ORGANIC COMPOUNDS OF POLYVALENT IODINE

REUBEN B. SANDIN

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

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The present review gives particular emphasis to recent work done in the field of organic compounds of polyvalent iodine. A brief historical survey is presented. The remainder of the survey deals with iodoso, iodoxy, and iodonium compounds under the following headings: (*a*) preparation; (*b*) properties; and (*c*) structures.

Phenyl iodide is a very interesting compound because of the polyvalency of its iodine atom. When it is treated with dry chlorine in anhydrous inert solvents, yellow crystalline phenyliodoso chloride, $C_6H_5ICl_2$, is formed. With bases the latter compound forms iodosobenzene or phenyliodoso oxide, C_6H_5IO. When iodosobenzene is heated, it undergoes disproportionation to give phenyl iodide and iodoxybenzene, $C_6H_5IO_2$. Treatment of iodosobenzene with phenylmagnesium bromide, or with silver oxide and iodoxybenzene, produces diphenyliodonium hydroxide, $(C_6H_5)_2IOH$, a strong base.

There is in existence, therefore, a group of organic iodides in which the halogen atom can exert a valence greater than one. Most of the work on compounds of polyvalent iodine was done between the years 1892 and 1912. During the past thirty years there has appeared only occasional reference to this group, a group certainly of considerable theoretical interest, especially from the standpoint of valence studies. The object of this paper is to discuss in a general way this group of compounds and to review the more important work done since 1914. The excellent monograph written by C. Willgerodt (85) and published in 1914 covers in detail the earlier work accomplished in this field, and no attempt has been made to repeat what has already been done.

I. HISTORICAL

In 1885 Willgerodt (86) prepared phenyliodoso chloride, $C_6H_5ICl_2$, the first organic compound containing polyvalent iodine to be recorded. The compound was obtained by the action of iodine trichloride on phenyl iodide. One year later, in 1886, Willgerodt (89) discovered that the same compound could be prepared by passing chlorine through a solution of phenyl iodide in chloroform, under which conditions it separated as light yellow needles.

In 1892 Meyer and Wachter (50) prepared *o*-iodosobenzoic acid by the oxidation of *o*-iodobenzoic acid with fuming nitric acid. This was the first iodoso compound to be discovered. In the same year Willgerodt (75) obtained iodosobenzene, C_6H_5IO, by treating phenyliodoso chloride with an aqueous solution of sodium hydroxide, and in the same report he mentioned the preparation of iodoxybenzene, the first iodoxy compound, by heating iodosobenzene.

Meyer and Wachter (50) in describing iodosobenzoic acid, the first iodoso compound, suggested the possibility of making aromatic iodoxy compounds by treating aromatic compounds with sulfuric acid and iodic acid, the latter acid corresponding to nitric acid. They actually added benzene to the mixture of acids and got a solid compound. However, it does not appear that the experiment was followed up. It was not until 1937 that Masson and Race (45) showed that in a number of cases this reaction, instead of producing the iodoxy compound, affords much the simplest and most economical way of making iodonium compounds.

In 1894 Hartmann and Meyer (25) dissolved iodosobenzene in cold concentrated sulfuric acid and so were the first ones to discover the existence of the remarkable class of polyvalent iodine compounds known as iodonium compounds. They showed that the reaction mixture contained the sulfate of the base, phenyl-*p*-iodophenyliodonium hydroxide, a derivative of the hypothetical base, H_2IOH. Later in the same year, Hartmann and Meyer (26) obtained diphenyliodonium hydroxide by shaking equivalent quantities of iodosobenzene and iodoxybenzene with water and silver oxide. Mixed aliphatic aromatic iodonium compounds were prepared by Willgerodt (80, 87) in 1895 by the action of aryliodoso chlorides on the compound of silver chloride and silver acetylide suspended in water. These compounds were described by Willgerodt as being dichloroethylaryliodonium compounds. It remained for Thiele and Haakh (65) to show that the compounds described by Willgerodt were dichlorovinyl compounds and not dichloroethyliodonium compounds. It also remained for Thiele and Haakh (65) to show that organic compounds of polyvalent iodine are not peculiar to the aromatic series. They found analogs to all of these compounds amongst the olefins, with chloroiodoethylene as their simplest parent substance. Thiele (66, 67) even demonstrated that methyl iodide at low temperatures could combine with chlorine. However, the product decomposed readily at −28°C., producing methyl chloride and iodine chloride. To have a stable compound of polyvalent iodine it was therefore necessary to have this element attached to a doubly bound carbon atom.

Many of the fundamental properties of the iodoso, iodoxy, and iodonium groups have remained obscure or else misapprehended since the pioneering discoveries of Willgerodt and Victor Meyer. However, the relatively recent and excellent contributions made by J. R. Johnson, Lucas and coworkers, Masson and coworkers, and others have done much to throw light on these groups and the relations which exist between them.

II. PREPARATION OF THE COMPOUNDS OF POLYVALENT IODINE

A. Iodoso compounds

Willgerodt (76, 79) and V. Meyer (2) obtained iodoso compounds readily by treating an iodoso salt, such as the iodoso chloride, with a dilute aqueous solution of an alkali hydroxide, an alkali carbonate or bicarbonate, calcium hydroxide or barium hydroxide:

$$C_6H_5ICl_2 + 2NaOH \rightarrow C_6H_5IO + H_2O + 2NaCl$$

It was found advisable to use aqueous sodium carbonate or bicarbonate instead of the alkali hydroxide for the preparation of the iodoso compounds from polyhalogen-substituted phenyliodoso chlorides (97). Thiele and Haakh (65) used the alkali carbonates instead of the alkali hydroxides for the preparation of the iodoso compounds from iodoethylene iodoso chloride and chloroethylene iodoso chloride. Lucas, Kennedy, and Formo (38) have given directions for the preparation of iodosobenzene in a 60 to 62 per cent yield, by the action of aqueous sodium carbonate and sodium hydroxide on phenyliodoso chloride. Ortoleva (54) prepared iodoso compounds by the action of water on a pyridine solution of the iodoso chloride.

Iodoso compounds have been made by the direct oxidation of the organic iodide. V. Meyer and coworkers (2, 50) used fuming nitric acid or potassium permanganate in dilute sulfuric acid as the oxidizing agent. Harries (23) oxidized phenyl iodide to iodosobenzene by means of ozone. Böeseken and Schneider (5, 6) carried out the oxidation of aromatic iodine compounds with 8 to 10 per cent solutions of peracetic acid in acetic acid. In no case did the oxidation proceed beyond the iodoso stage. The acetates of the following compounds were thus prepared: iodosobenzene, *o*-iodosotoluene, *o*-nitroiodosobenzene, *m*-nitroiodosobenzene, and *p*-iodosobenzoic acid. Similarly, *m*-diiodosobenzene tetraacetate was obtained from *m*-diiodobenzene and *o*-diiodosobenzene anhydride diacetate from *o*-diiodobenzene. Under similar conditions *o*-iodobenzoic acid and *o*- and *p*-iodobenzenesulfonic acids gave the corresponding iodoso compounds, which were believed to be internal salts without ring structure. With a 70 per cent solution of peracetic acid, monoiodofumaric acid gave iodosofumaric acid, which lost carbon dioxide in boiling water to form iodosoacrylic acid. Diiodofumaric acid took up two oxygen atoms, probably yielding the diiodoso acid, which lost no carbon dioxide in boiling water. Arbuzov (1) also reported the oxidation of phenyl iodide to the iodoso state by means of peracetic acid and perbenzoic acid.

Masson and Hanby (44) have carried out the direct substitution of aromatic hydrogen by the iodoso group, by the use of iodyl sulfate, $I_2O_3 \cdot SO_3$ or $(IO)_2SO_4$. The latter reagent was prepared from iodine, iodine pentoxide, and 96 per cent sulfuric acid. Nitrobenzene gave a 50 to 60 per cent yield of *m*-iodosonitrobenzene. Benzenesulfonic acid similarly gave iodosobenzenesulfonic acid and benzoic acid was likewise attacked, although with complications. In the direct formation of *m*-iodosonitrobenzene the missing 40 to 50 per cent yield was accounted for as *m*-iodonitrobenzene and iodonium salts. These products were experimentally traced to a relatively slow secondary decomposition of the primary iodoso compounds by sulfuric acid. The secondary decomposition was of the same kind as that discovered by Hartmann and V. Meyer (25) who, by treating iodosobenzene with concentrated sulfuric acid, obtained *p*-iodophenyl phenyliodonium sulfate, together with degradative consumption of oxygen and the formation of iodo compounds. Theirs was a rapid reaction, but in the case of the *m*-iodosonitrobenzene the *m*-nitro group made the decomposition slow and thus the *m*-iodosonitrobenzene was easily isolated before much of it was consumed.

Masson and Hanby, in their interpretation of the reaction, have considered it as being a number of ionic exchanges between the following ions: IO^+, iodyl;

I^{+++}, iodous; RI^{++}, iodoso; and R_2I^+, iodonium. The iodyl sulfate was regarded as the source of I^{+++} cations:

$$IO^+ + 2H^+ \rightleftarrows I^{+++} + H_2O$$

The formation of *m*-iodosonitrobenzene was expressed as a partial ion exchange:

$$I^{+++} + RH \rightarrow H^+ + RI^{++}$$

and, apart from the slow secondary decomposition, the reaction with a reagent which contained a *m*-directing substituent stopped there. With a compound containing an *o*,*p*-directing substituent the same reaction was considered to take place but was followed by a further step in ionic exchange:

$$RI^{++} + RH \rightarrow H^+ + R_2I^+$$

the total reaction being therefore

$$I^{+++} + 2RH \rightarrow 2H^+ + R_2I^+$$

It might be mentioned here that some of the above ions such as the iodous ion, I^{+++}, are unusual and interesting ions and lend themselves to much speculation.

B. Iodoso salts

Willgerodt (75) showed that one of the best methods for the preparation of the iodoso chloride was to lead dry chlorine gas into an ice-cold solution of the aryl iodide dissolved in chloroform, the reaction being analogous to the behavior of iodine monochloride:

$$ICl + Cl_2 \rightarrow ICl_3$$

$$C_6H_5I + Cl_2 \rightarrow C_6H_5ICl_2$$

Under these conditions the salt separated as a crystalline mass. If crystallization did not occur, the addition of low-boiling ligroin generally brought it about. Carbon tetrachloride, carbon disulfide, glacial acetic acid, and benzene were also used as solvents. The iodoso chlorides of benzene, of alkyl-, bromo-, chloro-, and nitro-substituted benzenes, and of naphthalene have been prepared in this way. The presence of several negative groups in the aromatic nucleus appears to prevent the addition of chlorine to the iodo group, for no iodoso chloride has been isolated from penta- and tetra-chloroiodobenzenes (97). Lucas and Kennedy (36) have prepared phenyliodoso chloride in 87 to 94 per cent yield by treating phenyl iodide in dry chloroform with chlorine at the temperature of an ice–salt mixture. The three tolyliodoso chlorides were prepared in good yields by similar methods. In order to prepare an alkyliodoso chloride, Thiele and Peter (66) worked at the temperature of liquid air or of a mixture of dry ice and ether. Töhl (68) used sulfuryl chloride as a source of chlorine. Satisfactory results were obtained by this method with phenyl iodide, *p*-tolyl iodide, 1,3,4-triiodo-*m*-xylene, and iodomesitylene. Willgerodt (75, 78) made iodoso chlorides by the action of hydrochloric acid on the corresponding iodoso or iodoxy compounds:

$$C_6H_5IO + 2HCl \rightarrow C_6H_5ICl_2 + H_2O$$

$$C_6H_5IO_2 + 4HCl \rightarrow C_6H_5ICl_2 + 2H_2O + Cl_2$$

p-Tolyliodoso fluoride (20) was prepared from *p*-iodosotoluene and 46 per cent hydrofluoric acid in acetic acid. This compound was used for fluorinating because it was an easily purified solid, it could be prepared and used in glass apparatus, and its chloroform solution was stable for several days.

By dissolving iodoso compounds in glacial acetic acid, the acetates have been obtained. Similarly, salts of other organic acids, such as formates, propionates, and benzoates, have been prepared. Nitrates have been made by treating iodoso compounds with dilute nitric acid; chromates by the addition of chromium trioxide to acetic acid solutions of the iodoso compounds. Basic salts have been obtained from aryliodoso compounds containing several negative substituents in the nucleus (78, 97).

C. Iodoxy compounds

Willgerodt (77) reported the preparation of iodoxy compounds by heating the corresponding iodoso compounds:

$$2C_6H_5IO \rightarrow C_6H_5I + C_6H_5IO_2$$

The heating was generally done in the presence of water, so that steam distillation could be carried out. The organic iodide which was produced by dismutation was carried over by the steam, the iodoxy compound being left behind. The latter was then crystallized from water, acetic acid, or formic acid. Lucas and Kennedy (37) have given directions for the preparation of iodoxybenzene in 92 to 95 per cent yield by the rapid steam distillation of iodosobenzene.

Hartmann and Meyer (24) found that *o*-iodosobenzoic acid, which did not undergo dismutation on heating, could be oxidized to *o*-iodoxybenzoic acid with alkaline potassium permanganate.

The method of preparing an iodoxy compound by heating the iodoso compound is not entirely satisfactory, because one half of the latter goes back into the state of the iodo compound. To overcome this difficulty Willgerodt (81) oxidized the iodoso compound directly to the iodoxy compound with hypochlorous acid, bleaching powder solution, or sodium hypochlorite. He also found that the iodoso chloride could be oxidized with sodium hypochlorite or with bleaching powder. A convenient method was to chlorinate the iodo compound in water; sodium hydroxide was then added to the iodoso chloride so formed and the oxidation was completed by passing in more chlorine. In all cases the iodoxy compound was obtained, and in many of them the yield was quantitative. Willgerodt regarded the oxidation of the iodoso chloride with bleaching powder or sodium hypochlorite solution to be a very good method:

$$C_6H_5ICl_2 + 2NaOCl \rightarrow C_6H_5IO_2 + 2NaCl + Cl_2$$

$$C_6H_5ICl_2 + 4HOCl \rightarrow C_6H_5IO_2 + 3Cl_2 + 2H_2O$$

$$C_6H_5IO + HOCl \rightarrow C_6H_5IO_2 + HCl$$

Formo and Johnson (17) have given directions for the preparation of iodoxybenzene in an 87 to 92 per cent yield, by the sodium hypochlorite oxidation of phenyliodoso chloride. Ortoleva (54) prepared iodoxybenzene by oxidizing phenyl iodide in aqueous pyridine with chlorine.

Iodoxy compounds have also been prepared by the direct oxidation of the organic iodide by means of Caro's acid (3):

$$C_6H_5I + 2H_2SO_5 \rightarrow C_6H_5IO_2 + 2H_2SO_4$$

In this way phenyl iodide and *o*-, *m*-, and *p*-iodotoluenes were oxidized to the corresponding iodoxy compounds. Masson and coworkers (46) used Caro's acid and carried out the quantitative oxidation of phenyl iodide to iodoxybenzene. They found that the iodoso compound was an intermediate product. An excess of Caro's acid was therefore used and the materials were ground once or twice during the operation. Böeseken and Schneider (5, 6) used perbenzoic acid in chloroform as the oxidizing agent and thus obtained the *o*-diiodoxybenzene and diiodoxyethylene from the corresponding diiodo compounds.

D. Iodonium compounds

Hartmann and Meyer (25) discovered the iodonium compounds when they added concentrated sulfuric acid to iodosobenzene and so obtained *p*-iodophenyl phenyliodonium bisulfate:

$$2C_6H_5IO + H_2SO_4 \rightarrow (C_6H_4I)(C_6H_5)I \cdot HSO_4 + H_2O + O$$

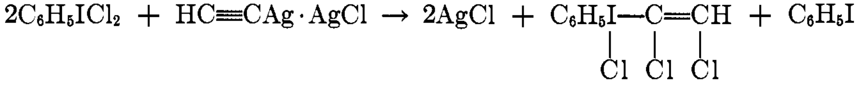
They showed that the oxygen in the above equation did not survive in any oxidizing agent, and that it was not evolved as such; but they did not pursue the point further, remarking "offenbar wird der Sauerstoff zur Oxydation eines kleinen Theiles der Substanz verbraucht."

The same workers (26) prepared diphenyliodonium hydroxide by shaking equivalent quantities of iodosobenzene and iodoxybenzene with water and silver oxide:

$$C_6H_5IO + C_6H_5IO_2 + AgOH \rightarrow (C_6H_5)_2IOH + AgIO_3$$

The filtrate from the reaction mixture contained the free base and its iodate, and on reduction of the iodate with sulfur dioxide the iodonium iodide was precipitated. Lucas and Kennedy (35) have prepared diphenyliodonium iodide in a 70 to 72 per cent yield by the action of iodosobenzene on iodoxybenzene in the presence of sodium hydroxide. The filtrate from the reaction mixture afforded diphenyliodonium iodide on treatment with aqueous potassium iodide. Similarly, mixed diaryliodonium compounds, such as the phenyl-*p*-anisyliodonium halides (59), have been made. Lucas and coworkers (39) found that silver oxide acts catalytically in the formation of di-*o*-tolyliodonium iodate from *o*-iodosotoluene and *o*-iodoxytoluene.

The double salt of diphenyliodonium chloride and mercuric chloride has been made by agitating a mixture of phenyliodoso chloride and mercury diphenyl with water and finally heating to the boiling point (83, 84). Mercury diethyl was substituted for mercury diphenyl in the hope of obtaining a phenylethyliodonium chloride, but this was not realized, the products of the reaction being ethyl chloride, phenyl iodide, and either ethylmercuric chloride or mercuric chloride. Aliphatic and mixed aliphatic–aromatic iodonium compounds (80, 90, 92, 93, 94, 95, 96) have been made by the action of the iodoso dichloride on the compound of silver chloride and silver acetylide:



$$2C_6H_5ICl_2 + HC{\equiv}CAg \cdot AgCl \rightarrow 2AgCl + C_6H_5\underset{\displaystyle Cl}{\underset{|}{I}}{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}\underset{\displaystyle Cl}{\underset{|}{CH}} + C_6H_5I$$

Hepworth (29) examined the action of various Grignard reagents on iodoso and iodoso chloride compounds. He found that small quantities of diphenyliodonium and phenyl-*p*-tolyliodonium bases were formed by the action of phenylmagnesium bromide on the corresponding iodosochloride and iodoso compounds. There were no indications of the formation of mixed aliphatic aromatic iodonium bases by the action of alkylmagnesium halides on the same compounds.

Freĭdlina and Nesmeyanov (19) have reported the preparation of diaryliodonium salts in quantitative yields by the action of aromatic organometallic compounds of tin on iodine trichloride in dilute hydrochloric acid:

$$ICl_3 + 2C_6H_5SnCl_3 \rightarrow (C_6H_5)_2ICl + 2SnCl_4$$

Similarly, they found that phenyliodoso chloride could be arylated:

$$C_6H_5ICl_2 + C_6H_5SnCl_3 \rightarrow (C_6H_5)_2ICl + SnCl_4$$

They also reported that diphenylmercury reacted with iodine trichloride to give the double salt of diphenyliodonium chloride and mercuric chloride. Freĭdlina and Nesmeyanov considered this method of synthesizing iodonium salts to have the advantage of simplicity and rapidity, as compared with other methods described in the literature.

Iodic acid as iodine pentoxide in suitable concentrations of sulfuric acid has been found by Masson and Race (43, 45) to attack benzene and its derivatives, with *o,p*-directing substituents which are not too highly activating (CH_3, Cl, Br, I), to give iodonium compounds in high yields:

$$HIO_3 + 2RH + H_2SO_4 \rightarrow R_2I \cdot HSO_4 + 2H_2O + O$$

In these particular cases it was the simplest method for preparing the iodonium compounds. The linkage between the aromatic nucleus and the iodine of the iodonium radical was always exclusively in the para position to the methyl or halogen substituent. Incidentally, this reaction furnishes a quick and delicate test for aromatic hydrocarbons in paraffins.

With anisole and other highly reactive benzene derivatives it was difficult to obtain more than traces of an iodonium product, and when the substituent was *m*-directing, scarcely any reaction was observed. As in nitrations, the practical success of the reaction depended upon the proper degree of hydration of the sulfuric acid and upon keeping the temperature from rising. For instance, with benzene the concentration of the acid was not weaker than $H_2SO_4:2H_2O$ and did not exceed $H_2SO_4:1.2H_2O$, and the temperature was kept below 10°C., preferably at 0°C.

Along with the iodonium compound, Masson and Race found an iodine-free reducing agent, which they considered to be an open-chain unsaturated acid and a product of the oxidation of part of the organic reagent. The above equation indicated that one-third of the initial oxygen atoms was unaccounted for. It was found that in the case of chlorobenzene the missing oxygen had broken the aromatic ring in 15 per cent of the organic reagent to form a chlorinated unsaturated fatty acid. Another byproduct was the iodo derivative of the aromatic reagent. This product could be largely suppressed by using the proper working conditions.

Evidence was given that the mechanism of the process consisted of a primary deoxidation of the iodic acid to the iodous stage (HIO_2) by a fraction of the aromatic reagent, which was thereby converted into the open-chain unstaurated substance. This was followed by the direct action of the iodous acid on the organic compound to give the diaryliodonium radical:

$$2RH + OIOH \rightarrow R_2IOH + H_2O$$

From an ionic standpoint the reaction was:

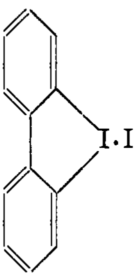
$$I^{+++} + 2RH \rightarrow 2H^+ + R_2I^+$$

or, alternatively,

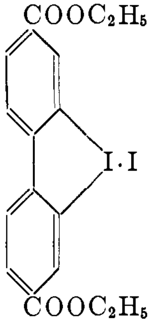
$$IO^+ + 2RH \rightarrow H_2O + R_2I^+$$

Masson and Race stated that the purpose of the sulfuric acid was to stabilize the iodous acid as an iodous sulfate and so the sulfuric acid prevented further reduction of the iodous compound by the organic reagent.

Mascarelli (41) prepared a number of iodonium bases and salts containing the iodonium iodine in a pentaatomic heterocyclic nucleus. He discovered that when 2,2′-diiodosobiphenyl or the tetrachloride was kept in water for some months the aqueous solution when treated with sulfur dioxide afforded diphenyleneiodonium iodide:



Searle and Adams (62), following the procedure of Mascarelli and Benati (42), diazotized 2,2′-diamino-4,4′-dicarboethoxybiphenyl, treated the resulting solution with sodium iodide, and so obtained a good yield of 4,4′-dicarboethoxydiphenyleneiodonium iodide:



Nesmeyanov (52) has prepared the double salts of phenyldiazonium iodide and mercuric iodide and has reported the formation of small yields of diphenyliodonium salts by the decomposition of these double salts.

III. PROPERTIES OF THE COMPOUNDS OF POLYVALENT IODINE

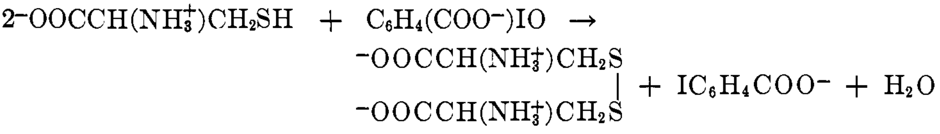
A. Iodoso compounds

The iodoso compounds function as oxidizing agents and ordinarily are reduced practically irreversibly. In this respect they resemble the hypoiodites. They are quantitatively reduced to iodo compounds in aqueous acid by added iodides, and the free iodine can be titrated:

$$C_6H_5IO + 2HI \rightarrow C_6H_5I + I_2 + H_2O$$

This was Willgerodt's method for the estimation or iodoso compounds, and it was confirmed by Victor Meyer. Iodoso compounds can be determined in the presence of iodoxy compounds by iodide reduction at room temperature in water saturated with borax, the iodoso compound alone being attacked even during 24 hr. (38, 46).

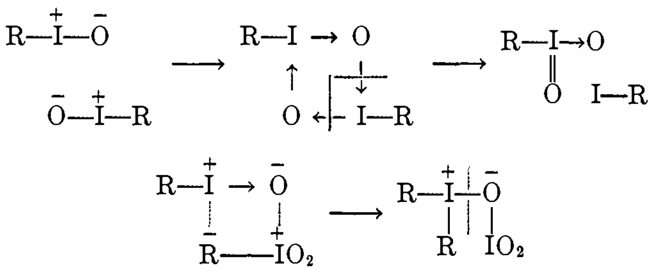
Aryliodoso compounds readily oxidize mercaptans. Hellerman, Chinard, and Ramsdell (28) have used this as a basis for a method of some precision for the estimation of cysteine, using standard *o*-iodosobenzoate:



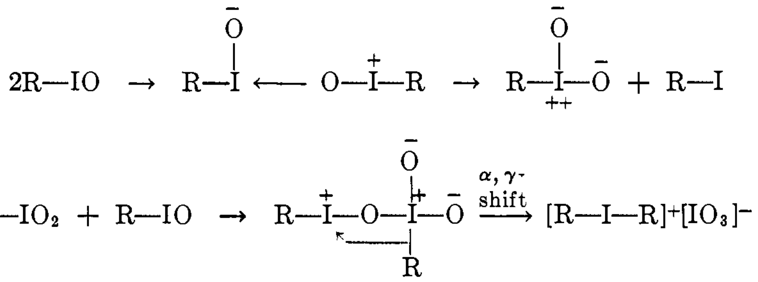
$$\begin{array}{l} 2\,{}^{-}OOCCH(NH_3^+)CH_2SH + C_6H_4(COO^-)IO \rightarrow \\ \qquad \begin{array}{r} {}^{-}OOCCH(NH_3^+)CH_2S \\ | \\ {}^{-}OOCCH(NH_3^+)CH_2S \end{array} + IC_6H_4COO^- + H_2O \end{array}$$

In addition, they have worked out the preparative details for the oxidation of cysteine to cystine by the *o*-iodosobenzoate ion. They also found that *o*-iodosobenzoate as an oxidizing agent has advantages over porphyrindine and in common with porphyrindine may be used in the estimation of 0.001 *N* ascorbic acid.

Iodoso compounds undergo self-oxidation and reduction (77), and they afford iodonium compounds when shaken with iodoxy compounds in the presence of wet silver oxide (26). Masson and coworkers (46) have explained these reactions as dipole additions:



Johnson (30) has explained the same reactions on the assumption that iodine in the link between iodine and the aryl group is capable of holding temporarily a decet of electrons but shows a strong tendency to revert to an octet:



Under suitable conditions iodoso compounds are oxidized to iodoxy compounds. With iodosobenzene this is brought about by heating at 90–100°C., or more conveniently by boiling with water (75). Oxidation of iodoso compounds is also effected readily by means of aqueous hypochlorite (81).

Iodoso compounds behave in general as the anhydrides of the hypothetical diacid base $RI(OH)_2$. An organic iodoso chloride is therefore the hydrochloric acid salt of the weak diacid base $RI(OH)_2$, of which other salts such as the acetate are also known. The preparation of iodoso salts from iodoso compounds brings out the analogy which exists between the iodoso compounds and such basic oxides as manganous oxide and lead monoxide:

$$C_6H_5I{=}O + 2HCl \rightarrow C_6H_5ICl_2 + H_2O$$

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O$$

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O$$

Tscherniac (69) found that phthalimide was readily transformed into anthranilic acid when shaken with alkali and iodosobenzene. The iodosobenzene in this case plays the part of the alkali hypochlorite in the ordinary Hofmann transformation of acid amides into amines.

In general, the iodoso compounds are yellow amorphous solids and explode or decompose with a puff on heating.

B. Iodoso salts

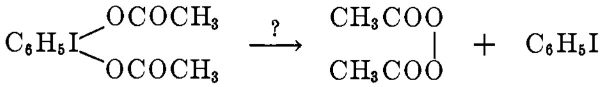
The iodoso salts, like the iodoso compounds, are oxidizing agents and liberate iodine from potassium iodide. Criegee and Beucker (8) have used aryliodoso acetates as oxidizing agents on unsaturated compounds such as anethole and have determined the reaction velocities at 20°C. The bimolecular coefficients decreased with time in all cases and were all of the same order, as was that for lead tetraacetate. Cyclopentadiene reacted with phenyliodoso acetate, *m*-4-xylyliodoso acetate, and *p*-nitrophenyliodoso acetate to give 52 to 73 per cent of diacetoxycyclopentenes. There was evidence that some 1,4-addition of two acetate groups to the conjugated system had occurred, which was also the case with lead tetraacetate. The fission of α,β-glycols by phenyliodoso acetate was found to occur much more slowly than with lead tetraacetate, and the reaction probably proceeded through a cyclic intermediate. Iodoso chlorides were found not capable of splitting glycols, and free iodosobenzene did not lend itself to this reaction because of its insolubility. In some respects the aryliodoso acetates were found to be better oxidizing agents than lead tetraacetate, especially from the standpoint of non-formation of inorganic products.

Aryliodoso chlorides decompose, on heating, usually into the iodo compound and chlorine. There is also the migration of chlorine to ring carbon with the formation of hydrogen chloride and a chlorine substitution compound. Phenyliodoso chloride, for example, decomposes at 120–121°C., giving up chlorine and hydrogen chloride. This property has been used in the characterization of aryl iodides (58). Leicester and Bergstrom (33), working on the thermal decomposition of triphenylselenonium iodide, characterized iodobenzene by its conversion into phenyliodoso chloride and further checked by a mixed melting point with a known sample of phenyliodoso chloride.

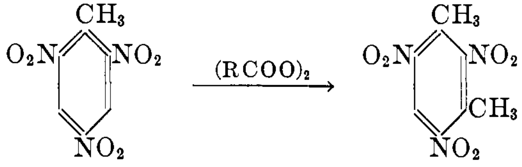
At low temperatures methyl iodide forms a solid chloride, CH_3ICl_2, which decomposes into methyl chloride and iodine monochloride at −30°C. Johnson (30) has expressed these reactions in the following way:

$$CH_3I + Cl_2 \xrightarrow{-80^\circ C.} \underset{\llcorner\!\!\longrightarrow\!\!\nearrow}{CH_3I \leftarrow ClCl} \xrightarrow{\alpha,\,\gamma\text{-shift}} ICl + CH_3Cl$$

Fieser and coworkers (12, 13, 15) have carried out some very interesting work on the alkylation of α-naphthoquinones and aromatic nitro compounds with tetravalent lead esters, such as lead tetraacetate. They have shown that with the latter reagent, 2-methyl-1,4-naphthoquinone, for example, can be converted into 2,3-dimethyl-1,4-naphthoquinone in yields as high as 50 per cent. By this method trinitrotoluene has been converted in yields as high as 32 per cent into trinitro-*m*-xylene, which appears to be an end product. Prompted by this work, the author of this review (58) has carried out some initial exploratory work on the behavior of phenyliodoso acetate towards compounds such as trinitrotoluene. It has been found that phenyliodoso acetate, like lead tetraacetate, behaves as a methylating agent, although the yield does not seem to be as high. It might be supposed that phenyliodoso acetate, like lead tetraacetate, undergoes decomposition to the acyl peroxide, which is the alkylating agent:



$$C_6H_5I\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix} \xrightarrow{?} \begin{matrix}CH_3COO\\|\\CH_3COO\end{matrix} + C_6H_5I$$



Lead tetraacetate is also known to be an acetoxylating agent. Reactive hydrocarbons, such as acenaphthene (11), anthracene (49), and 3,4-benzpyrene (14), undergo acetoxylation at temperatures below that at which the methylative action of lead tetraacetate becomes operative. Similarly, one might expect phenyliodoso acetate to function as an acetoxylating agent. This phase is now being investigated by the author.

Garvey, Halley, and Allen (20) have used phenyliodoso chloride as a chlorinating agent and have found that it gives the same products as chlorine, but that it is milder in its action. Unsaturated compounds, such as benzalacetophenone, *trans*-benzoylethylene, and 2-pentene, were found to add chlorine when heated with phenyliodoso chloride in ethylene chloride. Cinnamic acid and benzene did not react. Similarly, *p*-tolyliodoso fluoride was used as a fluorinating agent. This compound in chloroform reacted with simple olefins and stilbene to give mixtures. Rubber gave a white amorphous powder, apparently a monofluoro derivative. Indications were that the iodoso fluoride acted as a direct fluorinating agent at the double bond and that the resulting olefin fluoride decomposed with the evolution of hydrogen fluoride.

p-Tolyliodoso fluoride also reacted with certain aromatic polynuclear hydrocarbons and ketones to give two types of products, one formed by the substitution of hydrogen by fluorine and the other by a coupling reaction. Acenaphthene gave diacenaphthene. Anthrone formed dianthrone. Pyrone gave a monofluoropyrene and a bipyrenyl. Anthracene and benzanthrone gave only monofluoro derivatives.

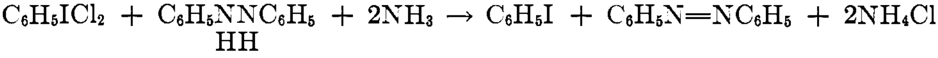
Bockemüller (4), in examining the behavior of aryliodoso fluorides on some organic compounds, found that α,α-diphenylethylene did not react in chloroform or nitrobenzene at ordinary temperatures. However, in the presence of a little anhydrous hydrogen fluoride or silicon tetrafluoride the formation of α,β-difluoro-α,α-diphenylethane occurred in 60 per cent yield, accompanied by the production of oily material which evolved hydrogen fluoride when distilled. α,α-Diphenyl-β-methylethylene was fluorinated with relative ease to α,α-diphenyl-β-methyl-α,β-difluoroethane in 77 per cent yield. Stilbene, α-methylstilbene, anthracene, and phenanthrene gave fluorine-containing compounds from which no definite products could be isolated. Diethylaniline was fluorinated to *p*-fluorodiethylaniline and dehydrogenated to tetraethylbenzidine.

The property of aryliodoso chlorides of liberating iodine from metal iodides and of acting as a chlorinating agent has been extended by Neu (53) to thiocyanates and to the chlorination of a number of organic compounds. Thus, phenyliodoso chloride with lead thiocyanate in acetic acid, methylene chloride, chloroform, carbon tetrachloride, and ethyl acetate formed solutions which gave the reactions of free thiocyanogen and with which organic compounds could be thiocyanated. For thiocyanation purposes phenyliodoso chloride was added, with cooling, to a suspension of 1.5 moles of dry lead thiocyanate in the organic solvent, shaken until the crystals or the yellow color of phenyliodoso chloride disappeared, and then filtered through a folded filter dried at 105°C. Atmospheric moisture was carefully excluded. Such a solution, added in small portions to aniline in chloroform and allowed to stand overnight, gave a 50 per cent yield of 1-amino-4-thiocyanobenzene. Other compounds, such as phenol, dimethylaniline, *o*-aminophenol, *m*-aminophenol, catechol, benzidine, *p*-phenetidine, thymol, anthranilic acid, β-naphthol, and β-naphthylamine, were similarly thiocyanated. Repeated attempts to thiocyanate *p*-aminophenol and salicylic acid were unsuccessful. Phenol, acetanilide, salicylic acid, and β-naphthol were readily chlorinated by phenyliodoso chloride in suitable solvents. Phenyliodoso acetate oxidized aniline to azobenzene with good yields and *p*-phenetidine gave a substance with the properties of a phenazine.

LeFèvre and Markham (32), in accord with Hepworth (29), found that no chlorobenzene was formed when phenyliodoso chloride reacted with phenylmagnesium bromide. Instead, there was produced mainly phenyl iodide and biphenyl. Chlorination of the ether also occurred, which was interesting, since phenyliodoso chloride and ether have been found not to react in the absence of the Grignard reagent.

Mel'nikov (48) isolated phenyl chloride, phenyl bromide, phenyl iodide, biphenyl, and diphenyliodonium chloride from the reaction product of phenyliodoso chloride and phenylmagnesium chloride. The reaction products from *p*-tolyliodoso chloride and phenylmagnesium chloride were phenyl chloride, phenyl bromide, *p*-tolylphenyl, and phenyl-*p*-tolyliodonium chloride.

Phenyliodoso chloride has been used as a nitridizing agent (10) in liquid ammonia. It reacted with ammonia in the liquid or gaseous state to give nitrogen, phenyl iodide, and ammonium chloride. In chloroform phenyliodoso chloride converted hydrazobenzene into a mixture of azobenzene and benzidine hydrochloride. In liquid ammonia it acted on hydrazobenzene according to the equation:



$$C_6H_5ICl_2 + C_6H_5\underset{H}{N}\underset{H}{N}C_6H_5 + 2NH_3 \rightarrow C_6H_5I + C_6H_5N{=}NC_6H_5 + 2NH_4Cl$$

On the supposition that iodoso compounds are like nitroso compounds, Pieroni (56) has examined the behavior of phenyliodoso chloride on aniline. When these two compounds were mixed in pyridine as the solvent, a deep brown color was produced and heat was evolved. The product was $C_6H_5NCl(C_6H_5ICl)_3$.

$$3C_6H_5ICl_2 + C_6H_5NH_2 \rightarrow 2HCl + C_6H_5NCl(C_6H_5ICl)_3$$

Sidgwick and Barkworth (63) determined the parachor of phenyliodoso propionate in order to find out the effect of an increase in valence on the parachor. The experimental value was found to be 583.5. The calculated value is 600.8, which gave a parachor defect of 17.3.

C. Iodoxy compounds

The iodoxy compounds, like the iodoso compounds and iodoso salts, are oxidizing agents and are comparable to iodates. They are quantitatively reduced in aqueous acid by added iodides, with the liberation of iodine which can be titrated:

$$C_6H_5IO_2 + 4HI \rightarrow 2H_2O + C_6H_5I + 2I_2$$

Masson, Race, and Pounder (46) found that in the estimation of nitroiodoxybenzene, where the reduction product is a solid, the addition of alcohol-free chloroform near the end of the titration with thiosulfate ensured a sharp end point by releasing mechanically engaged iodine.

The above workers called attention to two simple properties of iodoxybenzene: *viz.*, although it can be heated to 230°C., it neither melts nor vaporizes, and while it is slightly soluble in water, it is still less so in chemically inert solvents. These properties are shared by all iodoxy compounds. According to Masson and coworkers, the reason for this is not polymerization, because iodoxybenzene is monomeric in aqueous solution. The reason is probably due to internal polarity which is not ionic in nature, i.e., iodoxybenzene is not diphenyliodonium periodate. The high polarity must therefore have its source within the iodoxy group.

Willgerodt considered iodoxybenzene to be a neutral compound (88), and many textbooks have described the iodoxy compounds as having no basic properties. Masson (46) found iodoxybenzene to be amphoteric and that it afforded the following salts with acids: $C_6H_5IO_2 \cdot H_2SO_4$, m.p. 127°C., and the perchlorate, which was highly explosive. Iodoxybenzene is a stronger base than nitrobenzene, for, according to Masson, $C_6H_5IO_2 \cdot H_2SO_4$ is formed in an acid sufficiently dilute to hydrolyze $C_6H_5NO_2 \cdot H_2SO_4$ completely. Weinland and Stille (74) made the compound $C_6H_5IOF_2$ by treating iodoxybenzene with hot concentrated hydrofluoric acid:

$$C_6H_5IO_2 + 2HF \rightarrow H_2O + C_6H_5IOF_2$$

This reaction was considered by Masson and his coworkers to be a second stage in the reaction which gave them $C_6H_5IO_2 \cdot H_2SO_4$, a molecule of water having been eliminated, while hydrochloric acid went still further and was oxidized, a second molecule of water having been formed (78).

The formation of salts from iodoxy compounds and alkalies has been demonstrated by a combination of rapid measurements of solubility, conductivity, and freezing point (46). The reaction is

$$C_6H_5IO_2 + OH^- \rightleftarrows C_6H_5IO_2\cdot\overset{-}{O}H$$

Iodoxybenzene behaves as if it were a monobasic acid with a dissociation constant of the order of 1×10^{-11}. The slight conductivity measured for pure aqueous iodoxybenzene gives an apparent $K = 10^{-10.4}$. Masson has called the salts of iodoxy compounds and bases phenyliodoxylates. They change very rapidly irreversibly and quantitatively soon after their formation in cold alkali, according to the equation:

$$2C_6H_5IO_3^-H \rightarrow (C_6H_5)_2IO\cdot OH + IO_3^- + OH^-$$

The new compound, diphenyliodyl hydroxide, is amphoteric and is a strong oxidizing agent, being readily reduced by sulfur dioxide, hydrogen peroxide, hydrogen iodide, and dilute hydrochloric acid to form salts of diphenyliodonium hydroxide:

$$(C_6H_5)_2IO\cdot OH + 3HI \rightarrow (C_6H_5)_2I\cdot I + I_2 + 2H_2O$$

This is the origin of the iodonium salts obtainable from alkaline solutions containing iodoxy compounds on treatment with any of the reagents just mentioned, and it explains the qualitative results obtained by Willgerodt (82) in the action of iodoxybenzene with barium hydroxide or with boiling potassium iodide. With the latter compound the alkali needed is formed according to the equation:

$$C_6H_5IO_2 + 2KI + H_2O \rightarrow C_6H_5I + I_2 + 2KOH$$

The opinion expressed by Willgerodt as to the possible formation of "jodonate" by iodoxybenzene and barium hydroxide, although contradicted in his monograph, has definitely been justified by Masson and coworkers.

Considerable work has been done on the alkaline hydrolysis of iodoxy compounds, and all of the compounds examined yield the iodoxy group as iodate (24, 40, 46, 65, 71, 72, 73). With dilute sodium hydroxide at 15–20°C., *p*-iodoxynitrobenzene has been found to give the expected *p*-nitrophenol in only subordinate amounts. The main reaction was the replacement of the iodoxy group by hydrogen, with the formation of nitrobenzene and sodium iodate. With silver oxide in water at 15–20°C., silver iodate was formed in 98.8 per cent yield. The prolonged action of cold dilute alkali upon iodoxybenzene or the rapid action of 1 *N* alkali at 100°C. resulted in the formation of benzene and the alkali iodate. According to Masson, the reaction of iodoxybenzene, which is different from other iodoxy compounds in that it contains no activating substituents, indicates that the iodoxy group is "labile" in alkali and that its iodine is positive towards the organic residue. This fits in with the fact shown by Hartmann and V. Meyer (24) that *o*-iodoxybenzoic acid is a strong acid. It is highly probable that the alkaline hydrolysis of iodoxy compounds proceeds by way of the formation and subsequent decomposition of iodyl compounds. Diphenyliodyl acetate, when it is boiled with 1 *N* sodium hydroxide, affords benzene and iodate accompanied by less simple reactions (46).

Vorländer (70) found that iodoxybenzene was attacked by nitric acid only with great difficulty, indicating that the iodine atom of the iodoxy group is positive in character. By guarding against the presence of nitrous acid, which reduces the iodoxy to the iodo compound, it has been possible to carry out the mononitration of iodoxybenzene to an extent of not less than 98.6 per cent and the product is about 99.5 per cent the meta compound (46). This puts the iodoxy group on a par with that of free aromatic ammonium and similar cations and is more evidence in favor of the strongly dipolar character of the iodoxy group.

Because of their explosive properties, iodoxy compounds should be heated with extreme care. Iodoxybenzene is known to explode by impact. Morrison and Legge (51) have done work on the impact sensitivity of iodoxybenzene. They have found that it explodes on an anvil when struck with a hammer and that it undergoes decomposition when hit by a 500-g. weight falling through a distance of 100 cm. It was also found that its power in the sand-crushing test was very low. Iodoxybenzene deflagrates when touched with a hot wire.

Grossman (21) has described an iodoxy–iodosobenzene electrode for the determination of hydrogen- and hydroxyl-ion concentrations. It is analogous to the quinhydrone electrode and the underlying reaction is:

$$C_6H_5IO + 2OH^- + 2e \rightleftarrows C_6H_5IO_2 + H_2O$$

D. Iodonium compounds

The iodonium bases, such as diphenyliodonium hydroxide, are strong bases and form stable salts when neutralized with acids. In this respect they are analogous to the quaternary ammonium bases and the tertiary sulfonium bases.

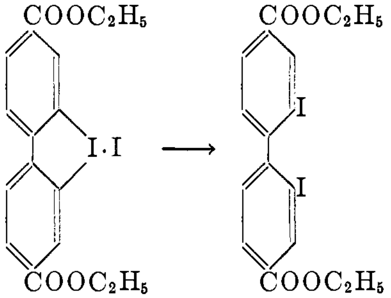
The iodonium compounds are decomposed by heat, and in this respect they again resemble other onium compounds. For example, diphenyliodonium iodide on heating decomposes to give iodobenzene:

$$(C_6H_5)_2I \cdot I \rightarrow 2C_6H_5I$$

The decomposition temperature of an iodonium salt depends upon the nature of the anion as well as the cation. Keeping the positive ion the same, we find roughly that the decomposition temperature of an iodonium salt varies with the electronegativity of the negative ion. For instance, di-*o*-tolyliodonium bromide decomposes at 178°C., the iodide at 155°C., and the sulfide at room temperature.

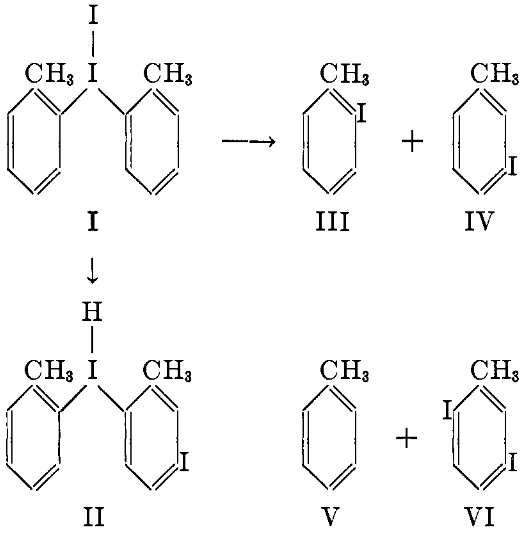
In the opinion of the reviewer this is reminiscent of the cleavage of thiamin by sodium bisulfite (98), and the cleavage of benzyldimethylphenylammonium chloride by sodium hydrosulfide, sodium sulfide, sodium thiosulfate, sodium bisulfite, and sodium sulfite (64).

Searle and Adams (62) heated 4,4′-dicarboethoxydiphenyleneiodonium iodide for 5 min. at 218°C. and obtained 2,2′-diiodo-4,4′-dicarboethoxybiphenyl:

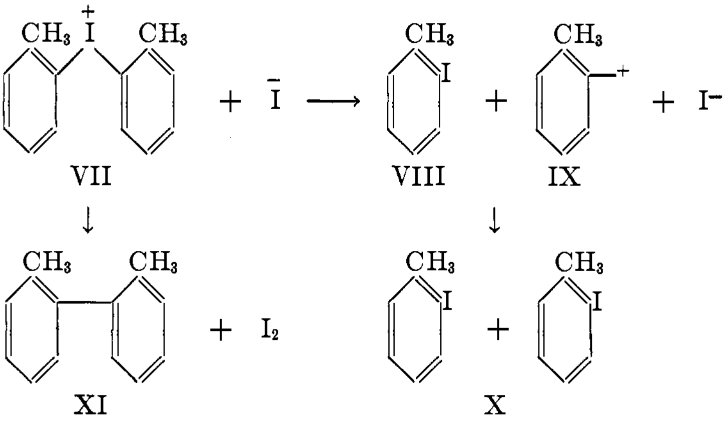


Lucas, Kennedy, and Wilmot (39) have worked with di-*o*-tolyliodonium iodide, which decomposes at 155°C. in a reaction which proceeds *via* the mechanism of an intermediate positively charged ion. There are, according to Lucas and coworkers, two possible mechanisms by which the decomposition might take place: (*a*) migration of the iodide iodine to one of the benzene rings in a position ortho or para to the C—I bond, followed by the scission of the C—I bond; (*b*) the scission of a C—I bond, followed by the attachment of the resulting positive organic ion to the negative iodide ion. The two mechanisms are pictured below:

(*a*) *Migration first:*

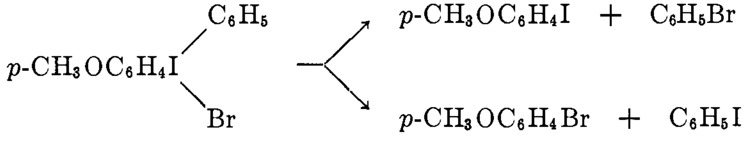


(*b*) *Scission first:*



If the two iodine atoms are held together by a covalent bond (I), the migration of iodine to an ortho or para position on the benzene ring is quite plausible. If migration is the first step, then scission of a C—I bond in the hypothetical intermediate (II) should lead to the formation of a mixture of equal parts of *o*-iodotoluene and *m*-iodotoluene (IV), or a mixture of equal parts of toluene (V) and 2,5-diiodotoluene (VI), or a mixture of the four compounds. However, if the original is ionized, then the iodide ion would not migrate to the ring. A mechanism might be the formation (*1*) of equal amounts of *o*-iodotoluene (VIII) and positive *o*-tolyl ion (IX) by the breakage of a C—I bond and (*2*) the combination of this ion with the negative iodide ion to form a second molecule of *o*-iodotoluene (X). This would afford pure *o*-iodotoluene. If both C—I bonds should break simultaneously, the products would be *o*,*o*′-bitolyl (XI) and iodine. Actually, Lucas and his coworkers found that the decomposition resulted in the formation of pure *o*-iodotoluene. This indicated that the iodonium ion split into *o*-iodotoluene and the positive *o*-tolyl ion by a scission of the C—I bond. The *o*-tolyl ion and the iodide ion then produced another molecule of *o*-iodotoluene.

The decomposition of compounds such as phenyl-*p*-anisyliodonium chloride, bromide, and iodide has been examined (59). In the case of phenyl-*p*-anisyliodonium bromide the decomposition may lead to *p*-iodoanisole and bromobenzene or to *p*-bromoanisole and iodobenzene:



$$p\text{-}CH_3OC_6H_4I(C_6H_5)Br \longrightarrow \begin{cases} p\text{-}CH_3OC_6H_4I + C_6H_5Br \\ p\text{-}CH_3OC_6H_4Br + C_6H_5I \end{cases}$$

Actually, at least 87 per cent and possibly more of the decomposition followed the first reaction scheme. Thus the decomposition occurred in such a way that the more electronegative radical (*p*-anisyl) remained attached to the iodine atom.

Sandin, McClure, and Irwin (60) have found that diphenyliodonium chloride and di-*p*-tolyiodonium chloride react with mercury in boiling *n*-propyl alcohol to produce phenylmercuric chloride and *p*-tolylmercuric chloride. With tellurium the same iodonium salts gave diphenyltellurium and di-*p*-tolyltellurium. Diphenyliodonium sulfide decomposed at room temperature in the presence of tellurium and antimony to give diphenyltellurium and triphenylstibinic sulfide.

In view of the results obtained, Sandin and coworkers assume that in the decomposition of an iodonium salt part of it at least can decompose by way of a non-ionic mechanism. The assumption is made that in the iodonium salt the central iodine atom is able, by expanding its valence shell, to act as an acceptor for the chloride or sulfide ion. Subsequent transformations of this complex result from the tendency of the central atom to revert to an octet. The following is suggested as a probable course of the reaction:

$$(C_6H_5)_2I^+Cl^- \rightarrow (C_6H_5)_2I{\leftarrow}Cl \rightarrow C_6H_5I + C_6H_5\bullet + \bullet Cl$$

Professor H. J. Lucas of the California Institute of Technology has kindly drawn attention to the important rôle played by the metal in the decomposition reactions. He suggests the possibility of an intermediate, undissociated complex which decomposes at a lower temperature than the salt would otherwise. Such a reaction mechanism would not necessarily involve the formation of free radicals. On this basis also, the decomposition with and without a metal would not necessarily have to proceed *via* similar mechanisms.

Fletcher and Hinshelwood (16) have studied the rate of decomposition of diphenyliodonium iodide in the solid state and in solution in iodobenzene. The activation energy for the reaction in the solid state was found to be 26,300 calories and that for the reaction in solution was 27,000 calories (uncorrected for change in viscosity). The decomposition in solution is probably unimolecular, as is the case for quaternary ammonium salts.

In the electrolysis of aqueous solutions of diaryliodonium hydroxide with a mercury cathode, no amalgam was formed. With the hydroxides of diphenyl-, *o*-dianisyl-, and *p*-dianisyl-iodonium, there was formed, in addition to the corresponding iodine derivatives, biphenyl, *o*,*o*′-bianisyl, and *p*,*p*′-bianisyl, respectively (102). The electrolysis of diphenyliodonium chloride in absolute ethanol with a mercury cathode has been shown to form some diphenyliodonium iodide (58).

Diphenyliodonium nitrate has been nitrated and the amount of meta nitration has been shown to be at least 82.5 per cent (7, 60, 70). This indicates the positive nature of the iodine atom towards the anion as well as both benzene nuclei. The nitration of a compound such as diphenyliodonium nitrate might be expected to be similar to the nitration of phenyltrimethylammonium nitrate, since the orienting group is $—IC_6H_5^+$. However, the iodine atom in $—I(C_6H_5)_2^+$ has unshared electrons and is at the same time the positive end of a dipole. On the basis of unshared electrons one might expect the formation of some ortho and para derivatives along with the meta compound. There is also another difference between phenyltrimethylammonium nitrate and diphenyliodonium nitrate to be considered. Since the positive electricity resides at the nucleus of the charged atom, the amount of damping action arising through the passage of the effect through the successive shells of electrons belonging to the charged atom itself would be smaller for the former than for the latter compound. On this basis it might be expected that the iodonium compound would show weaker meta reactivity. The results of Challenger and Rothstein (7) showed a para nitration which varied from 14 to 20.2 per cent. The work of Sandin, McClure, and Irwin (61) indicated a minimum of 18.5 per cent of para nitration. At least 10 per cent of the rearranged reaction mixture could be isolated as *p*-iodonitrobenzene.

Copley (9) has announced a rule which relates valency to orientation. If X is the atom attached to the benzene nucleus in the compound C_6H_5Y, then the group Y which contains X is an *o,p*-directing group when the valence of X is equal to or less than 4, and a *m*-directing group when the valence of X is greater than or equal to 4, a transition occurring at 4. The iodonium group is cited as an exception to this rule.

Medlin (47), by means of x-ray investigations, has shown that the distance between the iodine atoms in diphenyliodonium iodide is 3.55 Å., which is compatible with an ionic and not a covalent structure. The stability against interchange of the iodine atoms in diphenyliodonium iodide has been studied. Juliusburger, Topley, and Weiss (31) crystallized this salt from ethanol and water containing sodium iodide made radioactive by neutron bombardment. The resulting solid was strongly radioactive. Diphenyliodonium hydroxide derived from it was converted to the iodide with inactive sodium iodide and was inactive. Therefore the interchange occurred with the negative iodine only. Boiling for 20 min. in ethanol and water gave no interchange. In a solution of diphenyliodonium iodide (with the negative iodine radioactive) in iodobenzene no detectable exchange took place even under conditions so extreme that considerable decomposition into iodobenzene occurred. If both the decomposition and exchange reactions involve an activated complex, it is probable that the activation energy for the decomposition is less than for the exchange.

The ionizable iodine in iodonium iodides is capable of assuming fresh combining power quite as readily as the halogen in iodobenzene. The periodide of diphenyliodonium iodide, $(C_6H_5)_2I_4$, has been made by treating diphenyliodonium iodide with a solution of iodine in ethanol, a reaction which recalls the periodides of the alkylammonium bases. There has also been described the tetrachloride, dichloride, iodochloride, dibromide, and iodobromide of diphenyliodonium iodide, the iodide and dibromide of diphenyliodonium chloride, and the diiodide and dibromide of diphenyliodonium bromide (18, 27, 91).

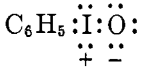
Iodonium compounds of the type $IR'\,R''\,R'''$ have not been separated into optically active components (55). The optical activity of diphenyliodonium tartrate has been investigated by Pribram (57) and the analogy of such salts with those of thallium has been pointed out. As the tartrate could not be obtained in the crystalline state, solutions of diphenyliodonium hydroxide and tartaric acid were mixed in equivalent proportions. The observed rotations in solutions of the iodonium tartrate were found to be in each case greater than that of solutions containing equivalent amounts of free tartaric acid.

Masson and Race (45) have called attention to the important fact that bis-(*p*-chlorophenyl)iodonium hydrogen sulfate can exist as an oily form and is partly soluble in chloroform in which it undergoes fission to some extent, producing the aromatic iodo compound. With reference to these properties, Masson and Race have made the important observation that it "points to marked polarisability of the anion by the cation," and that "it seems clear that any strong interionic polarisation, the effects of which are to induce, as has been mentioned, properties tending towards those of covalent compounds, must play an important part in initiating the wholly irreversible fission which all iodonium salts undergo when they are heated, $R_2I \cdot X \rightarrow RI + RX$, wherein the hitherto anionic X becomes covalently attached to one of the radicals R."

In case the reader has been wondering if there are chloronium and bromonium compounds, his attention is called to the very interesting work of Winstein and Lucas (99) and Lucas and Gould (34). These workers have shown that a cyclic positive ethylenebromonium ion is an intermediate when (+)-*threo*-3-bromo-2-butanol is converted into *dl*-2,3-dibromobutane by the action of hydrobromic acid. They have also shown that the concept of the cyclic chloronium ion is useful in accounting for *trans*-addition of chlorine and hypochlorous acid to the 2-butenes and for the purity of the resulting dichlorides and chlorohydrins.

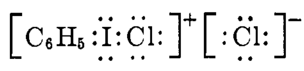
IV. STRUCTURES

The structure of an iodoso compound is shown best by means of an electronic formula. For example, iodosobenzene is given a structure which contains 2-covalent iodine:



$$C_6H_5:\underset{+}{\overset{..}{\underset{..}{I}}}:\underset{-}{\overset{..}{\underset{..}{O}}}:$$

Masson, Race, and Pounder (46) have considered the structure of the iodoso group in this way, when they refer to some of the reactions of iodoso compounds as being dipole additions. However, they have said, "We do not here prejudge the question whether the iodoso group contains a double bond or a single coordinate link, or whether the former is polarised into the latter by the reagent prior to its final conversion into an electrovalency." Similarly, the iodoso salts such as phenyliodoso chloride and phenyliodoso acetate are best represented by the structures:

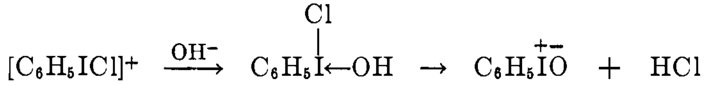


$$\left[C_6H_5:\overset{..}{\underset{..}{I}}:\overset{..}{\underset{..}{Cl}}:\right]^+\left[:\overset{..}{\underset{..}{Cl}}:\right]^- \quad \text{and} \quad [C_6H_5I(OCOCH_3)]^+(OCOCH_3)^-$$

Johnson (30) has represented the formation of phenyliodoso chloride from iodobenzene and chlorine by the equation:

$$C_6H_5I \;+\; Cl_2 \;\rightarrow\; C_6H_5I\leftarrow ClCl \;\rightarrow\; [C_6H_5ICl]^+Cl^-$$

He has indicated the change of phenyliodoso chloride into iodosobenzene by the following:



$$[C_6H_5ICl]^+ \xrightarrow{OH^-} C_6H_5\overset{Cl}{\overset{|}{I}}\leftarrow OH \rightarrow C_6H_5\overset{+-}{IO} + HCl$$

The dipole moments of phenyliodoso chloride and its derivatives have been determined by Guryanova and Syrkin (22). As a result of their work, they have considered these compounds to be mixtures of homopolar and internally ionized structures. The values of the dipole moment in excess of the vector sum are believed to be due to resonance effects.

Zappi and Degiorgi (101) studied the reaction between phenyliodoso chloride and methylmagnesium iodide in various solvents and from their results were led to the belief that phenyliodoso chloride is ionized in solution:

$$C_6H_5ICl_2 \rightleftarrows ClH_5ICl^+ + Cl^-$$

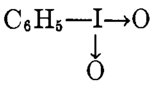
They provisionally assigned the structure $[C_6H_5ICl]^+Cl^-$ to phenyliodoso chloride. Later, Zappi and Cortelezzi (100) determined the molecular weight and electrical conductivity of phenyliodoso chloride in various solvents and came to the conclusion that any dissociation which occurred was molecular:

$$C_6H_5ICl_2 \rightleftarrows C_6H_5I + Cl_2$$

They decided that the ionic formula for phenyliodoso chloride should be discarded.

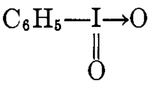
Askenasy and Meyer (2) ascribed the extremely feeble acidic properties of *o*-iodosobenzoic acid to internal-ring formation, with which view Willgerodt agreed. Solely on the basis of the polarity of the I—O group, *o*-iodosobenzoic acid might have been expected to be a strong acid. That *o*-iodosobenzoic acid yields salicylate and not benzoate when boiled with alcoholic sodium hydroxide has been explained by Masson, Race, and Pounder (46) to be due to the easy reduction of iodyl compounds by hot alcohol to iodo compounds, and to the fact that *o*-iodobenzoic acid is capable of alkaline hydrolysis to salicylic acid. Therefore the properties of *o*-iodosobenzoic acid are not in contradiction with the belief that the iodine of the iodoso group is positive in character.

Of the three structures for iodoxybenzene



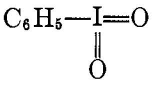
$$C_6H_5-\underset{\overset{\downarrow}{O}}{I}\rightarrow O$$

I



$$C_6H_5-\underset{\overset{\|}{O}}{I}\rightarrow O$$

II

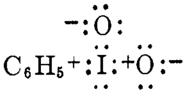


$$C_6H_5-\underset{\overset{\|}{O}}{I}=O$$

III

Masson, Race, and Pounder (46) prefer structure II. In this structure there is the opportunity for resonance, which would explain the greater stability of iodoxy compounds over that of the iodoso compounds. Structures I and II both indicate internal polarity, which fits in with the refractory properties of the iodoxy compounds.

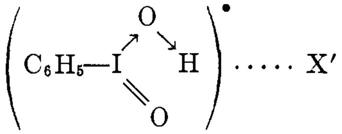
Johnson (30) has used structure I, which contains 3-covalent iodine, in his equations showing the dismutation of iodoso compounds and the formation of iodonium compounds. Electronically structure I is



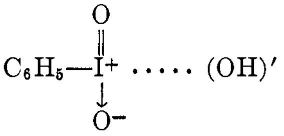
$$\begin{array}{c} {}^{-}{:}\ddot{O}{:} \\ C_6H_5{}^{+}{:}\underset{..}{\ddot{I}}{:}^{+}\underset{..}{\ddot{O}}{:}^{-} \end{array}$$

Before a final choice between these structures can be made, chemical evidence needs to be supported by data from x-ray work. Masson has pointed out the difficulty of carrying out the parachor and dipole-moment measurements.

The structure of the salt of an iodoxy compound and an acid is represented by Masson, Race, and Pounder (46) as:

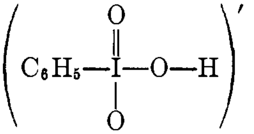


The iodoxy compound in this case plays a cationic part in which univalent hydrogen is associated with the resonance between the two oxygen linkages, the anion remaining as such. On the other hand, the salt of an iodoxy compound and a base is shown as:



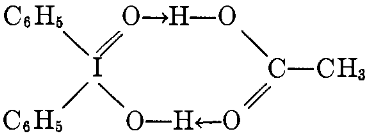
$$\begin{array}{c} O \\ \| \\ C_6H_5-I^{+} \cdots\cdots (OH)' \\ \downarrow \\ O^{-} \end{array}$$

In the first type of salt, one end of the dipole $\overset{+}{I}-\overset{-}{O}$ has coördinated H; in the second case, the other end of the same dipole has combined with OH^-, the cation of the alkali remaining as such. Masson and coworkers say that they have no evidence to justify a supposition that in the latter type of salt (iodoxylates) the union with the OH can become covalent:

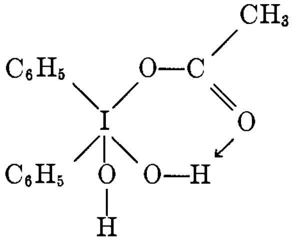


$$\left(\begin{array}{c} O \\ \| \\ C_6H_5-I-O-H \\ | \\ O \end{array} \right)'$$

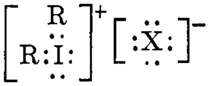
To account for the fact that the salts of the stronger acids and diphenyliodyl hydroxide seem to be less stable than the carbonate and the acetate, Masson *et al.* (46) have suggested for the carbonate and acetate coördinated ring structures such as:



and



There seems to be no doubt regarding the ionic structure of the iodonium compounds (31, 47), and here again we notice the similarity between iodonium compounds and other onium compounds. Electronically the iodonium compounds are represented:



$$\left[\begin{array}{c} R \\ R:\ddot{\underset{\cdot\cdot}{I}}: \end{array}\right]^{+}\left[:\ddot{\underset{\cdot\cdot}{X}}:\right]^{-}$$

Like the iodoso compounds, they contain 2-covalent iodine.

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