrically. It is shown that acetonitrile forms 1:1 complexes with iodine monochloride, iodine bromide and iodine, and that the respective formation constants are 6.9 ± 0.3, 1.40 ± 0.03 and 0.57 ± 0.02. Experimental evidence indicates that in the absence of impurities or of ultraviolet radiation there is a slow transition of the "outer complex" $CH_3CN \cdot IX$ to the "inner complex" $[CH_3CN \cdot I]^+X^-$. This slow transition is responsible for the gradual increase in conductance of the solutions and for the changes in the absorption spectra.

## Introduction

When iodine or iodine halides are dissolved in polar solvents, they usually act as weak electrolytes and the resulting solutions show an appreciable electrical conductance. However, one of the puzzling aspects of such solutions is the fact that the conductance does not remain constant, but rather it tends to increase with time.[2] It also has been observed that there are time-dependent changes occurring in the absorption spectra of these solutions which roughly parallel the changes in the electrical conductance. These phenomena have been especially evident in acetonitrile solutions.

In general, this behavior has been ascribed to the reaction of the halogens either with the solvent or with a trace impurity remaining in the solvent. In recent years, however, a number of cases of similar slow change in solution properties have been reported where the solutes were much less reactive than the halogens and where a specific chemical reaction between the solvent and the solute is highly improbable.[3] Also, careful purification of the solvents did not do away with the gradual increase in conductance.[2] It was therefore decided to re-investigate the behavior of iodine and iodine halides in acetonitrile solution under carefully controlled conditions in an attempt to establish the reasons for the gradual changes in the absorption spectrum and in conductance.

## Experimental Part

**Iodine Halides.**—Iodine monochloride was prepared by the method of Cornog and Karges.[4] It was first purified by sublimation in the usual manner. The resulting product was then introduced into a glass vacuum apparatus and further purified by several fractional crystallizations. The final product was sealed in a series of glass ampules until needed. The m.p. was 27.2°, identical with the literature value.[4]

Iodine bromide was obtained as previously described[2] and was purified by fractional crystallization until the same melting point was obtained on several repeated crystallizations. The final m.p. was 41.5°, rep. 42°.[5] Iodine of A.R. grade was purified by sublimation from a mixture of barium oxide and potassium iodide.

**Solvents.**—Acetonitrile and carbon tetrachloride were purified by standard methods.[2,6] The specific conductance of acetonitrile was 0.5 to 1.2 × $10^{-7}$ ohm$^{-1}$ cm.$^{-1}$. The best literature value is 0.5 to 0.9 × $10^{-7}$ ohm$^{-1}$ cm.$^{-1}$.[7]

**Absorption Spectra.**—Absorption spectra were obtained on a Cary recording spectrophotometer model 11, using stoppered silica cells of path length 1.00 ± 0.01 cm. In certain cases, 2, 5 and 10 cm. silica cells of comparable precision were used. In one series of experiments with con-

---

(1) Abstracted from the Ph.D. Thesis of William A. Deskin, State University of Iowa, June, 1957.

(2) A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3722 (1955).

(3) C. M. French and L. G. Roe, *Trans. Faraday Soc.*, **49**, 314, 791 (1953).

(4) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 165.

(5) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

(6) A. I. Popov, D. H. Geske and N. C. Baenziger, THIS JOURNAL, **78**, 1793 (1956).

(7) V. A. Pleskov, *Zhur. Fiz. Khim.*, **22**, 351 (1948).

centrated solutions modified infrared sandwich cells with silica windows and a polyethylene spacer were used. The optical path length was 0.153 ± 0.002 cm. The data reported here were obtained at room temperature of approximately 25°.

**Conductivity Measurements.**—The conductance measurements were obtained with a Leeds and Northrup apparatus consisting of a Campbell-Shackelton ratio box, an adjustable air capacitor, an audiofrequency oscillator, a tuned audiofrequency amplifier and a decade resistance box. The over-all accuracy of the resistance measurements was ±0.1%. Conductance cells of the Jones-Bollinger type having constants of 0.1276, 0.1162 and 0.04145 were used to keep the resistance of the solutions between 1000 and 15000 ohms. An additional cell was constructed with a constant of 0.0012 and was used to measure the specific conductance of solvent. The cells were calibrated in the usual manner with potassium chloride solutions using specific conductance values given by Shedlovsky.[8] The cell constants were corrected for the Parker effect. The conductance cells were maintained at 25.00 ± 0.01° in an oil-bath.

A closed system electrical conductance apparatus was also prepared which permitted one to carry out purification of the solvents, preparation of solutions and to make conductance measurements at various dilution with all of the operations being carried out under a dry nitrogen atmosphere. The detailed description of this apparatus is given elsewhere.[9] The apparatus was also fitted with an adapter which made it possible to fill a Cary absorption cell with the studied solution again avoiding all contact with atmospheric moisture.

## Experimental Results

A series of conductance measurements were made on iodine monochloride solutions in acetonitrile at concentrations varying from $1 \times 10^{-3}$ to $3 \times 10^{-2}$ *M*. The solutions were prepared, and the conductance cells were filled in a dry-box under nitrogen atmosphere. The concentrations were determined by iodometric titrations. The results were similar to those previously reported, *i.e.*, the conductances increased with time and would not reach a constant value even after a number of days. In general the specific conductance extrapolated to zero time, varied between 0.5 to $3 \times 10^{-5}$ ohm$^{-1}$ but showed considerable variation from solution to solution. On occasions, more concentrated solutions exhibited smaller specific conductances than the dilute ones. The rate of increase was likewise variable, but was apparently faster for more dilute solutions. Conductance measurements carried out in closed system showed essentially the same behavior, but the rate of change was noticeably slower.

Since these measurements often took more than two weeks to complete, there was remaining always a possibility that notwithstanding the precautions taken, traces of atmospheric moisture could penetrate into the conductance cells of the apparatus and be responsible for the change in conductance. In order to avoid this possibility the apparatus was fitted with a separate cell which was attached to the draining tube of the solution chamber. This cell was filled with a portion of the previously prepared solution, and immersed in a Dry Ice-chloroform-carbon tetrachloride bath in order to freeze the solution. The cell was then sealed with a hand torch, warmed to room temperature and immersed in a constant temperature bath. The electrical conductance of this solution as well as of the solution in the apparatus was then measured periodically; the results are shown in Fig. 1. Although even after 310 hours the conductance does not reach a constant value, the variation of conductance is identical in both cases within the limits of experimental data.

After this run was completed the solutions were removed and the total halogen concentration of each solution was determined by iodometric titration. These concentrations were found to be identical to those of the original solution within the limits of experimental error. Both solutions, likewise, showed an absorption maximum at 227 mμ, characteristic of the $ICl_2^-$ ion. This absorption was approximately five times as great as the absorption of the original solution.

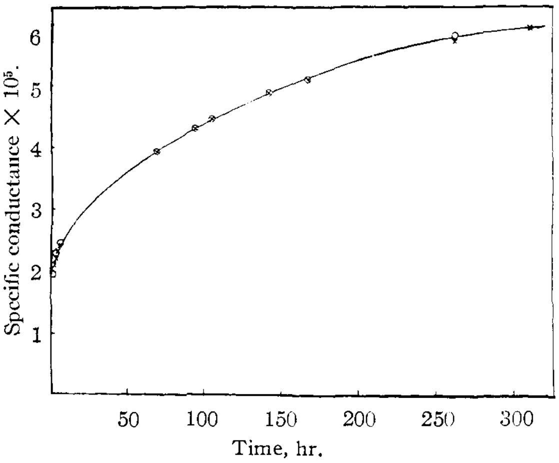

Fig. 1.—Variations in electrical conductance of iodine monochloride solutions in acetonitrile: o, closed system; x, sealed cell.

In another experiment a $1.03 \times 10^{-3}$ *M* solution of iodine monochloride in acetonitrile was divided into several portions some of which were kept in the dark, others exposed to daylight in a dry box, and still others were placed in a Pyrex flask and in a silica cell and were irradiated by ultraviolet lamp. The absorption spectra of these solutions were studied after varying intervals of time. All of the solutions showed a rapid increase in intensity of the absorption band at 227 mμ; however, the irradiated solution showed much greater initial increase in absorption which, after reaching a maximum value in 25 hours, began to decrease in intensity.

Simultaneously a growth of an absorption peak at 260 mμ, characteristic of the $I_2Cl^-$ ion was observed. If the exposure to ultraviolet radiation is continued, the absorption changes further to that characteristic of $I_3^-$ ion (absorption maxima at 360 and 290 mμ). Other solutions did not show either the $I_2Cl^-$ or $I_3^-$ bands even after 100 hours.

Since acetonitrile behaves as a "brown" (*i.e.*, complexing) solvent with iodine and iodine halides, it was of interest to establish the empirical formula of such complexes and also to evaluate their stability constant.

A series of solutions were prepared in carbon tetrachloride in which the concentration of iodine monochloride was kept constant at $1.36 \times 10^{-2}$ *M* but the concentration of acetonitrile progressively increased from $0.382 \times 10^{-2}$ to $6.63 \times 10^{-2}$ *M*. The absorbence of these solutions was then determined at 350, 360 and 370 mμ and the data obtained for each wave length were plotted against the mole ratio $CH_3CN/ICl$. In all three cases a clear break in the plot was observed at equimolar concentrations of the two components, showing the complex to be $CH_3CN \cdot ICl$ (Fig. 2). The increase in absorption beyond the stoichiometric amount of acetonitrile indicates that the complex is quite unstable.

The stability of this constant was determined by the Benesi-Hildebrand[10] method as modified by Scott.[11] These authors have shown that when two species A and B react to form a 1:1 complex AB in solution, and provided that the (a) complex shows an absorbence at a wave length where A and B do not absorb, and (b) the concentration of one of the components in a series of solutions is considerably larger than that of the other component, *i.e.*, [A] >> [B], the relationship between the two original concentrations, the molar absorbtivity ($a_m$) and the formation constant ($K_f$), in a cell of path length $b$, is given by

$$\frac{[B]b}{A_s} \times [A] = \frac{[A]}{a_m} + \frac{1}{K_f a_m}$$

A plot of $([B]b/A_s)$ [A] *vs.* [A] should give a straight line with a slope of $1/a_m$ and an intercept $1/K_f a_m$.

A series of solutions were prepared in carbon tetrachloride in which the concentration of acetonitrile was always considerably greater than that of iodine monochloride. The absorbence was measured at several wave lengths and the

---

(8) T. Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

(9) A. I. Popov, W. A. Deskin and N. E. Skelly, *Proc. Iowa Acad. Sci.*, **64**, 242 (1957).

(10) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949).

(11) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

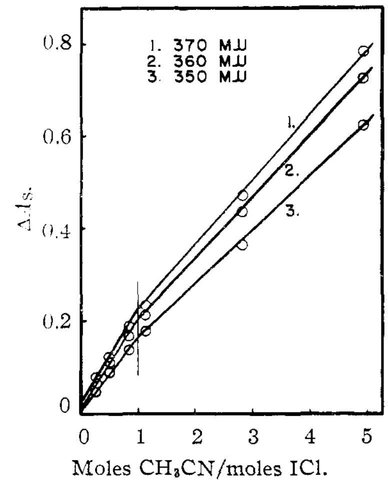

Fig. 2.—Mole ratio plot of ICl-$CH_3CN$ system in carbon tetrachloride.

factor ($[B]/A_s$)$[A]$ was plotted *vs.* [A]. Typical results are shown in Table I. The plots are given in Fig. 3 and it is seen that satisfactory straight lines were obtained. The calculated values of the molar absorptivity and of the formation constant are given in Table I.

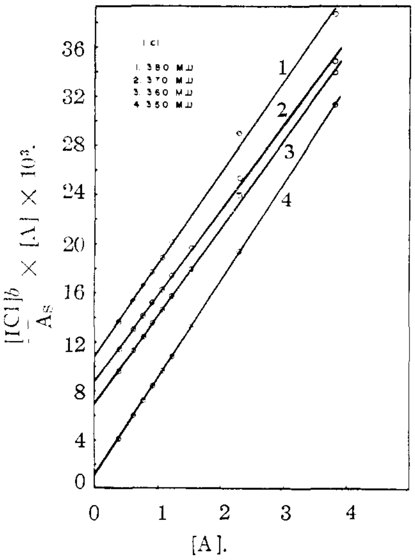

Fig. 3.—Benesi-Hildebrand-Scott plot for ICl-$CH_3CN$ system. Ordinate values are given for 350 mμ. Subtract 6, 8 and 10 × $10^{-3}$ for curves 360, 370 and 380 mμ, respectively.

The use of the Benesi-Hildebrand-Scott method in this particular case was complicated by two factors. In the first place, iodine monochloride shows some absorption at the wave lengths used, secondly, in solutions containing appreciable amounts of acetonitrile, it partially formed the iododichloride ion $ICl_2^-$. The first difficulty was largely circumvented by neglecting the absorption due to free iodine monochloride in the first approximation, and calculating the approximate value of $K_f$. Subsequently, this $K_f$ value is used to calculate the fraction of free iodine monochloride in each solution, and from its known molar absorptivity calculating the correction factor for the total absorbence. The Benesi-Hildebrand-Scott equation is replotted and a more exact value of $K_f$ is obtained. Further successive approximations are used until a convergent value of $K_f$ is obtained.

Since the conversion of iodine monochloride to the $ICl_2^-$ ion is time and concentration dependent, correction in this case appears to be impossible to obtain with any degree of accuracy. However, if the data at 350 mμ were used, the correction becomes unnecessary since at this wave length the molar absorptivity of iodine monochloride is one-half of that of the iododichloride ion, and the absorbence due to iodine monochloride remains constant irrespective of the fraction in the $ICl_2^-$ form. It thus seems that the values of $K_f$ obtained at 350° mμ are more reliable than those at other wave lengths but in practice it was noted that the difference was rather small.

For comparison purposes the formation constants of iodine bromide and of iodine complexes with acetonitrile were obtained in the similar manner. Again, the wave lengths were so chosen as to avoid a correction for $IBr_2^-$ and $I_3^-$ ions, respectively. The experimental results are shown in Figs. 4 and 5, and the formation constants are, respectively, 6.9 ± 0.3, 1.40 ± 0.03 and 0.57 ± 0.02 for iodine monochloride, iodine bromide and iodine.

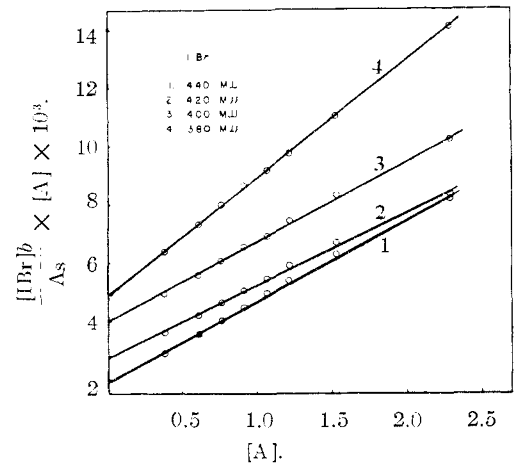

Fig. 4.—Benesi-Hildebrand-Scott plot for IBr-$CH_3CN$ system. Ordinate value given for 440 mμ. Subtract 1 × $10^{-3}$ for 420 mμ and 2 × $10^{-3}$ for 400 and 380 mμ.

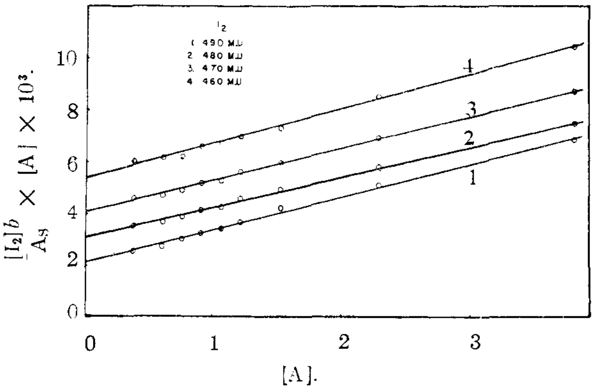

Fig. 5.—Benesi-Hildebrand-Scott plot for $I_2$-$CH_3CN$ system. Ordinate value given for 490 mμ. Subtract 1, 2 and 3 × $10^{-3}$ for 480, 470 and 460 mμ, respectively.

## Discussion

It seems that the experimental results described above give a rather strong indication that the change in the absorption spectra and in the conductance of halogen solutions in acetonitrile are *not due entirely* to an interaction of the iodine halides either with trace impurities or with the solvent itself. The fact that this change occurs even in rigorously purified solvents and under completely anhydrous conditions and also that under these circumstances the concentration of total titratable halogen remains essentially constant in spite of the changes in conductance and in absorption spectra

TABLE I

SPECTROPHOTOMETRIC DATA FOR THE REACTION OF IODINE MONOCHLORIDE AND ACETONITRILE IN CARBON TETRACHLORIDE SOLUTION AT 25°[a]

| | | $\frac{[\mathrm{ICl}]b}{A_s}$ | | | |
|---|---|---|---|---|---|
| [ICl] × 10³, moles/l. | $A$, moles/l. | 350 mμ | 360 mμ | 370 mμ | 380 mμ |
| 0.68 | 3.81 | 31.34 | 27.97 | 26.81 | 28.69 |
| 1.36 | 2.29 | 19.39 | 17.94 | 17.34 | 18.99 |
| 3.41 | 1.53 | 13.28 | 11.99 | 11.64 | 12.52 |
| 5.46 | 1.22 | 10.81 | 9.76 | 9.45 | 10.14 |
| 6.82 | 1.07 | 9.65 | 8.65 | 8.29 | 8.88 |
| 8.18 | 0.915 | 8.43 | 7.58 | 7.24 | 7.71 |
| 10.23 | .763 | 7.24 | 6.44 | 6.14 | 6.54 |
| 12.28 | .610 | 6.00 | 5.32 | 5.06 | 5.35 |
| 13.64 | .382 | 4.11 | 3.65 | 3.44 | 3.64 |
| | $K_f$ | 6.84 | 6.87 | 7.05 | 7.26 |
| | $a_m$ | 126 | 140 | 145 | 135 |

[a] Values of $K_f$ and $a_m$ are calculated by the method of least-squares.

seems to offer sufficient justification for the above conclusions. It therefore becomes necessary to postulate some other mechanism for the changes observed in these solutions.

It is interesting to note that other substances such as picrates[3] or hydrogen chloride[12] in acetonitrile solutions also show increase in conductances and changes in absorption spectra with time.

In the case of picric acid solutions it has been shown by French and Roe[3] that increase in conductance of these solutions is accompanied by the changes in absorption spectra from that of undissociated picric acid to that of the picrate ion. It has been postulated therefore that these authors observed a "slow ionization" Pic.H → Pic⁻ + H⁺. It seems that the changes observed in halogen solutions are essentially of the same type, that is, we may have a "slow ionization" of the acetonitrile halogen complex.

As in the case of other halogen complexes, this complex appears to be of the "charge-transfer" type. According to Mulliken[13] there are two types of charge complexes, the outer complex $B{\cdot}X_2$ and the inner complex $BX^+{\cdot}X^-$. Mulliken points out[14] that in the case of pyridine–iodine complex slow increase in conductance is due to a slow passage from outer to inner complex over a barrier of considerable height. It seems that a similar explanation would be valid for iodine halides–acetonitrile complexes, *provided that the solvent is pure* and the solutions are not exposed to ultraviolet radiation. It thus becomes possible to postulate the following reactions in acetonitrile solutions of iodine halides

$$\mathrm{CH_3CN + IX \rightleftharpoons CH_3CN{\cdot}IX} \qquad (1)$$

$$\mathrm{CH_3CN{\cdot}IX \rightleftharpoons CH_3CN{\cdot}I^+X^-} \qquad (2)$$

$$\mathrm{CH_3CN{\cdot}I^+{\cdot}X^- \rightleftharpoons [CH_3CN{\cdot}I]^+ + X^-} \qquad (3)$$

$$\mathrm{IX + X^- \rightleftharpoons IX_2^-} \qquad (4)$$

Reaction 2, which illustrates the formation of the inner complex, is slow, all other reactions are fast.[15]

Because of the reactive nature of iodine halides, it is quite obvious that in the presence of impurities or of ultraviolet radiation other reactions do take place. The fact that exposure of iodine halide solutions in acetonitrile to radiation results in the formation of $I_2Cl^-$ and eventually $I_3^-$ absorption bands can be explained by the chlorination reaction of the solvent. Indeed, in this case, we can have

$$\mathrm{RH + ICl \longrightarrow RCl + H^+ + I^-} \qquad (5)$$

$$\mathrm{I^- + ICl \longrightarrow I_2Cl^-} \qquad (6)$$

$$\mathrm{2I_2Cl^- \longrightarrow I_3^- + ICl_2^-} \qquad (7)$$

The fact that diiodochloride ion can disproportionate into $I_3^-$ and $ICl_2^-$ has been shown previously.

An alternate explanation for the slow formation of the $ICl_2^-$ ion could be the iodination of the solvent according to

$$\mathrm{RH + ICl \longrightarrow RI + HCl} \qquad (8)$$

$$\mathrm{HCl + ICl \longrightarrow H^+ + ICl_2^-} \qquad (9)$$

However, it appears to be extremely unlikely that in iodoacetonitrile the iodine would be sufficiently positive to be titratable iodometrically.

**Acknowledgment.**—The authors are indebted to the Research Corporation for the support of this work.

IOWA CITY, IOWA

---

[12] G. J. Janz and S. S. Danyluk, to be published.

[13] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[14] Ref. 13, p. 812.

[15] It is also possible that there are two molecules of acetonitrile coördinated to the "positive" iodine, and the reactions 3 and 4 may be represented by $\mathrm{2CH_3CN{\cdot}I^+{\cdot}X^- \rightleftharpoons [(CH_3CN)_2I]^+ + IX_2^-}$. See THIS JOURNAL, **79**, 570 (1957).