499. *Unstable Intermediates. Part XV.* Interaction between Strong Acids and Various Compounds Containing Iodine.*

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Spectrophotometric, conductometric, cryoscopic, and magnetic studies of solutions of a wide range of iodine-containing compounds in sulphuric acid and in oleum provide evidence for the ions I_5^+, I_3^+, and $H_2IO_3^+$, in addition to I^+. Some indication that IO^+ is formed in 65% oleum is adduced, and it is suggested that white crystals obtained from such solutions are the ionic compound $(IO)HS_2O_7$.

Various oxidation–reduction equilibria in these solutions have been elucidated.

In our search for the iodine cation [1] a variety of unusual iodine-containing compounds and their reactions in sulphuric acid and oleums have been studied, and in this paper we attempt to systematise and explain some of our observations. Earlier work in this field includes that of Masson and Argument [2] and of Masson [3] who studied the interaction between iodine and iodine pentoxide in sulphuric acid and oleum, and the interaction between the resulting iodine-containing species and various aromatic compounds. In particular, they considered that brown solutions rich in iodine contained the ions I_3^+ and I_5^+, and that yellow solutions corresponding to tervalent iodine contained the ions IO^+ and, possibly, I^{3+}.

Dasent and Waddington [4] recently reported details of the infrared spectra of yellow iodous sulphate (iodosyl sulphate), $(IO)_2SO_4$, and related compounds, and concluded that IO^+ ions are not present, but that the sulphate has a network structure involving I–O–I bridges. Symons [5] found that iodous sulphate was diamagnetic, like the oxide I_2O_4,[6] and pointed out that one might expect that IO^+ would be paramagnetic, having a triplet ground state.

Lehmann and his co-workers have prepared $I_2O_5,2SO_3$ by interaction between liquid sulphur trioxide and potassium iodate or iodine pentoxide at 100°.[7] The constitution of $I_2O_5,2SO_3$ has been represented [1] as iodyl sulphate $([IO_2]^+)_2[S_2O_7]^{2-}$. The evidence in favour of this formulation is inconclusive. The compound formed by interaction of I_2O_4 with SO_3 has been formulated [7] as $[IO]^+[IO_2]^+[S_2O_7]^{2-}$.

A considerable weight of evidence in favour of the postulate that blue solutions of

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* Part XIV, *J.*, 1962, 237.

[1] Arotsky, Mishra, and Symons, *J.*, 1961, 12.
[2] Masson and Argument, *J.*, 1938, 1702.
[3] Masson, *J.*, 1938, 1708.
[4] Dasent and Waddington, *J.*, 1960, 3350.
[5] Symons, *J.*, 1957, 2186.
[6] Willmarth and Dharmatti, *J. Amer. Chem. Soc.*, 1950, **72**, 5789.
[7] Lehmann and Hesselbarth, *Z. anorg. Chem.*, 1959, **299**, 51.

iodine in 65% oleum contain the solvated iodine cation, I^+, has now been collected,[1] and in this paper it will be assumed that this identification is correct; and the visible and ultraviolet spectrum given for this ion [1] will be used for its characterisation.

Our studies of septivalent iodine compounds in strong acids have been reported separately.[8]

EXPERIMENTAL

Materials.—Water was distilled twice from alkaline permanganate under nitrogen. Sulphuric acid was purified as described previously [1] whenever ultraviolet spectra were required; for other purposes " AnalaR " sulphuric acid proved to be equivalent within experimental error. Commercial oleum was refluxed for several hours with chromium trioxide, and sulphur trioxide distilled at atmospheric pressure and condensed as a liquid. This was then refluxed with potassium persulphate and distilled slowly into purified sulphuric acid. Concentrations of the resulting oleums were estimated approximately by the " fog-clear " method [9] or accurately from their conductivities.[10]

Carbon tetrachloride was fractionately distilled from phosphorus pentoxide after refluxing, and acetic acid was distilled from 100% sulphuric acid. Benzene was dried with sodium and fractionated. Chlorobenzene, nitrobenzene, and nitromethane were dried with calcium sulphate and distilled.

Potassium chloride was crystallised several times from purified water, dried at 120°, and fused in a platinum crucible. Silver sulphate was crystallised from hot aqueous sulphuric acid and dried at 400°. Potassium pyrosulphate was obtained by heating potassium hydrogen sulphate to 600°, and the resulting solid was reheated after being moistened with sulphur trioxide.

Iodine, iodic acid, potassium iodate, and potassium sulphate were of " AnalaR " grade. The former pair were dried for several days *in vacuo* over magnesium perchlorate, and the latter at 120° for several hours.

Iodine tetroxide was prepared by Muir's method,[11] the yellow solid being stable and non-hygroscopic. The oxide I_4O_9 was obtained by heating iodic acid with orthophosphoric acid.

Iodous sulphate was prepared by Masson and Argument's method [2] from iodine and iodine pentoxide, or by shaking iodine with equivalent quantities of potassium iodate or potassium persulphate. These alternatives had the advantage that reaction was complete in a relatively short period (about 6 hr. at room temperature). The resulting yellow solid was washed rapidly with acetic acid or nitromethane and dried on porous plate over sulphuric acid [Found: I, 65·8; S, 8·4; $(IO)_2SO_4$ requires I, 66·5; S, 8·4%].

A colourless tervalent iodine compound was obtained by dissolving yellow iodous sulphate in dilute oleum and warming the mixture to about 60°. On cooling, colourless crystals separated, which were filtered off and dried on sintered glass in an atmosphere of dry nitrogen. After being washed with nitromethane they were stored *in vacuo* over sulphuric acid. In an alternative preparation, 30% oleum (50 ml.), iodine (25 g.), and 100% (fuming) nitric acid (10 ml.) were stirred together at 60° for several hours. The blue solution formed initially slowly became pale yellow and colourless crystals were deposited on cooling. These were unchanged in contact with 100% sulphuric acid, but 96% acid reacted to give a pale yellow solution from which yellow iodous sulphate, $(IO)_2SO_4$, was slowly deposited. In contact with 98% sulphuric acid the white crystals changed very slowly into yellow $(IO)_2SO_4$ without any change in the oxidation state of iodine.

Preparation of Solutions.—Solutions thought to contain I_3^+ as the only or major iodine compound were prepared by shaking stoicheiometric amounts of iodine with iodic acid, iodine pentoxide, potassium iodate,· or iodous sulphate in 100% sulphuric acid or dilute oleum.

In certain instances, some properties of solutions of iodine compounds in oleum changed slowly with time, without an overall change in the oxidation state, and also varied with the method employed for preparing the solutions. This type of problem has been encountered before in our studies connected with the formation of carbonium ions,[12,13] and was apparently

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[8] Mishra and Symons, *J.*, 1962, 1194.
[9] Brand, *J.*, 1946, 585.
[10] Arotsky and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1426.
[11] Muir, *J.*, 1909, **95**, 656.
[12] Grace and Symons, *J.*, 1959, 958.
[13] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205; *J.*, 1961, 1.

overcome by preparing solutions in such a manner that product ions were kept from contact with reactants during the process of dissolution. We have followed this principle in the present study, and, in general, stable solutions resulted which had higher conductivities than those prepared by conventional methods. For example, direct addition of iodic acid to oleum gave solid iodine pentoxide which dissolved slowly on shaking to give a non-conducting solution. However, iodic acid dissolves readily in 100% sulphuric acid (probably as $H_2IO_3^+$) and when sulphur trioxide was added to these solutions to give 65% oleum clear solutions resulted whose conductivity was close to that required for a species having one positive charge per iodine atom.

Reduction of these colourless conducting solutions containing I^V with sulphur or formic acid gave successively pale yellow solutions of I^{III} and blue solutions of I^+, there being no change in conductivity during the reduction.

The blue solutions were slowly oxidized by persulphate to I^{III}, again with no change in conductivity. (I^V was not formed in 65% oleum although persulphate gives I^V rapidly in 100% sulphuric acid.) Significant results of this type are specified in the Tables and figures.

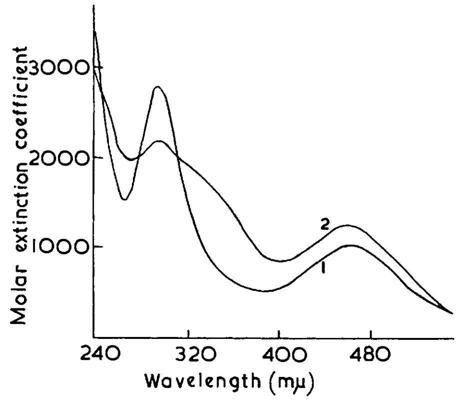

FIG. 1. Ultraviolet spectra attributed to the ions I_3^+ and I_5^+ in sulphuric acid.

(1) I_3^+. (2) $I_5^+ + I_3^+$.

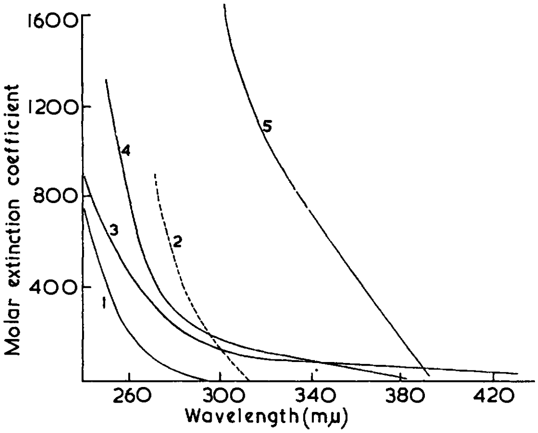

FIG. 2. Ultraviolet spectra of various tervalent and quinquevalent iodine compounds in sulphuric acid and oleum.

(1) $H_2IO_3^+$ in 100% H_2SO_4. (2) IO_2^+ or $IO(HS_2O_7)_2^+$ in 65% oleum. (3) $(IO)_2SO_4$ in 96% H_2SO_4. (4) $IO(HSO_4)$ in 100% H_2SO_4. (5) IO^+ in 65% oleum.

Ultraviolet Spectra.—Spectrophotometric measurements in the visible and ultraviolet region were made with Unicam S.P. 500, S.P. 600, and S.P. 700 spectrophotometers. Cells were calibrated at frequent intervals and were cleaned by repeated rinsing with oleum followed by test solutions. Care was taken to avoid striations in the solutions since their presence seriously altered the ultraviolet spectra. Optical densities were confined to the region 0·2 to 0·8 by a suitable choice of cells and concentrations.

Diffuse reflectance spectra in the ultraviolet region were obtained with the precautions described earlier,[14] potassium sulphate being used as diluent and reference surface.

Because of the high reactivity of the colourless tervalent iodine compound obtained from 65% oleum, and the presence of traces of oleum, diffuse reflectance spectra obtained at room temperature were irreproduceable and changed with time. However, by using a modified sample holder,[15] in which samples could be cooled to near 77° K, reproducible spectra were obtained. Results are given in Figs. 1—3. The spectrum for solutions having stoicheiometry corresponding to I_5^+ is not simply due to absorption by this ion since the equilibrium $I_5^+ \rightleftharpoons I_3^+ + I_2$ lies sufficiently far to the right to interfere. The spectrum assigned to AgI_2^+, not given in the Figures, is characterised by a band in the visible having $\lambda_{max.}$ 520 mμ and ε 900,

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[14] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

[15] Symons and Trevalian, *Spectrovision*, 1961, **10**, 8

which may be compared with the first band for iodine in this solvent ($\lambda_{\text{max.}}$ 505 mμ; ε 800). In addition, there is a weak shoulder in the 420 mμ region and an intense, rising ultraviolet absorption, not found for either of the separate components in this medium. There is no sign of the band in the 640 mμ region characteristic of the iodine cation.

Infrared Spectra.—Unicam S.P. 100 and Perkin-Elmer " Infracord " spectrophotometers fitted with sodium chloride optics were used. Solutions in sulphuric acid and oleums were contained in bags made from " Fluon " sheets 0·0015 " thick and wedged between silver chloride plates. Solids were mulled either with Nujol or, for more reactive compounds, with sulphuric acid or oleum, in which case " Fluon " bags were again used.

Results are given in Table 1. The formation of the hydrogen sulphate ion and sulphuric acid in Nujol mulls of pyrosulphates was probably caused by reaction with traces of moisture. We do not understand our failure to detect certain characteristic bands for the pyrosulphate ion in sulphuric acid and oleum mulls. In may be that the particle size was too large or that intense absorption by the medium interfered. We have had similar experience in related studies and it seems that this mulling is of limited applicability.

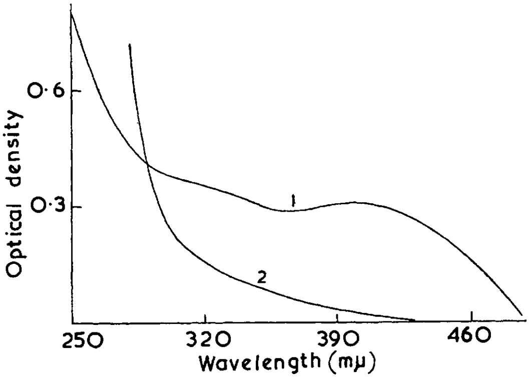

FIG. 3. Reflectance spectra.
(1) Yellow $(IO)_2SO_4$.
(2) Colourless $IO(HSO_4)$ at 77° K.

Magnetic Susceptibility.—A sensitive susceptibility balance was used with stabilised power supply as described earlier.[1] Results are compiled in Table 2.

TABLE 1.

Infrared frequencies for certain sulphates and pyrosulphates.

Compound	Medium	Vibration frequencies (cm.$^{-1}$)
K_2SO_4	Nujol mull	1105
$KHSO_4$	Nujol mull	850, 880, 1005, 1065, 1110, 1280, 1640, 2340, 2900
$KHSO_4$	H_2SO_4 mull	890, 1050
$(IO)_2SO_4$ *	Nujol mull	1036
H_2SO_4	—	910, 970, 1165, 1370, 2400, 2980
$K_2S_2O_7$	Nujol mull	855, 875, 1015, 1080, 1170, 1280, 2480, 3100
KHS_2O_7	Nujol mull	725, 850, 870, 1080, 1200, 1620
KHS_2O_7	Oleum mull	890, 1090
$(IO)HS_2O_7$	Nujol mull	125, 766,† 845, 890, 1080, 1200, 1600
$(IO)HS_2O_7$	Oleum	770,† 895, 1090
20% Oleum	—	805, 906, 970, 1190, 1370, 2425, 3000

* Result in agreement with that obtained by Dasent and Waddington.[4]
† Frequency assigned to I–O stretching frequency.

TABLE 2.

Magnetic susceptibilities (χ_g and χ_M) for some tervalent iodine and related compounds.

	$(IO)_2SO_4$	KHS_2O_7 *	$(IO)HS_2O_7$ *	IO^+ *	I_2O_4 †	I_4O_9	TeO	$Ag_2SO_4 + I_2$ ‡
$10^6\chi_g$	−0·21	−0·37	−0·10	+0·26	−0·22	−0·3	−0·12	−0·29
$10^6\chi_M$	−80·2	−79·9	−28·9	+37·7	−72·2	−196·5	−17·2	−105

* Value for the postulated ion, IO^+, was estimated from these results and a value for K^+ of 13 × 10^{-6}. † Also given by Willmarth and Dharmatti.[6] ‡ Saturated solution in sulphuric acid.

Conductance Measurements.—The apparatus and experimental procedures for measuring conductivities of dilute solutions in 65% oleum have already been described.[10]

Cells for measuring conductivities of solutions in 100% sulphuric acid or dilute oleums were based on that used by Gillespie and his co-workers.[16] The electrode chamber was 1·0—1·5 cm. in diameter and 10—25 cm. long with platinised platinum electrodes pinch-sealed into each end. The cell constants were 30—40 cm.$^{-1}$ for 100% sulphuric acid and 50—70 cm.$^{-1}$ for dilute oleums, and were obtained by using solutions of potassium chloride as recommended by Fuoss and others.[17] This method was preferred to that of Jones and Bradshaw [18] because cell constants could be determined over a range of resistances in order to estimate the importance of stray currents.

All measurements were made at 25·00° ± 0·01°, and cells were cleaned by standard methods after prolonged washing with purified sulphuric acid. Weighed portions of dilute oleums were added to known weights of 98% sulphuric acid in the cell until minimum conductivity was obtained. Thereafter, the exact amount of dilute oleum required to form 100% sulphuric acid or low percentage oleums was introduced through a weight-burette. Powdered solutes or their concentrated solutions in the required acid were mixed with the solvent out of contact with the atmosphere.

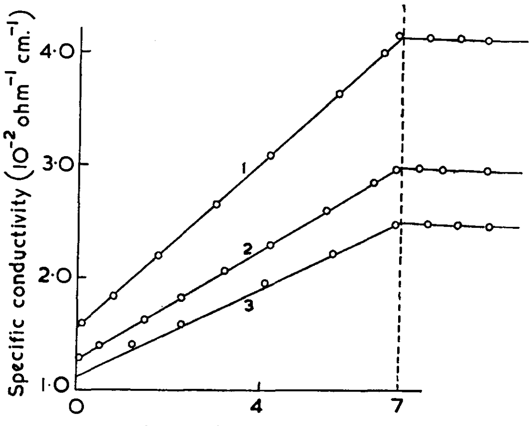

FIG. 4. Change in specific conductivity on adding iodine to a solution of iodic acid in 100% sulphuric acid.

A molar ratio of seven corresponds to the formation of I_3^+.

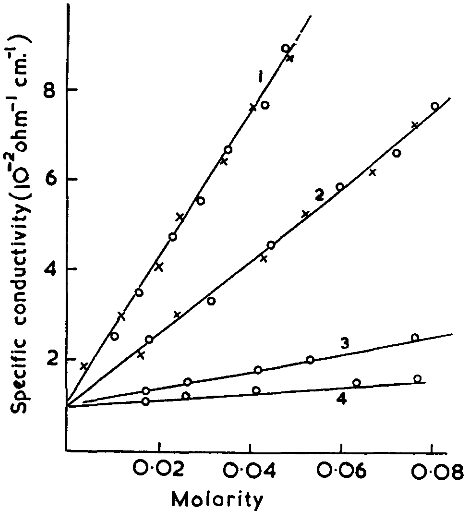

FIG. 5. Specific conductance as a function of concentration of various ter- and quinque-valent iodine compounds in oleum.

(1) (×) $K_2S_2O_7$, (○) KIO_3. (2) (×) $KHSO_4$, (○) $IO(HSO_4)$. (3) $(IO)_2SO_4$. (4) HIO_3.

(1, 2) Conducting solutions prepared as described in the Experimental section. (3, 4) Solutions prepared by direct addition of powered solids to oleum.

Errors involved in the measurement of conductance were not large enough to affect our conclusions concerning the mode of ionization of solutes in 100% sulphuric acid or 65% oleum, but in several instances, because of the very high intrinsic conductivity of the medium and the relatively low solubility of the solutes, measurements on solutions in oleums in the region of 15% were subject to large errors. Nevertheless, the results constitute a useful guide taken in conjunction with other information.

Results are displayed in Figs. 4—6.

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[16] Gillespie and Wasif, *J.*, 1953, 221.

[17] Lind, Lwolenik, and Fuoss, *J. Amer. Chem. Soc.*, 1959, **81**, 1557.

[18] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

Cryoscopy.—A standard cell of the type described by Gillespie and his co-workers,[19] was fitted with a calibrated solid-stem thermometer which could be read to ±0·001° with the aid of a cathetometer. Both the Beckmann and the equilibrium method were used to estimate the freezing-point depression effected by the solutes, which were added from a weight-pipette as concentrated solutions. To remove uncertainty regarding the composition of solutions at equilibrium, samples were withdrawn after each addition of solute and analysed either chemically or by means of their conductivity.

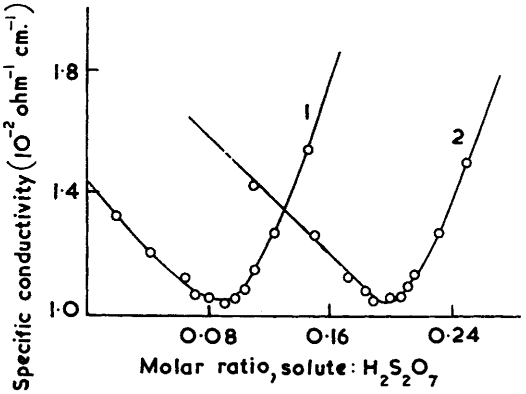

FIG. 6. Conductimetric titration in dilute oleum.
(1) HIO_3. (2) $KHSO_4$.

Results obtained by these alternative procedures are compared in Table 3. The values of ν, the number of moles of ions formed from one mole of solute were obtained by using the equation,[19]

$$\theta/m_2 = g_r \nu K_f\{1 - \theta\,(1/T_0 - \Delta C_p/2\Delta H_0^f)\}\{1 + m_2(2S_2 - \nu)/2m_1\}$$

which relates ν to the freezing-point depression (θ), the molalities of solvent (m_1) and solute (m_2), the cryoscopic constant of the solvent (K_f), the freezing point of pure solvent (T_0), the difference between the heat capacities of solid and liquid solvent (ΔC_p), the rational osmotic coefficient of the solvent (g_r), and S_2, the total number of moles of solvent required to react with and solvate the ions formed by one mole of solute.

Iodination.—A variety of organic compounds react to form iodo-, iodoso-, or iodonium derivatives when treated with solutions of the type under consideration.[3] We have confirmed and extended this work because the nature of the products gives some guide to the nature of the reagent. Of particular significance when solutions thought to contain the ions I_3^+ or I_5^+ are used is the formation of molecular iodine in quantitative accord with the equations

TABLE 3.

Number of ions formed from one mole of various solutes in sulphuric acid as estimated from cryoscopic measurements.

	Compound						
Method	HIO_3	KIO_3	I_2O_5	$(IO)_2SO_4$	I_2O_4	Ag_2SO_4	$Ag_2SO_4 + I_2$
Equilibrium ...	2·1	4·1	4·4	2·1	—	3·8	3·8
Beckmann	2·3	4·3	4·4	—	3·3	—	—

$$RH + I_3^+ \longrightarrow RI + H^+ + I_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

and

$$RH + I_5^+ \longrightarrow RI + H^+ + 2I_2 \quad \ldots\ldots\ldots\ldots \quad (2)$$

where RH is the aromatic compound concerned.

The products were isolated and identified by standard procedures, and some details are recorded in Table 4.

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[19] Gillespie, Hughes, and Ingold, *J.*, 1950, 2504.

TABLE 4.

Iodination of aromatic compounds, C_6H_5X, in sulphuric acid.

X = (i) H, (ii) Cl, and (iii) NO_2.

Reagent	Postulated reaction	Identification
1. $Ag_2SO_4 + I_2$	$C_6H_5X + AgI_2^+ + HSO_4^- \longrightarrow$ *o*/p-$C_6H_4XI + AgI + H_2SO_4$	M. p. and mixed m. p.
2. $(IO)_2SO_4$ (1 part) + I_2 (9 parts)	$C_6H_5X + I_3^+ + HSO_4^- \longrightarrow$ *o*/*p*-$C_6H_4XI + I_2 + H_2SO_4$ *	M. p. and determin. of I_2 liberated
3. (IO_2SO_4) (1 part) + I_2 (14 parts)	$C_6H_5X + I_5^+ + HSO_4^- \longrightarrow$ *o*/*p*-$C_6H_4XI + 2I_2 + H_2SO_4$ *	,, ,,
4. $(IO)_2SO_4$	$2C_6H_5X + IO{\cdot}HSO_4 \longrightarrow (C_6H_4X)_2I^+HSO_4^- + H_2O$ †	Ultraviolet spectra and m. p.
5. I_2O_5	$3C_6H_5X + H_2IO_3^+ + HSO_4^- \longrightarrow (C_6H_4X)_2I^+HSO_4^-$	M. p. and analysis
6. I_2O_4	Mixture of 4 and 5	,, ,,

* When X = Cl, the tri-iodo-derivative was the main product. † When X = NO_2, the iodoso-compound was the main product from cold, and a mixture of iodonium and iodo-compound from hot solutions.

DISCUSSION

Valency States between Zero and +1.—Our results are in accord with previous conclusions that mixtures of tervalent iodine and molecular iodine in sulphuric acid give I_3^+, and probably I_5^+.[2,5] Conductivity results are significant in that the steady increase in conductivity on addition of iodine to iodic acid in sulphuric acid stops at the stage required by the equation

$$HIO_3 + 7I_2 + 8H_2SO_3 = 5I_3^+ + 3H_3O^+ + 8HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The spectrum of solutions at this stage (Fig. 1) is similar in the 400—600 mμ region to that previously deduced for I_3^+ in dilute oleums and shown in Fig. 2 of ref. 1. If this spectrum is accepted as being characteristic of I_3^+, then the appearance of a shoulder in the 330 mμ region when more iodine is added is evidence that a new species is being formed. Comparison of such spectra as a function of the concentration of excess iodine suggests that the equilibrium

$$I_3^+ + I_2 \rightleftharpoons I_5^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is involved, I_5^+ being characterised by maxima at ~330 and 450 mμ (Fig. 1). This marked change in spectrum implies that I_5^+ differs in structure from I_3^+, and we tentatively suggest that it may be cyclic.

Solutions of iodine in sulphuric acid, originally transparent in the 330 mμ region, slowly develop a maximum at 330 mμ and a shoulder at 280 mμ. We think that the band at 330 mμ is due to I_5^+ and that that at 280 mμ is due to sulphur dioxide formed by the slow reaction

$$5I_2 + 5H_2SO_4 \rightleftharpoons 2I_5^+ + 2H_3O^+ + 4HSO_4^- + SO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Absorption in this region has been observed previously for solutions of iodine in sulphuric acid,[20] and this has been discussed in terms of the formation of I_4.[21]

Our attempts to isolate salts of these cations have been unsuccessful. However, the solid $(ICl_2)SbCl_6$ has been shown to contain bent, discrete ICl_2 units having an angle close to 90°.[22] This is in accord with expectation for ICl_2^+, which is structurally similar to I_3^+.

Tervalent Iodine.—Our optical results for solid iodous sulphate $(IO)_2SO_4$ are the same as those of Dasent and Waddington [4] and we accept their interpretation. Yellow solutions

[20] Bower and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 3583.
[21] Keefer and Allen, *J. Chem. Phys.*, 1956, **25**, 1059.
[22] Vonk and Wiebenga, *Acta Cryst.*, 1959, **12**, 867.

in sulphuric acid are also non-ionic, and cryoscopic results support the formulation $(IO)HSO_4$:

$$(IO)_2SO_4 + H_2SO_4 \rightleftharpoons 2(IO)HSO_4 \qquad (6)$$

Further evidence for this reaction is that ultraviolet spectra of its solutions in sulphuric acid vary markedly with the concentration of added water in the 95—100% acid region. In 95% acid, the spectrum is closely similar to that of solid $(IO)_2SO_4$, having poorly resolved bands in the 300 and 400 mμ regions, whilst absorption at 400 mμ falls to nearly zero in 100% sulphuric acid (Fig. 2). However, when prepared under carefully controlled conditions, solutions in 65% oleum are ionic, the conductivity approaching that required for one positive charge per iodine atom. The simplest explanation is that the ion IO^+ is formed:

$$(IO)HSO_4 + H_2S_2O_7 \rightleftharpoons IO^+ + HS_2O_7^- + H_2SO_4 \qquad (7)$$

and the marked change in the ultraviolet spectrum of solutions on going from 100% sulphuric acid to 65% oleum also shows that there is a definite alteration in the bonding to iodine.

Doubtless IO^+ is strongly solvated, and this formulation may be an oversimplification. Strong solvent interaction could affect the electronic structure in such a manner as to lower the energy of a singlet state below that of the triplet predicted for this ion.[5] However, it is conceivable that, even in the absence of a solvent field, IO^+ would have a singlet ground state. Calculations by Griffith [23] suggest that the hypothetical ion I_2^{2+} would have a singlet ground-state, and similar reasoning can be applied to IO^+, though the situation is less clear in this instance.

If the ground state is a singlet, however, there should still be a low-lying triplet level which would make a temperature-independent paramagnetic contribution to the magnetic susceptibility of the ion IO^+. Our results, given in Table 2, show that the diamagnetism of the colourless solid obtained from solutions of tervalent iodine in 65% oleum is considerably less than that of yellow iodous sulphate. If this solid is formulated as $(IO)HS_2O_7$, and a reasonable value for the magnetic susceptibility of $HS_2O_7^-$ is subtracted from the total susceptibility, then the iodine-containing fragment is found to be very weakly paramagnetic, in accord with the above postulate.

Similar arguments can be applied to solvated iodine cations in a strong axial field; [1] thus the small magnetic moment of 1·5 B.M. assigned to this ion may arise because the $^3\Sigma$-ground state is split so that $M_S = 0$ lies below $M_S = \pm 1$,[23] rather than for the reasons outlined earlier.[1]

Finally, the infrared spectrum of this colourless solid is markedly different from that of $(IO)_2SO_4$. All the features found for the ion $HS_2O_7^-$ from our study of KHS_2O_7 (Table 1) are also found in this instance, and there is an additional band at 770 cm.$^{-1}$ which could be the I–O stretching frequency for IO^+ in the crystal lattice. Absence of any other absorption which can be assigned to an iodine-containing species implies considerable simplicity, but, as Dasent and Waddington [4] have pointed out, one would expect the stretching frequency for IO^+ to be slightly greater than that of TeO, which is found [24] from infrared measurements to be 796 cm.$^{-1}$. In fact, if our identification is correct, the order is reversed: this may be an indication of strong cation–anion interactions in the crystal, which would weaken the I–O bond.

The ion I^{3+} is sometimes postulated as an important component of solutions of tervalent iodine in strongly acidic media.[3,25] We have found no evidence for this ion and consider that its formation is improbable in any circumstances since this involves the loss of

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[23] Griffith, personal communication.

[24] Haranath, Rao, and Sivarmamurty, *Z. Physik*, 1959, **155**, 507.

[25] Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul, London, 1938, 1st edn., p. 331.

two *p*-electrons from the cation I^+, leading to a configuration $5s^2,5p^2$. There is no feature which would stabilise this in relation to the configuration $5s^2,5p^4$ of I^+, and the ionization potential for the loss of two further electrons must be very large. Indeed, we should expect that if I^+ could lose electrons then I^{2+} would be favoured since its ground state is ^4S which should have special stability. There is no evidence for bivalent iodine in any of the solutions studied.

Quinquevalent Iodine.—Conductivity measurements established that IO_2^+ is not an important constituent of solutions of quinquevalent iodine compounds in 100% sulphuric acid, since reactions such as

$$HIO_3 + 2H_2SO_4 \longrightarrow IO_2^+ + H_3O^+ + 2HSO_4^- \quad (8)$$

would give twice the observed conductivity. Our data fit equally reactions 9 and 10:

$$HIO_3 + H_2SO_4 \longrightarrow H_2IO_3^+ + HSO_4^- \quad (9)$$

and

$$HIO_3 + 2H_2SO_4 \longrightarrow (IO_2)HSO_4 + H_3O^+ + HSO_4^- \quad (10)$$

These should be distinguishable by cryoscopy and our results (Table 3) are in better accord with (9) than with (10). However, our measurements were made on dilute solutions, because of very limited solubility, and we therefore sought further information about these systems.

In the 0—4% oleum region one can treat the medium as a solution of $H_3SO_4^+HS_2O_7^-$ in pure sulphuric acid. On addition of water the reaction

$$H_3SO_4^+ + HS_2O_7^- + H_2O \longrightarrow 3H_2SO_4 \quad (11)$$

occurs leading to 100% sulphuric acid. However, addition of potassium hydrogen sulphate leads to the loss of $H_3SO_4^+$ only:

$$K^+ + HSO_4^- + H_3SO_4^+ + HS_2O_7^- \longrightarrow K^+ + HS_2O_7^- + 2H_2SO_4 \quad (12)$$

$$HS_2O_7^- + H_2SO_4 \rightleftharpoons H_2S_2O_7 + HSO_4^- \quad (13)$$

The bisulphate ion thus formed by solvolysis gives rise to an increment in the conductivity which is sufficiently large to enable a clear choice to be made by comparison with the results for potassium hydrogen sulphate. Our results, given in Fig. 6, are in accord with the formation of $H_2IO_3^+$ rather than of $(IO_2)HSO_4$.

Solutions in oleum are less well characterised. There is a strong tendency to form solid iodine pentoxide but, as described in the Experimental section, solutions can be obtained whose conductivities approach that required for one positive charge per iodine atom. This species has an ultraviolet spectrum which is quite different from that assigned to $H_2IO_3^+$, and one alternative would be IO_2^+ (Fig. 2). Another is that the cation $IO(HS_2O_7)_2^+$ is formed:

$$H_2IO_3^+ + 4H_2S_2O_7 \longrightarrow IO(HS_2O_7)_2^+ + 2H_2SO_4 \quad (14)$$

We favour the latter alternative since, by analogy with the spectrum of the isoelectronic molecule TeO_2, we should have expected a well-defined spectrum for IO_2^+. On the other hand, the change observed is in accord with reaction (14) if the intensity arises from transitions involving electron-transfer from the oxide ligand to iodine.

Intermediate Valency States.—Our results show that compounds of iodine in valency states other than those already considered are not important constituents of these solutions.

In particular I_2O_4, which is thought to be polymeric in the solid state,[6] appears to dissolve according to the reaction

$$I_2O_4 + 2H_2SO_4 \longrightarrow (IO)HSO_4 + H_2IO_3^+ + HSO_4^-$$

This equation satisfactorily accounts for the conductance, the freezing-point depression, and the reactions of these solutions with aromatic compounds.

Effect of Silver Salts.—We find no evidence for the formation of iodine cations when silver sulphate is added to iodine in 100% sulphuric acid. However, the pronounced change in spectrum and greatly enhanced solubility of both components strongly suggest that a complex, such as AgI_2^+, is formed. Our conductometric results for these solutions are in accord with the reactions

$$Ag_2SO_4 + H_2SO_4 \longrightarrow 2Ag^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$Ag^+ + I_2 \rightleftharpoons AgI_2^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

the conductivities being independent of the concentration of iodine, as required. These solutions are powerful iodinating agents,[26] their reactivity being comparable with that of solutions containing I_3^+, as might be expected if AgI_2^+ is the effective reagent.

Oxidation–Reduction Equilibria.—The complex nature of the spectral data for solutions in dilute oleum and sulphuric acid shows that various of the species discussed above are in equilibrium with each other. By studying the effect of changing temperature, concentrations, and medium, and of adding bases, we have deduced that the important equilibria are:

$$4I^+ + 3HS_2O_7^- + 2H_2SO_4 \rightleftharpoons (IO)HS_2O_7 + I_3^+ + 3H_2S_2O_7 \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$3I_3^+ + 3HS_2O_7^+ + 2H_2SO_4 \rightleftharpoons (IO)HS_2O_7 + 4I_2 + 3H_2S_2O_7 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The first equilibrium is reached rapidly, but the second slowly at room temperature. The former is of particular significance in the 5—50% oleum region and the latter in the 100% sulphuric acid region.

The following are qualitatively in accord with equilibrium (18): (i) Addition of iodous sulphate or pyrosulphuric acid results in loss of I_3^+ and corresponding gain of I^+. (ii) Addition of potassium pyrosulphate has the opposite effect. (iii) Dilution favours the formation of I^+ at the expense of $(IO)HS_2O_7$ and I_3^+. Similarly in 100% sulphuric acid, provided sufficient time is allowed for the attainment of equilibrium, dilution and the addition of base result in the loss of I_3^+, but the addition of pyrosulphuric acid has the reverse effect.

Generally, the law of mass action is obeyed, but the systems are complicated because the equilibria occur simultaneously, slight changes in the medium can alter them considerably and are difficult to control, and other subsidiary reactions, such as the formation of I_5^+, have to be taken into account.

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[26] Derbyshire and Waters, *J.*, 1950, **3694**.