

boron. It is proposed that a similar steric interaction toward the N_2O_2 group prevents the formation of stable adducts with these amines. Small amounts of the alkyl ammonium nitrites are obtained instead.

Some definite trends in the stability of the amine-nitric oxide products have been noted. The ammonium salts of the straight chain primary amines show a stepwise increase in stability from methylamine through *n*-butylamine. The *n*-amylamine product is comparable in stability to that of methylamine. Isopropylamine and cyclohexylamine form compounds which are more stable than those of the straight chain primary amines. The stability difference of the *sec*-butylamine and isopropylamine product is surprising.

The nitric oxide products of symmetrical, straight chain secondary amines exhibit a steady increase in stability from the diethylamine through the di-*n*-hexylamine products; relatively, the latter two members of the series are very stable. Two branched-chain analogs, diisopropylamine and di-

sec-butylamine do not form product but give very low yields of the alkylammonium nitrites.

These observations on "stabilities" are purely qualitative and are based upon visual observation of the ease of decomposition of the material. It has not been possible to correlate all of the "stabilities" described above with any single property of the amine donor. The basicity of the amine, crystal lattice effects, steric effects and volatility of the amine are all important considerations. With few exceptions, the stability of the products parallel the basicity of the amines as measured by the heat of formation of the trimethylboron adducts. There are some exceptions to this general rule in instances where one or more of the above factors become controlling.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA]

Stability of the Chloro-complexes of Iodine in Aqueous Solution¹

BY D. L. CASON AND H. M. NEUMANN²

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Spectrophotometric measurements have been used to study the stability in aqueous solution of the chloro-complexes of iodine in the (0), (I) and (III) oxidation states. The ion I_2Cl^- is characterized by absorption maxima at 248 and 437 $m\mu$. Qualitative observations were made on the conditions necessary for disproportionation of I_2Cl^- to I^- and ICl_2^- and for the air oxidation of I_2Cl^- to ICl_2^- . The dissociation constant for I_2Cl^- was determined by a spectrophotometric method, and the value so obtained was compared with the variety of values in the literature. The most probable value is 0.60. The ion ICl_2^- is characterized by absorption maxima at 224 and 343 $m\mu$, and the spectral data on its dissociation are consistent with the work of Faull. Spectral evidence for ICl_1^- could not be found, either in solutions prepared from ICl_3 or from KI , KIO_3 and HCl . Solutions equivalent to iodine (III) in terms of oxidation were found to be equimolar mixtures of ICl_2^- and IO_3^- .

The existence of chloro-complexes of iodine in the (0), (I) and (III) oxidation states has been well established. However, there are a number of conflicting statements in the literature as to the stability of these complexes in aqueous solution. The purpose of this work is to determine the conditions under which these complexes exist in aqueous solution. It was hoped that this evidence would aid in interpreting the behavior of astatine in chloride solutions. Evidence for the existence of a chloro-complex of astatine has been presented,³ but it has been difficult to make arguments about the oxidation state without further information about the behavior of iodine.

The work reported here has established the nature and amount of the iodine species in chloride solutions where the iodine concentration is in the range 10^{-5} to 10^{-3} *M*. In addition to the experimental work, which has principally involved spectrophotometric measurements, the earlier data in the literature has been evaluated.

Experimental

Materials.—A sample of commercial iodine was ground into powder and treated with successive portions of water to

dissolve salts. It was then thoroughly dried and purified by sublimation.

Iodine monochloride was made by treating the purified iodine with condensed chlorine according to the method of Cornog and Karges.⁴ It was purified by two or three recrystallizations.

A modification of the method of Booth and Morris⁵ was used for the preparation of iodine trichloride. Small amounts of liquid ICl were added, a drop or two at a time, to condensed chlorine. After all the ICl was added, most of the excess chlorine was allowed to evaporate from the solid ICl_3 . When solutions of ICl_3 were desired some ICl_3 crystals would be shaken out onto a piece of paper, allowed to stand for a few seconds to let the excess Cl_2 escape and then added to the solvent without further delay.

All other chemicals were commercial materials of reagent grade. The concentrations of stock solutions were determined by the standard iodometric method.

Spectral Measurements.—The absorption spectra were determined with either a Beckman Model DU spectrophotometer or a Beckman Model DK-1 spectrophotometer. Most of the measurements were made with matched, fused silica cells having a light path of 1.000 ± 0.003 cm. A water jacket was used to keep the cells at a constant temperature of $25.0 \pm 0.5^\circ$. Even though the cells were cleaned repeatedly, fluctuations in readings occasionally appeared due to impurities in the cells. This difficulty with iodine solutions has been observed and discussed by other workers.⁶

(1) Taken in part from a thesis submitted by Dennis Lamar Cason in partial fulfillment of the requirements for the M.S. degree, June 1959.

(2) Requests for reprints should be addressed to this author.

(3) H. M. Neumann, *J. Inorg. Nuclear Chem.*, **4**, 349 (1957).

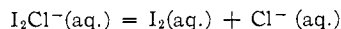
(4) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 165.

(5) H. S. Booth and W. C. Morris, *ibid.*, p. 167.

(6) J. H. Wolfenden, *Anal. Chem.*, **29**, 1098 (1957).

The data are expressed in terms of the absorbancy, A , of a particular solution or in terms of the molar absorbancy index, a , of a particular species. For a solution containing a single absorbing species these will be related by the equation, $A = a c l$, where c is the molar concentration of the species and l is the cell thickness in cm.

Dissociation Constant Experiments.—For the equilibrium



the dissociation constant is given by

$$K = \frac{[\text{I}_2][\text{Cl}^-]}{[\text{I}_2\text{Cl}^-]}$$

if activity coefficients are ignored or by

$$K_a = \frac{[\text{I}_2][\text{Cl}^-]y_{\text{I}_2}y_{\text{Cl}^-}}{[\text{I}_2\text{Cl}^-]y_{\text{I}_2\text{Cl}^-}} = \frac{[\text{I}_2][\text{Cl}^-]}{[\text{I}_2\text{Cl}^-]} F = KF$$

if they are not.

For absorption at a wave length where I_2Cl^- and I_2 are the only absorbing species

$$A = (a_{\text{I}_2\text{Cl}^-}[\text{I}_2\text{Cl}^-] + a_{\text{I}_2}[\text{I}_2])l$$

To determine the dissociation constant, a series of experiments is performed in which the stoichiometric concentration of iodine is fixed at c_0 , *i.e.*, $c_0 = [\text{I}_2] + [\text{I}_2\text{Cl}^-]$, but in which $[\text{Cl}^-]$ is varied. Letting $A_{\text{I}_2} = a_{\text{I}_2}c_0l$ and $A_{\text{I}_2\text{Cl}^-} = a_{\text{I}_2\text{Cl}^-}c_0l$, appropriate substitution and manipulation give

$$A = A_{\text{I}_2\text{Cl}^-} - \frac{K_a(A - A_{\text{I}_2})}{F[\text{Cl}^-]}$$

If A_{I_2} is known and F can be estimated reasonably well, A can be plotted *versus* $(A - A_{\text{I}_2})/F[\text{Cl}^-]$. The slope of such a plot will be $-K_a$, and the intercept on the A -axis will be $A_{\text{I}_2\text{Cl}^-}$. Thus, in addition to providing a determination of K_a , the spectrum of I_2Cl^- can be reconstructed. The method used in estimating F will be discussed in the section on the solubility of I_2 .

One series of measurements was made in the visible region, using the DU spectrophotometer and the one cm. cells. In this series the slit width was kept constant at any one wave length so that the readings would be comparable.

A second series was made in the ultraviolet region, using the DK spectrophotometer and 1 cm. cells containing 0.9 cm. silica plugs to reduce the light path to 0.1 cm. In the latter series dust impurities were particularly troublesome. After a thorough initial cleansing the cells and plugs were kept immersed in a 6 *M* HCl solution when not in use. Rubber gloves were worn during handling operations.

The spectra were recorded immediately after filling the cells and then periodically during the next 30 minutes. The data were considered invalid if the spectrum changed by more than a few per cent. during this time interval.

Results

Spectral Characteristics.—Table I records the values of λ_{max} and a_{max} determined for species of interest in this study. Comparison with values previously reported in the literature have been made where possible.

TABLE I

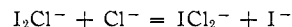
Species	λ_{max}	a_{max}	Ref.
ICl_2^-	343	243	This work
	343	275	^a
	224	47,000	This work
I_2Cl^-	437	1,100	This work
	247	...	^b
	248	55,000	This work
I_2	460	728	This work
	460	746	^c
	270	121	^c

^a Ref. 33. ^b L. I. Katzin, *J. Chem. Phys.*, **20**, 1165 (1952). ^c A. D. Awtry and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842(1951).

Iodine(0).—When solid I_2 is dissolved in hydrochloric acid the iodine solutions present initially as I_2 and I_2Cl^- , and the spectral characteristics

are those of the mixture. If the solution is allowed to stand the absorption maximum at about 440 $m\mu$ drops and a new peak rises near 340 $m\mu$. The titer of the solution, as determined by iodometric titration, changes at the same time; when the 440 $m\mu$ peak has entirely disappeared, the titer has doubled its original value. Trial runs with various concentrations of HCl in the range 1–12 *M* showed that the rate of disappearance of I_2 was strongly dependent on the acidity, and incidentally also on the volume of air in the closed flask. These facts suggest that the reaction is air oxidation to ICl_2^- . From the practical point of view it was observed that the spectrum of a 3 *M* HCl solution only changes 10% over a period of 11 days, so that it is feasible to make stock solutions at this or lower acidities.

Both the ultraviolet and visible peaks of solutions of I_2 in 3 *M* HCl were found to deviate from Beer's law at sufficiently low iodine concentrations. The visible peak adhered satisfactorily to the law for iodine concentrations greater than 10^{-4} formal. Solutions about 10^{-5} formal in I_2 have a peak in the ultraviolet at 248 $m\mu$ (I_2Cl^-) with a hump on the short wave length side suggesting the presence of some ICl_2^- . This spectrum may be observed within minutes after preparation of the solution, and it does not change with time. The spectrum is the same in both 3 *M* HCl and 3 *M* KCl. When the iodine concentration is reduced further, the peak appears at 224 $m\mu$ with a hump at 248 $m\mu$. These effects provide evidence of the disproportionation reaction



Dissociation Constant of I_2Cl^- by Spectral Method.—Several conflicting values of the dissociation constant of I_2Cl^- have been reported, so that an independent measurement and a re-evaluation of previous results seemed in order. The principle of the spectral method has been outlined in the experimental section. Measurements were made in the region of both the ultraviolet and visible peaks, using HCl solutions in the concentration range 0.1–6 *M*. The iodine concentrations were compromise values; large enough to keep the extent of disproportionation small but small enough to give reasonable absorbancy readings with the cells available. Figure 1 shows the spectra obtained in the visible region for a series of solutions in which the stoichiometric iodine concentration, C_0 , is 5.33×10^{-4} formal and the light path is 1 cm. Determination of the dissociation constant from data in this region has the advantage that species which might be present as minor constituents, such as I^- , I_3^- , ICl_2^- or HOI , do not absorb strongly in this region; but has the disadvantage that the spectra of I_2Cl^- and I_2 overlap to a considerable extent. Figure 2 shows the spectra obtained in the ultraviolet region for a series of solutions in which C_0 is 2.60×10^{-4} formal and the light path is 0.1 cm. In this region the absorption by I_2Cl^- is considerably greater than that by I_2 , which is a favorable circumstance; but the possible minor constituents absorb strongly.

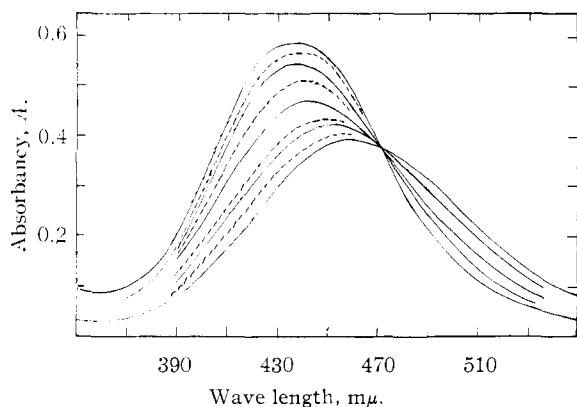


Fig. 1.—Spectra in the visible region. Curves, from top to bottom at 440 $m\mu$, are: reconstructed spectrum of I_2Cl^- , spectra in 5.7, 3.07, 1.23, 0.75, 0.31, 0.20, 0.098 M HCl and in 0.12 M $HClO_4$.

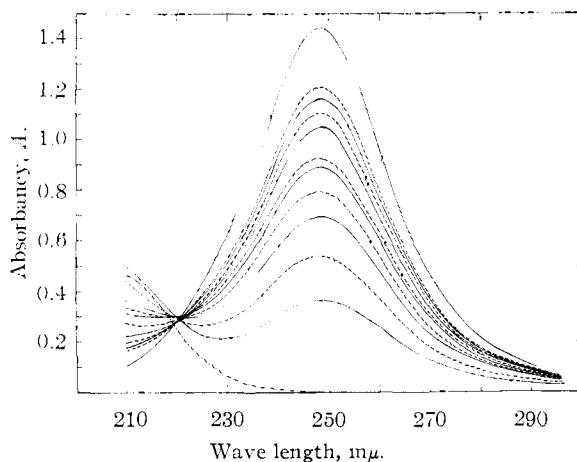


Fig. 2.—Spectra in the ultraviolet region. Curves, from top to bottom at 250 $m\mu$, are: reconstructed spectrum of I_2Cl^- , spectra in 2.90, 2.45, 2.02, 1.55, 1.12, 0.94, 0.75, 0.57, 0.39, 0.20 M HCl and in 0.10 M $HClO_4$.

In order to provide information on how the spectrum of iodine is affected by acidity, the spectra of 1.15×10^{-4} formal solutions of I_2 in 0.1–1 M $HClO_4$ were examined, using 1 cm. cells. A lower I_2 concentration was used in the $HClO_4$ experiments than in the HCl experiments to make the spectra more comparable from the point of view of possible disproportionation, since $[I_2]$ is less than c_0 in the HCl solutions. In the visible region the spectra of the $HClO_4$ solutions were nearly identical. There was, however, a small increase (10% at most) in absorbance with increasing acidity in the region of 520 $m\mu$. This observation suggests that a small fraction of the I_2 may exist in a non-solvated condition⁷ in $HClO_4$ solutions.

The spectra of these solutions are sufficiently alike so that any one of them could be used to give A_{I_2} for the determination of the dissociation constant. The curve shown in Fig. 1 is for a 0.12 M $HClO_4$ solution, corrected for the difference in c_0 . The presence of an isosbestic point at 470 $m\mu$ is strong evidence for only two major forms of iodine in these solutions. In Fig. 3 are shown plots

(7) J. G. Bower and R. L. Scott, *J. Am. Chem. Soc.*, **75**, 3583 (1953).

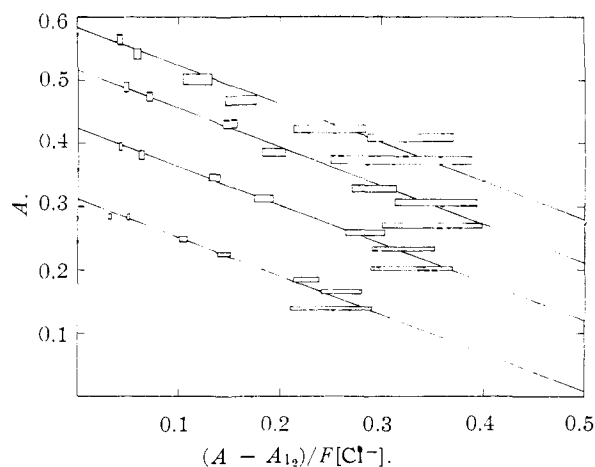


Fig. 3.—Determination of the dissociation constant for I_2Cl^- from data in the visible region; data for wave lengths of 440, 420, 410 and 400 $m\mu$.

of A vs. $(A - A_{I_2})/F[Cl^-]$ for selected wave-lengths. The slope which best satisfies all of the data is -0.60 . The intercepts from plots such as these give the reconstructed spectrum of I_2Cl^- shown in Fig. 1.

The spectra of the $HClO_4$ solutions showed greater variability among themselves in the ultraviolet region, but this was chiefly in the region around 260 $m\mu$ where the absorption is small compared to that of I_2Cl^- . This is apparent in Fig. 3 where the spectrum in 0.1 M $HClO_4$, appropriately corrected for iodine concentration, is shown. It is clear that there is no real isosbestic point; the minor constituents I^- and ICl_2^- are contributing to the observed spectra in the HCl solutions. Figure 4 shows the plots of A vs. $(A - A_{I_2})/F[Cl^-]$ from these spectra. In this case the slope is again -0.60 . In both cases the slope is not very sensitive to the values chosen for F , and the same slope is obtained by taking F as unity.

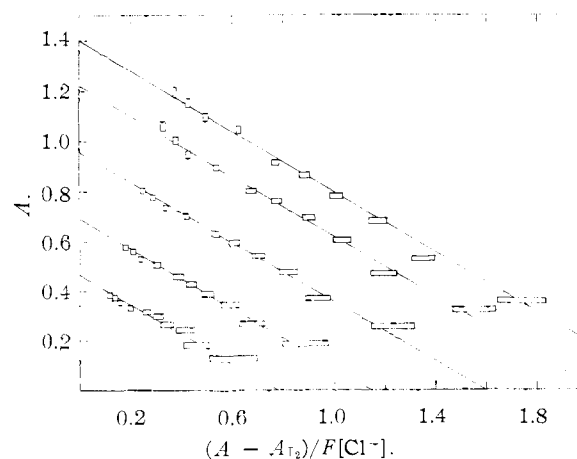


Fig. 4.—Determination of the dissociation constant for I_2Cl^- from data in the ultraviolet region. Data for wave lengths of 250, 255, 260, 265 and 270 $m\mu$.

The principal limitation of this method is the difficulty in attaining conditions where only I_2 and I_2Cl^- are present. However, the value of

K_a , 0.60, is in good agreement with the results obtained by Ray and Sarkar⁸ in distribution experiments. They obtained an average value of 0.62 from a variety of experiments using the non-aqueous solvents CS_2 , CCl_4 and $CHCl_3$, and HCl solutions 0.06—1 M in concentration.

Solubility of I_2 in Chloride Solutions.—The solubility of iodine in aqueous solutions of many chlorides has been determined by a variety of workers.⁸⁻¹⁹ Several of the workers used their own data to calculate the dissociation constant of I_2Cl^- . Among the values which have been stated explicitly or which can be obtained by simple conversions are

at 20°	0.48 (HCl) ¹³
25°	.60 (HCl), ⁸ 0.55 (HCl), ¹¹ 0.81 (HCl) ¹⁹
	.68 (NaCl), ¹⁴ 0.67 (NaCl), ¹¹
	.63 (KCl), ¹⁴ 0.63 (KCl), ¹⁵ 0.63 (KCl) ¹⁸
30°	.53 (HCl) ¹³
35°	.77 (HCl) ¹⁹
45°	.72 (HCl) ¹⁹

Although a value of about 0.6 is strongly suggested at 25°, certain of the original data have subsequently been re-examined and re-calculated to give other values. For example, Sidgwick²⁰ gives 0.48 and Korenman²¹ 0.29. These last two values, or values of ΔF^0 calculated from them, have subsequently appeared in articles of a review nature.²²⁻²⁴

Considering the large amount of data available, the solubility measurements should yield a good value for the dissociation constant. For this purpose the solubilities reported were first all reduced to the basis of molar concentration for comparison of consistency. Density data were necessary for some of these conversions; the densities of the chloride solutions were taken from the International Critical Tables, and the assumption was made that the presence of I_2 did not change the density. There is enough overlapping of data at 25° from references 8, 10, 11, 14, 15 and 18 to confirm the reliability of their data. Certain of these data are shown in Fig. 5. The data of Winther,¹³ Ray¹⁷ and Sandved¹⁶ at temperatures other than 25° are not inconsistent with these, but the extent to which they can be compared is limited.

(8) P. Ray and P. V. Sarkar, *J. Chem. Soc.*, 1449 (1922).

(9) E. Oliveri-Mandala and A. Angenica, *Gazz. chim. ital.*, **50**, (1), 273 (1920).

(10) J. S. Carter, *J. Chem. Soc.*, 2861 (1925).

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(13) C. Winther, *Z. physik. Chem.*, **3B**, 299 (1929).

(14) A. v. Kiss and A. Urmanczy, *Z. anorg. allgem. Chem.*, **202**, 172 (1931).

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(16) K. Sandved, *Kgl. Norske Videnskab. Selskabs Forh.*, **6B**, 165 (1933).

(17) S. K. Ray, *J. Indian Chem. Soc.*, **11**, 115 (1934).

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(21) I. M. Korenman, *J. Gen. Chem. (U.S.S.R.)*, **17**, 1608 (1947).

(22) R. L. Scott, *J. Am. Chem. Soc.*, **75**, 1551 (1953).

(23) R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. III, D. Van Nostrand Co., 1954, p. 185-216.

(24) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, 1956, p. 837.

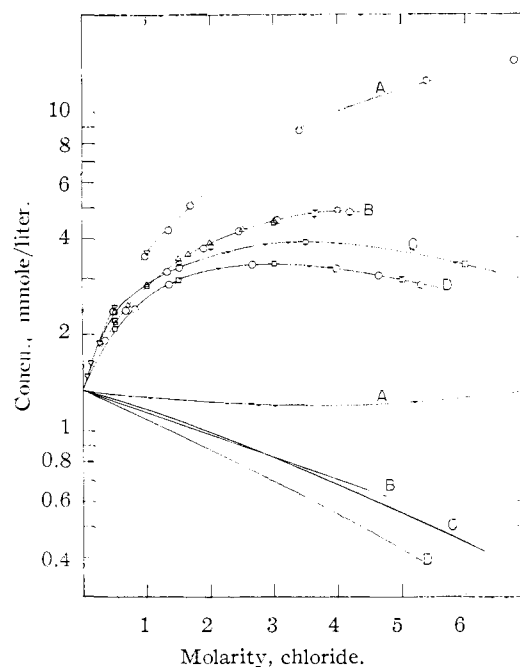


Fig. 5.—Solubility of iodine in chloride solutions (upper curves) and estimated concentrations of I_2 (lower curves). A, HCl; B, KCl; C, LiCl; D, NaCl. Data of Ray and Sarkar,⁸ ∇ ; Carter and Hoskins,^{10,11} \circ ; Dawson and Spivey,¹⁵ Δ ; and Kiss and Urmanczy,¹⁴ \square .

The data of Lee and Chen¹⁹ appear self-consistent, but the values at 25° are all lower than the reliable data, and the values at 25° and 35° are not compatible with the data of Winther¹³ at 20° and 30°.

The extensive measurements of Herz and Hiebethal¹² at 25° parallel the curves of Fig. 5 but do not agree with them. If their term "Molmengen" is translated as "gram-moles," their values are all high by a factor of about 1.85; if the translation is "gram-atoms" their values are low by 10-20%. The values of Oliveri-Mandala and Angenica⁹ are clearly inconsistent with the other sets of data, being low by a factor of 1.3 to 1.6.

Several investigators have called attention to the fact that the solubility is affected not only by the formation of the complex I_2Cl^- but also by the salting-out of I_2 . For systems where complex formation does not occur, the solubility, S , of a non-electrolyte is often given by the Setchenow equation.

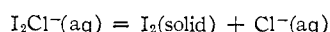
$$\log S = \log S_0 - kC$$

where S_0 is the solubility in pure water, C is the molar concentration of the salt used and k is a constant. Plots like Fig. 5 (using data from ref. 10 and 14) for the solubility of I_2 in non-complexing salts give the linear relation corresponding to this equation, with the values of k : KNO_3 , 0.058; $NaNO_3$, 0.075; Na_2SO_4 , 0.28.

Most workers have at this point assumed that the Setchenow equation applies to molecular I_2 in the chloride solutions and made estimates of the k 's. Our estimates of the concentration of molecular I_2 in the chloride solutions were made in a different manner. It was first necessary to choose

as a reference solute a non-electrolyte which was salted-out in a fashion similar to iodine. N_2O was chosen because (1) the salting coefficients for I_2 in non-complexing salts are not much different from the corresponding values for N_2O ,²⁵ (2) both I_2 and N_2O are salted-out by H_2SO_4 and salted-in by HNO_3 ,^{10,26} and (3) extensive data are available for N_2O .²⁶⁻²⁸ We then applied the principle suggested by Markham and Kobe²⁸ that two salt solutions that are equivalent in terms of their having the same salting effect on one solute, will also be equivalent for a second solute. From the N_2O data solutions of LiCl, NaCl and KCl of certain concentrations could then be equated to certain solutions of KNO_3 , $NaNO_3$ or Na_2SO_4 . Knowing the solubility of I_2 in the latter then gave the solubility in the former. Similarly HCl was compared to H_2SO_4 . The results of these estimates are shown in Fig. 5.

These systems may be described in terms of the equilibrium



with equilibrium constants

$$K' = \frac{[Cl^-]}{[I_2Cl^-]}$$

and

$$K_a' = \frac{[Cl^-]y_{Cl^-}}{[I_2Cl^-]y_{I_2Cl^-}} = K' \frac{y_{Cl^-}}{y_{I_2Cl^-}} = K' \frac{f_{Cl^-}}{f_{I_2Cl^-}}$$

as well as in terms of K and K_a . (The y 's are the activity coefficients on a molar basis; and the f 's on the rational basis.) Using concentrations taken from the smoothed curves of Fig. 5 values of K and K' have been calculated. These are shown in Table II.

The values of K agree generally with those previously calculated by workers with reliable data.^{8,14,15,18} Of these only Ray and Sarkar⁸ ignored the salting-out effect, but they used data only from HCl solutions, and Fig. 5 shows that salting-out by HCl is so small that neglect of it cannot lead to much error.

Although the solubility data of Winther¹³ appear reliable, in his calculation of K he assumed that disproportionation to I^- and I^+ is appreciable. Treating his limited solubility data in HCl by our method gives values of K in 1-3 M HCl of 0.51 at 20° and 0.53 at 30°. Within experimental error these are equal to the values of Table II for 25°.

Korenman²¹ treated solubility data for NaCl and KCl solutions by a method using several concepts now obsolete. In addition much of the solubility data he used appears to be that of Herz and Hiebenthal.¹²

The trends in K and K' evident in Table II indicate that activity coefficients cannot be ignored. In order to obtain values for the thermodynamic equilibrium constants K_a and K_a' , it is necessary to consider the behavior of K and K' as

(25) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 736.

(26) G. Geffcken, *Z. physik. Chem.*, **49**, 271 (1904).

(27) W. Manchot, M. Jahrstorfer and H. Zepter, *Z. anorg. allgem. Chem.*, **141**, 45 (1924).

(28) A. E. Markham and K. A. Kobe, *J. Am. Chem. Soc.*, **63**, 449 (1941).

TABLE II

[Cl ⁻]	SOLUBILITIES AND EQUILIBRIUM CONSTANTS					
	HCl			LiCl		
	S	K	K'	S	K	K'
0.5	0.00243	0.57	442	0.00233	0.57	459
1.0	.00358	.56	435	.00292	.67	585
1.5	.00462	.56	445	.00325	.69	673
2.0	.00576	.54	441	.00348	.75	779
2.5	.00685	.53	439	.00366	.78	884
3.0	.00794	.53	445	.00380	.81	997
3.5	.00903	.54	448	.00387	.81	1115
4.0	.01005	.54	452	.00384	.84	1254
4.5	.01085	.57	468	.00375	.85	1420
5.0	.01170	.59	478	.00363	.87	1618
5.5	.01240	.61	493	.00347	.90	1846
6.0	.01310	.64	506	.00327	.93	2120
6.5	.01375	.68	522			
	NaCl			KCl		
0.5	0.00208	0.68	568	0.00217	0.65	532
1.0	.00258	.71	662	.00284	.66	588
1.5	.00296	.73	754	.00341	.66	636
2.0	.00321	.74	855	.00385	.68	697
2.5	.00331	.76	984	.00424	.66	749
3.0	.00333	.77	1133	.00450	.67	818
3.5	.00329	.80	1306	.00474	.67	882
4.0	.00320	.81	1504	.00485	.67	966
4.5	.00308	.83	1731			
5.0	.00294	.83	1984			

a function of $[Cl^-]$. For this purpose it is better to use K' since it is less sensitive to the correctness of the estimates of salting. In addition the numerical value of K' is independent of the units used in expressing the concentrations of Cl^- and I_2Cl^- . In Fig. 6 is plotted the variation of K' with $[Cl^-]$. With the exception of HCl at concentrations greater than 3 M , there is a linear relation between $\log K'$ and $[Cl^-]$, with each chloride giving a different intercept.

This behavior can be rationalized by using several theoretical ideas and empirical observations discussed in Harned and Owen²⁹ and in Robinson and Stokes³⁰ for mixtures of electrolytes. Consider the equilibrium in a solution of a particular chloride, MCl.

$$K_a' = K' \frac{f_{M^+} f_{Cl^-}}{f_{M^+} f_{I_2Cl^-}} = K' \frac{(f_{MCl})^2}{(f_{MI_2Cl})^2}$$

where f_{MCl} and f_{MI_2Cl} are the mean ionic activity coefficients in the mixture. In a solution containing only MCl, or in one in which MCl is the predominant salt

$$\log f_{MCl} = - \frac{0.5115\sqrt{C}}{1 + 0.3291 a_{MCl}\sqrt{C}} + b_{MCl}C$$

where a_{MCl} is the distance of closest approach of the M^+ and Cl^- ions, b is a parameter characteristic of the salt and C is the molar concentration.

In a solution containing only MI_2Cl

$$\log f_{MI_2Cl} = - \frac{0.5115\sqrt{C}}{1 + 0.3291 a_{MI_2Cl}\sqrt{C}} + b_{MI_2Cl}\sqrt{C}$$

but in a mixture that has a small amount of MI_2Cl in a large amount of MCl

(29) Ref. 25, chapters 12 and 14.

(30) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions, 2nd Ed., Academic Press, Inc., New York, N. Y., 1959, Chapters 9 and 15.

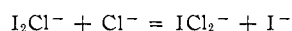
$$\log f_{M_1_2Cl} = -\frac{0.5115\sqrt{C}}{1 + 0.3291 a_X \sqrt{C}} + \frac{1}{2}(b_{MCl} + b_{M_1_2Cl})C$$

where C is the concentration of MCl , and a_X is a parameter intermediate in value between a_{MCl} and $a_{M_1_2Cl}$. It follows that

$$\log K' = \log K'_a - \frac{1.0230\sqrt{C}}{1 + 0.3291 a_X \sqrt{C}} + \frac{1.0230\sqrt{C}}{1 + 0.3291 a_{MCl}\sqrt{C}} + (b_{M_1_2Cl} - b_{MCl})C$$

It would then be expected that $\log K'$ will appear to be a linear function of C in a concentration range where the difference in the second and third terms is either constant or changing only slowly with C . In general $a_{M_1_2Cl}$ would be expected to be greater than a_{MCl} , so that the intercept from the extrapolation to $C = 0$ will be higher than $\log K'_a$ by this difference. The zero slope of the HCl curve, which results from $b_{HCl} = b_{H_1_2Cl}$, suggests that $a_{HCl} = a_{H_1_2Cl}$, since a correlation has been observed between values of a and b . The best estimate of K'_a is then the intercept of the HCl curve, 440. Corresponding to this K'_a will have a value of 0.59. A further implication is that only in 0-3 M HCl does $f_{Cl^-} = f_{I_2Cl^-}$. In this region $F = \gamma_{I_2}$, and the estimates of F for use with the spectral data then follow from the estimates of the salting-out of I_2 in HCl .

Considering the evidence in total, 0.60 appears to be the best value for K_a . Using this value and free energy of formation values tabulated by Latimer,³¹ we calculate that ΔF^0 for I_2Cl^- is -27.73 kcal. and that the equilibrium constant for the reaction

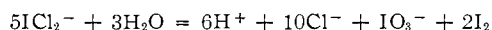


is 7.3×10^{-7} . The previously mentioned spectral evidence for the disproportionation is consistent with the latter value.

Iodine(I).—In solutions where the HCl concentration is 0.5 M or greater, iodine(I) exists predominantly as the dichloriodate(I) ion, ICl_2^- . Such solutions are very stable, retaining their titer and spectral characteristics for prolonged periods. The dissociation constant for the reaction



was determined to be 6×10^{-3} by Faull³² by means of a distribution method. Because of the rather high formal concentration of ICl (0.1-0.4) and low concentrations of HCl (<0.4 M) the hydrolysis reaction



was quite extensive in his experiments even though 1-5.5 M $HClO_4$ was also present. Spectrophotometric measurements, utilizing the 343 $m\mu$ peak, can be made at ICl concentrations of $10^{-3}F$, decreasing the complications caused by the hydrolysis. Gillam and Morton³³ report that the absorbance of ICl in this region does not change in the

(31) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., 2nd Ed., 1952, p. 54 and 63.

(32) J. H. Faull, *J. Am. Chem. Soc.*, **56**, 522 (1934).

(33) A. E. Gillam and R. A. Morton, *Proc. Roy. Soc. (London)*, **A132**, 152 (1931).

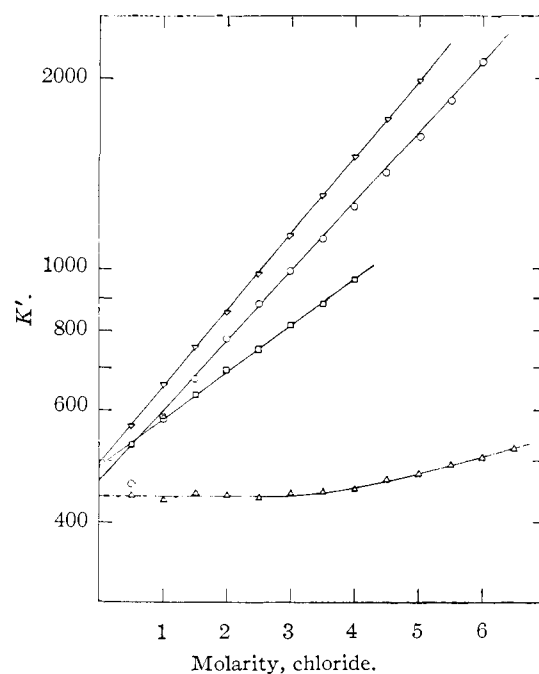


Fig. 6.—Values of K' as a function of chloride concentration, HCl , Δ ; KCl , \square ; $LiCl$, \circ ; $NaCl$, ∇ .

HCl solutions in the concentration range 0.2-10 M . We observe a decrease in absorbance as the chloride ion concentration decreases from 1 to 0.01 M , while $[H^+]$ is maintained at 2 M , which is not inconsistent with Faull's value for the dissociation constant of ICl_2^- .

A recent investigation,³⁴ involving potentiometric measurements of solutions of ICl in HCl of variable concentration, was interpreted as providing evidence for the existence of ICl_6^{5-} . Few experimental details are given about the measurements, but it appears that iodine was added only as ICl . The authors assume that I^- is present in all the experiments in some constant, but unknown, amount, to provide the reduced form of iodine in the couple being measured. This assumption is highly questionable; in fact, the half-reaction at the electrode is completely unknown. The authors claim to justify their assumptions by similar measurements on the I_3^- complex. The experiments are not analogous, however; in the I_3^- case iodine is added both as I_2 and I^- so that the electrode half-reaction is known, as well as the amounts of the oxidized and reduced forms of the couple.

Iodine (III).—There are two known iodine(III) species, iodine trichloride, ICl_3 , and its complexed form, the tetrachloriodate(III) ion, ICl_4^- , which might possibly exist in aqueous solutions containing chloride ion. Many salts containing the ICl_4^- ion have been crystallized from aqueous media,³⁵ and it is apparent that this ion does exist in aqueous solutions under some conditions. However, there has been no quantitative investigation of the equilibria involving ICl_4^- in such

(34) E. Pungor, K. Burger and E. Schuelek, *J. Inorg. Nuclear Chem.*, **11**, 56 (1959).

(35) See A. I. Popov and R. E. Buckles, "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1957, p. 167.

media, and it is not clear from the preparative procedures what solution conditions are most favorable for forming ICl_4^- .

Solutions prepared by dissolving ICl_3 in 0.5 and 1 *M* HCl are quite stable, and the λ_{max} values coincide with those of ICl_2^- . Assuming that the absorption is due to ICl_2^- alone leads to the conclusion that half of the ICl_3 is converted to ICl_2^- . The spectra and titer of these solutions remained unchanged over a period of 27 days. There was no evidence that Cl_2 could be lost from the solutions either by aging or heating.

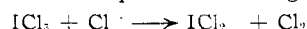
On the other hand, when ICl_3 is dissolved in 3 *M* HCl, a definite odor of chlorine can be detected. The spectrum of a freshly prepared solution is not identical to that of ICl_2^- but has a contribution from another substance (Cl_2 and/or Cl_3^-) in the region around 335 $m\mu$. As the solution ages, the spectrum approaches that of ICl_2^- , the extent of absorption indicating that all of the ICl_3 is converted to ICl_2^- .

The iodine content of these solutions was determined by reducing to iodide and then performing a potentiometric titration with AgNO_3 . This value was then compared with the oxidizing power determined by iodometric titration. These experiments showed that in 0.5 *M* HCl the iodine is present in a form or forms equivalent in oxidizing power to ICl_3 , whereas in 3 *M* HCl loss of chlorine reduces the oxidizing power to almost that equivalent to ICl_2^- .

All these facts are consistent with the following reaction occurring in 0.5 *M* HCl



In 3 *M* and higher HCl concentrations, on the other hand, the ICl_3 decomposes according to

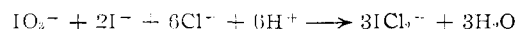


This interpretation is also consistent with the behavior of IO_3^- when added to HCl solutions. If the concentration of HCl is 3 *M* or greater, the 224 $m\mu$ peak of ICl_2^- appears within the order of minutes, along with the odor of Cl_2 . If the HCl concentration is 0.5 *M*, there is no evidence of reaction.

A study of the potentiometric titration³⁶ of IO_3^- with KI in hydrochloric acid revealed that the end-point appeared prematurely when the HCl concentration was greater than 2 *M* and that the exact position of the end-point depended on the time taken for titration. This effect can now be seen to result from the formation and loss of chlorine gas.

Fialkov and Kagan³⁷ report the use of solutions of ICl_3 for volumetric analysis. Their solutions were prepared either by dissolving solid ICl_3 in 0.2-0.4 *M* HCl or by adding KI and KIO_3 in a mole ratio of 1:2 to the acid solution. On the basis of the evidence presented so far it would appear that such solutions do not contain ICl_2^- or ICl_4^- , but instead, equal amounts of ICl_2^- and IO_3^- .

As a further test of this view solutions in 0.5 *M* HCl were prepared by adding KIO_3 and KI in 4:2 and 1:2 mole ratios, keeping the amount of KI the same in both. If the only reaction that occurs is



excess IO_3^- ions will remain in the 4:2 solution, and the two solutions ought to have identical spectra in regions where IO_3^- does not absorb. On mixing the solutions a rather intense yellow-brown color developed immediately, probably due to the formation of I_3^- . Within a few minutes it was replaced by the expected light lemon-yellow color characteristic of ICl_2^- . Spectral measurements in the 270-400 $m\mu$ range showed the two solutions to be identical except for the small range 270-290 $m\mu$, where the 4:2 solution had a slightly higher absorbance. This could be ascribed to absorbance by the excess IO_3^- ions.

Thus under the conditions employed in these experiments no evidence was found for the existence of ICl_3 or ICl_4^- . Of course, other conditions, such as the presence of excess Cl_2 , may prove favorable to their existence.

(36) H. T. S. Britton, R. E. Cockaday and J. K. Foreman, *J. Chem. Soc.*, 3877 (1952).

(37) Y. A. Fialkov and P. E. Kagan, *Ukrain. Khim. Zhur.*, **19**, 55 (1952).

[CONTRIBUTION NO. 1645 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY, NEW HAVEN, CONNECTICUT

Electrolytic Conductance of Salts of Several Cyanocarbon Acids

BY JOHN E. LIND, JR.,¹ AND RAYMOND M. FUOSS

RECEIVED NOVEMBER 12, 1960

The conductance at 25° of the tetraethylammonium salts of 1,1,2,3,3-pentacyanopropene and of 1,1,2,4,5,5-hexacyano-3-azapentadiene have been measured in acetonitrile and in ethylene dichloride; the penta-salt was also measured in water. The electrolytic behavior is typical for that of salts of strong acids. Association is negligible in water and in acetonitrile ($D = 36.01$); in ethylene dichloride ($D = 10.35$), association constants are 2600 and 2000 for the penta- and hexa-salts, respectively. These values, as well as the contact distances derived from them, show that the negative charge is widely distributed in both anions.

A number of cyanocarbon acids² have been prepared recently, as well as a variety of their salts. Briefly described, these acids are essentially

(1) Du Pont Postdoctoral Research Fellow, 1960-1961.

(2) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

hydrocarbons in which all hydrogens except one or two have been replaced by nitrile groups; the resulting carbanion is so highly stabilized by resonance among a large number of canonical structures that the compounds are stable strong acids with pK_a about 2. One would therefore