670. *Iodine Oxygen Compounds. Part II.* Iodosyl and Related Compounds.*

By W. E. Dasent and T. C. Waddington.

The preparation and infrared and visible spectra of iodosyl sulphate, iodosyl selenate, iodine dioxide, and μ-oxo-dinitratodiphenyldi-iodine are reported

Because of the similarity of the infrared and visible spectra of the iodosyl compounds and iodine dioxide to those of the organic iodine compound, it is concluded that the " IO " cation is polymeric with I–O–I bridges.

The existence has been reported of a small number of compounds conjecturally formulated as salts of the iodosyl cation IO^+. These are (*a*) the sulphate, $(IO)_2SO_4$, a hygroscopic, bright yellow substance variously regarded as a monohydrate,[1] a hemihydrate,[2,3] and an anhydrous [4] salt; (*b*) a poorly defined, highly unstable bright yellow nitrate obtained [5,6] from iodine and fuming nitric acid; and (*c*) the pale yellow " iodine dioxide," I_2O_4, formed [7] by slow hydrolysis of iodosyl sulphate. Iodine dioxide has usually been regarded [5] as iodosyl iodate, $IO{\cdot}IO_3$, although there has been little evidence to support this. Early investigators [5] of the nitrate were unable to decide between the formulæ $IO{\cdot}NO_3$ and $I(NO_3)_3$; subsequent work by Kikindai [6] seems to support its formulation as an iodosyl salt, though his analyses allow for contamination by up to 1·8 moles of free nitric acid. A recent brief report [8] of the preparation of $I(NO_3)_3$ as a yellow product of the reaction between iodine trichloride and $ClNO_3$ sheds no light on the problem.

To obtain further information as to the constitutions of these compounds we have studied their infrared spectra, together with those of a diverse range of related compounds. Unfortunately, the iodosyl nitrate, $IO{\cdot}NO_3$, proved to be too unstable and reactive for a satisfactory infrared spectrum to be obtained. We have attempted to prepare further compounds analogous to $(IO)_2SO_4$, using the procedure of Masson and Argument,[4] with different acids in place of sulphuric acid; only in the case of selenic acid was the method successful and led to the preparation of the new iodosyl selenate, $(IO)_2SeO_4$, which is isomorphous with, and very similar in properties to, the sulphate.

We consider it unlikely that these compounds contain the simple iodosyl cation, IO^+, on the following grounds:

(1) Apart from the small solubility of the sulphate and selenate in the concentrated

---

* Part I, *J.*, 1960, 2429.

[1] Bahl and Partington, *J.*, 1935, 1258.
[2] Chrétien, *Compt. rend.*, 1896, **123**, 814.
[3] Fichter and Dinger, *Helv. Chim. Acta*, 1936, **19**, 607.
[4] Masson and Argument, *J.*, 1938, 1702.
[5] Kappler, *Ber.*, 1911, **44**, 3496.
[6] Kikindai, *Compt. rend.*, 1954, **238**, 1229.
[7] Muir, *J.*, 1909, **95**, 656.
[8] Schmeisser, Fink, and Bandle, *Angew. Chem.*, 1957, **69**, 780.

parent acid, none of the iodosyl compounds showed any sign of solubility (without decomposition) in any of a wide range of solvents tested, including those, like nitromethane, which dissolve nitrosonium salts. Unfortunately, the ultraviolet absorption spectrum of the nearly colourless solution of iodosyl sulphate in concentrated sulphuric acid is ill defined [9] and sheds no light on the nature of the species present. This insolubility is surprising if the compounds are indeed salts containing a univalent cation, and strongly suggests a polymerized structure.

(2) By analogy with the oxygen molecule, which contains the same number of valency electrons, the IO^+ ion might be expected to have a $^3\Sigma^-$ ground state and hence be paramagnetic, as Symons [9] has pointed out. Iodosyl sulphate [9] and iodine dioxide [10] are both diamagnetic and so is iodosyl selenate.

(3) Completely isoelectronic compounds have very similar vibration frequencies. Changes in charge only affect these slightly. Thus we have in the series NO_2^+, CO_2, NCO^-, NCN^{2-} the following values for ν_3 (in cm.$^{-1}$) 2390, 2349, 2170, 2150, and for NO^+, CO, CN^- the stretching frequency has the values (cm.$^{-1}$) 2200, 2144, 2080. Now molecular TeO [11,12] has a fundamental vibration frequency of 796 cm.$^{-1}$ so we might reasonably expect for the isoelectronic IO^+ a vibration frequency of about 800 cm.$^{-1}$ or a little higher. In iodosyl sulphate and selenate, and in iodine dioxide, the only absorption attributable to the IO group occurs in the frequency range 553—658 cm.$^{-1}$. This is considerably lower than any I=O stretching frequency (values of which are given below) let alone the stretching frequency to be expected of IO^+.

	I=O asym. str. (cm.$^{-1}$)	I=O sym. str. (cm.$^{-1}$)
IO_3^- (metallic iodates) [13]	743—796	695—780
IO_2 (complex iodates) [13]	757—808	719—758
IO_2 (iodoxy-benzenes) [14]	762—795	716—744

μ-Oxo-dinitratodiphenyldi-iodine.—The preparation of the compound, wrongly identified by Willgerodt [15,16] as iodosobenzene dinitrate, $C_6H_5I(NO_3)_2$, and its analysis and identification as the oxygen-bridged compound $[C_6H_5I(NO_3)]_2O$ have been reported in a separate preliminary communication.[17] The infrared spectrum of this compound, containing as it does an I–O–I bridge, throws a good deal of light on the structure of the inorganic iodosyl compounds. The spectrum has been examined and an almost complete assignment made. This will be discussed in detail. Apart from the usual aromatic C–H peaks the usual monosubstituted benzene-ring peaks occur at 1583, 1565, 1472, and 1447 cm.$^{-1}$ in the sodium chloride region and at 735, 677, and 656 (w) cm.$^{-1}$ in the potassium bromide region [cf. iodobenzene 727, 683, and 653 (s) cm.$^{-1}$; iodosobenzene 734, 690, and 655 (vw) cm.$^{-1}$; iodosobenzene diacetate, 739 and 683 cm.$^{-1}$, any peak at 655 cm.$^{-1}$ being obscured by absorption by the acetate group]. A C–I vibration frequency is found at 457 cm.$^{-1}$ (cf. iodobenzene, 447 cm.$^{-1}$; iodosobenzene, 489 cm.$^{-1}$; iodosobenzene diacetate, 463 cm.$^{-1}$). The six fundamental frequencies characteristic of a covalent nitrate group are also found and are assigned by comparison with the data for metal nitrato-complexes [18,19] and methyl nitrate in Table 1, from which it will be seen that the frequencies in the organic complex lie much closer to those in the metal nitrato-complexes than to those in methyl nitrate. There are also a large number of weak combination frequencies in the sodium chloride

---

[9] Symons, *J.*, 1957, 2186.

[10] Willmarth and Dharmatti, *J. Amer. Chem. Soc.*, 1950, **72**, 5789.

[11] Herzberg, " Molecular Spectra and Molecular Structure, I, Diatomic Molecules," Prentice-Hall, 1939.

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

[13] Dasent and Waddington (Part I), *J.*, 1960, 2429.

[14] Furlani and Sarton, *Ann. Chim.* (*Rome*), 1957, **47**, 124.

[15] Willgerodt, *Ber.*, 1892, **25**, 3498.

[16] Willgerodt, *Ber.*, 1893, **26**, 1308.

[17] Dasent and Waddington, *Proc. Chem. Soc.*, 1960, 71.

[18] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

[19] Gatehouse and Comyns, *J.*, 1958, 3965.

region which can be reasonably assigned. Only two peaks are left, *viz.*, 585 cm.$^{-1}$ (vs) and 427 cm.$^{-1}$ (ms); 585 cm.$^{-1}$ can very reasonably be assigned to the I–O–I asymmetric stretching frequency. There should also be a symmetric stretching frequency; this could be the 427 cm.$^{-1}$ frequency, but this frequency might equally reasonably be due to I–ONO_2.

TABLE 1. *Nitrato-frequencies in μ-oxo-dinitratodiphenyldi-iodine and other nitrato-compounds.*

	–O·NO_2 in the iodine complex (cm.$^{-1}$)	–O·NO_2 in metal nitrato-complexes (cm.$^{-1}$)	–O·NO_2 in methyl nitrate (cm.$^{-1}$)
ν_1	1270	1290—1253	1287
ν_2	993	1034—970	854
ν_4	1427 *	1531—1481	1672
ν_6	802	800—781	759
ν_3	706	706—721	578 †
ν_5	717	736—749	657

* Overlapped by benzene ring vibration.
† Calculated from overtones.

Iodosyl Sulphate and Selenate.—The infrared spectrum of iodosyl sulphate between 4000 and 400 cm.$^{-1}$ is relatively uncomplicated; the positions of the maxima are listed in Table 2. The simplicity of the spectrum is significant in view of what may be expected if the symmetry of the sulphate ion were altered by covalent bond formation. The symmetrical tetrahedral ion SO_4^{2-} has T_d symmetry and four fundamental vibrations:

	ν_1	ν_2	ν_3	ν_4
Group symmetry	A_1	E	F_2	F_2
Frequency (cm.$^{-1}$) [15]	981	451	1104	613

Only ν_3 and ν_4 are infrared active. If the sulphate ion acts as a monodentate group, *i.e.*, if it forms one covalent bond, the symmetry is changed to C_3 and six infrared active fundamentals should be observed, *viz.*, ν_1, ν_2, and four new fundamentals resulting from the splitting of both the triply degenerate frequencies ν_3 and ν_4 into a non-degenerate and a doubly degenerate vibration. If the sulphate ion functions as a bidentate group, *i.e.*, if it forms two covalent bonds, the symmetry is again altered, to C_2; nine fundamental vibration frequencies (all but one of which are infrared active) would then occur, resulting from the splitting of the remaining doubly degenerate vibrations. So if the sulphate group were forming one or two covalent bonds, the forbidden frequencies ν_1 and ν_2 should appear in the spectrum, together with extensive splitting of both ν_3 and ν_4. Some instances [21-23] of this have been reported.

Now there is no evidence for this state of affairs in iodosyl sulphate or selenate. In iodosyl sulphate, ν_3 (1035 cm.$^{-1}$) appears as a rather broad band at somewhat lower frequencies than is usual for a typically ionic sulphate; ν_4 (633 cm.$^{-1}$) is also slightly displaced, but the possibility that the nearby maximum (577 cm.$^{-1}$, which we have assigned to the IO group) results from a splitting of ν_4 can be rejected in the absence of any other indications of asymmetry, such as the appearance of ν_1 and ν_2. There is some sign of frequency splitting in iodosyl selenate; ν_3 has a pair of poorly resolved peaks at 825 and 798 cm.$^{-1}$ (again the frequencies are rather lower than in the alkali-metal selenates) and the weak peak at 471 cm.$^{-1}$, which we have assigned to ν_4, could be the higher frequency of a split vibration. However, the absence of ν_2 indicates that the ion is unlikely to be asymmetric and the splitting of ν_3 may very well be an effect of the symmetry of the lattice. A comparison of the frequencies in the iodosyl sulphate and selenate with those in other sulphates and selenates is made in Table 2.

---

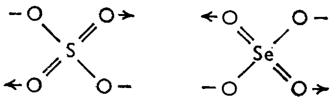
[20] Brand and Cawthorn, *J. Amer. Chem. Soc.*, 1955, **77**, 319.
[21] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[22] Mizushima and Quagliano, *J. Amer. Chem. Soc.*, 1953, **75**, 4870.
[23] Bertin, Penland, Mizushima, and Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 3818.

TABLE 2. *Vibration frequencies and assignments in iodosyl sulphate and selenate and in some other selenates and sulphates.*

Compound	I–O (cm.$^{-1}$)	SO_4^{2-}		SeO_4^{2-}	
		ν_3 (cm.$^{-1}$)	ν_4 (cm.$^{-1}$)	ν_3 (cm.$^{-1}$)	ν_4 (cm.$^{-1}$)
$(IO)_2SO_4$	562 577	1035	633		
SO_4^{2-} ion [24]		1104	613		
K_2SO_4		1110	617		
$(Me_4N)_2SO_4$		1136	607		
$(IO)_2SeO_4$	553 600			825 798	471 [a]
Na_2SeO_4				884	426
K_2SeO_4				874	427
$(Me_4N)_2SeO_4$				851	413
Ag_2SeO_4				835	408

[a] This is a weak peak and the assignment tentative: ν_4 may lie below 400 cm.$^{-1}$.

It may be safely concluded that in iodosyl sulphate and selenate, the tetrahedral symmetry of the sulphate and selenate groups is essentially undisturbed, and that all four SO and SeO bonds are equivalent. This does not necessarily mean that tetrahedral *ions* are present, since structures in which all four oxygen atoms form covalent bonds, *i.e.*,



would likewise retain the T_d symmetry, provided that the differences in bond order implied by the classical formulæ were removed by resonance.

Now the absorption attributable to the IO group in these two compounds lies in the lower frequency region expected for an I–O *single* bond, as can be seen from the following values:

I–O in complex iodates	630—697 cm.$^{-1}$
I–OH in iodic acid	577—650 cm.$^{-1}$
I–O–I in μ-oxodinitratodiphenyldi-iodine	588 cm.$^{-1}$

In formulating iodosyl sulphate and selenate, therefore, one has to assign structures in which the iodine atoms form essentially single bonds, and in which the sulphate and selenate groups are present either as discrete anions, or as four-covalent groupings. Although it is not possible to allot definitive structures on this basis alone, yet reasonable postulates can be made which are in agreement with the known properties of the compounds; the most plausible of these involves polymerized IO chains, between which the sulphate and the selenate groups are accommodated, by either ionic or covalent bonds. It may well be that the I···O–S bonds, represented by broken lines in Figure 1, are intermediate in character. *X*-Ray powder photography merely reveals that iodosyl sulphate and selenate are isomorphous, with very complicated unit cells; the method of preparation of the compounds precludes the growth of single crystals for detailed *X*-ray studies.

Iodine Dioxide.—The infrared spectrum of iodine dioxide can be readily interpreted on the basis of a structure (similar to those of iodosyl sulphate and selenate) for the compound, composed of iodate and polymerized I–O groups. A satisfactory assignment of the entire observed spectrum can be made if it is assumed that the compound consists of a network of IO_3 groups and polymerized I–O chains, in which the iodate groups are linked to the chains by bonds comparable in covalent character with the iodate–metal bonds in metallic iodate complexes, or the iodate–hydrogen bonds in iodic acid. The assignments

[24] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., New York, 1945, p. 167.

are shown in Table 3, along with the corresponding frequencies in comparable compounds. The relevant parts of the infrared spectra are shown in Fig. 2.

TABLE 3. *Frequencies and assignments in* I_2O_4 *and comparison compounds.*

Compound	OIO_2 ν_1	OIO_2 ν_2	OIO_2 ν_{3a}	OIO_2 ν_{3b}	I–O–I stretch
Iodine dioxide	622 s 658 m	408	825 w 783 s	745 s	578 s
Iodato-complexes [14]	630—697	not obs.	757—808	719—759	—
Iodic acid [14]	577—650	not obs.	804—835	718—763	—
Iodosyl sulphate and selenate	—	—	—	—	553—600
μ-Oxo-dinitratodiphenyldi-iodone	—	—	—	—	585

The formulation of I_2O_4 as iodosyl iodate is thus satisfactory if it is remembered that the IO group is not present as a discrete cation, and that the IO_3 group forms bonds which are at least semicovalent. Again, the method of preparation of the compound precludes the growth of single crystals for detailed *X*-ray studies. There is chemical evidence that the IO group present in iodosyl sulphate is similarly constituted to that in iodine dioxide, since the latter is prepared by the controlled, slow hydrolysis of the sulphate. If iodosyl sulphate is treated with an excess of water, the hydrolysis

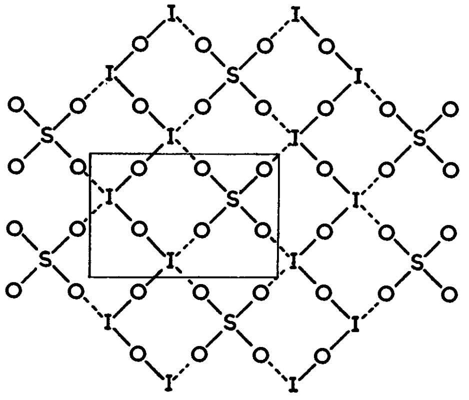
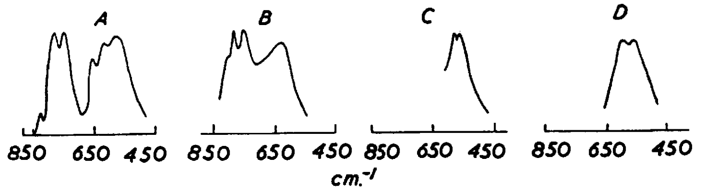


FIG. 1. *Two-dimensional representation of type of structure postulated for iodosyl sulphate (the selenate is similar, with* Se *replacing* S). *The repeating unit (boxed) is* $I_2O_2SO_4$.

FIG. 2. *Infrared spectra of* I_2O_4 *and reference compounds.*



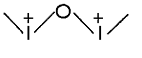
A, $IO{\cdot}IO_3$. *B*, IO_3 *in* $K_2Mn(IO_3)_6$. *C*, IO *in* $(IO)_2SO_4$. *D*, IO *in* $(IO)_2SeO_4$.

$$5(IO)_2SO_4 + 8H_2O = 2I_2 + 6HIO_3 + 5H_2SO_4 \quad (1)$$

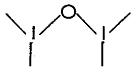
proceeds rapidly to completion. But if the hydrolysis is performed slowly, *e.g.*, by exposing the sulphate to moist air, considerable amounts of I_2O_4 are produced. This suggests [5] that under these conditions the iodate produced in reaction (1) has time to react with the iodosyl group of unchanged iodosyl sulphate, producing $IO{\cdot}IO_3$ by metathesis:

$$(IO)_2SO_4 + 2HIO_3 = 2IO{\cdot}IO_3 + H_2SO_4$$

Ultraviolet and Visible Spectra.—There is evidence that the yellow colour of all three iodosyl compounds and of μ-oxo-dinitratodiphenyldi-iodine can be associated with the presence of the postulated I–O–I bridges. The infrared spectrum of the solid complex shows that the two nitrate groups are linked to the iodine atoms by bonds which resemble the partially covalent nitrate–metal linkages in metallic nitrato-complexes such as $Co(NO_3)(NH_3)_5^{2+}$ rather than the more fully covalent carbon–nitrate bond in methyl nitrate. The solid compound is yellow. The colours of its solutions, however, vary in a striking way with the dielectric constant of the solvent. In liquids of low dielectric constant (chloroform, methylene dichloride) the compound readily dissolves (and can be recovered unchanged), but the solutions are quite colourless. Solutions in liquids of higher dielectric constant (*e.g.*, ethanol) have a perceptible yellow colour, which is intensified in liquids of even greater ionizing power (*e.g.*, dimethylformamide). The variation is colour can only be related to the degree of ionization of the nitrate groups, since the nitrate group itself is colourless, either as the free anion or in methyl nitrate. The source of the colour must lie in the extent to which the iodine atoms of the bridge carry a partial positive charge, a tendency towards (*a*) intensifying and towards (*b*) diminishing (or shifting to shorter wavelengths) the absorption responsible for the yellow colour.



(*a*) Yellow



(*b*) Colourless

This is precisely the structural element postulated in iodosyl sulphate, selenate, and iodate.

Attempts to measure the yellow colour quantitatively were only partly successful, since the inorganic iodosyl compounds are insoluble, while in the organic nitrato-complex the comparatively low intensity of the I–O–I absorption is partly obscured by the much more intense absorption of the benzene rings which lies just beyond it in the ultraviolet region. However, qualitatively it can be seen that there is no detectable absorption apart from that of the benzene rings in the ultraviolet spectra of the complex in methylene dichloride and chloroform. In ethanol there is some indication of absorption just above that of the benzene rings, and in dimethylformamide the absorption spectrum of the complex shows a broad plateau of low intensity at 400 mμ. The reflectance spectra of solid samples of the three inorganic compounds were determined. For iodine dioxide, absorption begins at about 450 mμ, rises to a rather broad maximum in the region of 350 mμ, and then decreases again. The sulphate and selenate show a generally similar spectrum, but it is displaced about 50 mμ to longer wavelengths, absorption beginning at about 500 mμ and rising to a maximum at about 400 mμ, in accordance with the rather brighter yellow colour of the two compounds. If our postulate as to the origin of the yellow colour is correct, the shorter-wavelength absorption in iodine dioxide implies a higher degree of covalent bonding between the iodate groups and the I–O bridges; the infrared spectra also suggest this.

EXPERIMENTAL

All hygroscopic materials were handled throughout in a dry box containing phosphorus pentoxide. Samples for infrared determinations were dried *in vacuo* over suitable desiccants, mulled with Nujol or hexachlorobutadiene, and smeared between sodium chloride or potassium bromide plates. In the case of the μ-oxo-dinitratodiphenyldi-iodine it was necessary to protect the plates with a thin sheet of Polythene to prevent exchange of the nitrate group with the halide in the plates (cf. refs. 18 and 19). A thin sheet of Polythene was introduced into the other beam for purposes of compensation. The spectra were all measured on a Perkin-Elmer 21 double-beam recording spectrophotometer with sodium chloride and potassium bromide optics.

The ultraviolet reflectance spectra were measured on a recording Beckman DK spectrophotometer. The ultraviolet absorption spectra were measured on a Cary recording spectrophotometer.

X-Ray powder photographs of iodosyl sulphate and selenate were taken with Cu-K_α radiation, on a 19 cm. Debye–Scherrer camera, samples being filled into thin-walled Pyrex capillaries which were then sealed with picein wax.

Analyses for iodine were performed by standard volumetric procedures; selenium was determined as the element, and sulphur as barium sulphate. Carbon, hydrogen, and nitrogen in the organic complex were determined by standard microcombustion methods.

The following compounds were either pure commercial samples or were prepared by standard metathetical reactions: potassium and tetramethylammonium sulphates; potassium, sodium, silver, and tetramethylammonium selenates.

Iodosyl sulphate was prepared [4] by shaking the theoretical quantities of finely powdered iodine pentoxide and iodine in concentrated sulphuric acid. Most of the adhering acid was removed from the yellow product by spreading the crystals on a porous tile, and the remainder by washing them quickly several times with glacial acetic acid. It was stored over concentrated sulphuric acid (Found: I, 65·6; S, 8·4. Calc. for I_2SO_6: I, 66·5; S, 8·4%).

Iodosyl selenate. Iodine (1·269 g., 0·005 mole) and iodine pentoxide (2·504 g., 0·0075 mole) were finely powdered and added to commercial selenic acid (25 ml.; 97·4% of H_2SeO_4 by titration), and the mixture was warmed sufficiently to melt any solid acid (re-solidification did not occur on cooling). The mixture was shaken intermittently for several days, after which the reactants had dissolved to a brown solution. After 9 days, bright yellow crystals began to separate and precipitation was complete after a further day. The liquid was poured off, and the very hygroscopic crystals spread on a porous plate for several hours, then washed rapidly with glacial acetic acid and stored over concentrated sulphuric acid (Found: I, 58·3; Se, 18·7. I_2SeO_6 requires I, 59·2; Se, 18·4%).

Iodine dioxide was prepared by a slight modification of Muir's method.[7] The yellow product obtained by heating iodic acid with concentrated sulphuric acid was freed as much as possible from sulphuric acid by suction through a sintered-glass funnel, washed quickly with cold glacial acetic acid, and allowed to hydrolyse slowly on a porous tile exposed to air. The product, apparently a mixture of iodine dioxide, iodine, iodic acid, and sulphuric acid, was finely powdered and washed quickly with several small portions of cold water until the washings were free from sulphate, and then with ethanol to remove iodine. Since iodine dioxide reacts slowly with cold water, it was impossible to prevent slight decomposition during the washing process; the iodic acid cannot be removed in any other way than by washing the mixture with water (Found, in a typical specimen: I, 79·2. Calc. for IO_2: I, 79·9%).

Iodosobenzene and iodosobenzene diacetate were prepared as described by Mann and Saunders, " Practical Organic Chemistry," 3rd edn.

Iodobenzene nitrate.[15, 16] Iodobenzene diacetate (3 g.), dissolved in glacial acetic acid (10 ml.), was added to a mixture of nitric acid (*d* 1·42; 1·4 ml.), water (1·4 ml.), and glacial acetic acid (3 ml.). The resulting pale yellow solution was allowed to evaporate in a warm place. The yellow crystals formed were dried on a porous tile (KOH and silica gel) and had m. p. 105—106° [Found: C, 26·3; H, 2·4; N, 4·9%; *M*, by vapour-pressure lowering in CH_2Cl_2, 550, 555 (two separate preparations). $C_6H_5I(NO_3)\cdot O\cdot I(NO_3)\cdot C_6H_5$ requires C, 26·3; H, 1·8; N, 5·1%; *M*, 548]. Acidimetric equivalent (by potentiometric titration with tetrabutylammonium hydroxide in benzene–methanol, 274. By potentiometric titration of a separate preparation with potassium hydroxide in methanol–water, 276. Calc. 274. The compound reported by Willgerodt as yellow crystals, m. p. 105—106°, was assigned by him the formula $C_6H_5I(NO_3)_2$ (Calc.: C, 21·95; H, 1·5; N, 8·5%; *M*, 328; equiv., 164). Willgerodt records only nitrogen analyses, agreeing with his formulation. Attempts were made to obtain a product with Willgerodt's formula by using iodosobenzene in place of the diacetate, and by varying the concentration of nitric acid (and the proportions of acetic acid) in the reaction mixture over a very wide range. In all cases, analyses, which varied slightly according to the method of preparation, of the yellow crystals were within the limits C, 25·60—26·75; H, 2·19—3·29; N, 4·6—4·9. We can only conclude that Willgerodt's compound, in spite of its identical appearance and melting point, was different from our own, or that Willgerodt's analyses for nitrogen were in error. The molecular weight (Found: 330. Calc.: 322) and acidimetric equivalent (Found: 166. Calc.: 161) of iodobenzene diacetate were determined by the same method as used for the nitrate, and were found to agree with the accepted formula $C_6H_5I(OAc)_2$.

We thank Dr. A. R. Caverhill for measurement of the reflectance spectra. One of us (W. E. D.) acknowledges the award of a Fellowship from the Nuffield Foundation.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, February 8th,* 1960.]