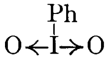
398. *The Iodoxy-group and its Relations.*

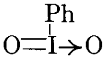
By Irvine Masson, Edward Race, and (in part) F. E. Pounder.

The enquiries here described arose from the observation that iodic acid very readily attacks benzene and its derivatives in media like those in which nitric acid does so; but that instead of forming iodoxy-compounds, as would be the case if the analogy between HIO_3 and HNO_3 were maintained, the reaction forms diaryliodonium salts in large yield. An account of this will soon be submitted; but reactions encountered early in its study showed that many fundamental properties of the iodoxy-, iodoso-, and iodonium groups, and the connexions between them, have remained obscure, or else misapprehended, since the pioneering discoveries of Willgerodt and of Victor Meyer more than forty years ago. The present summary of several of our investigations, dealing particularly with the iodoxy-group IO_2, and establishing hitherto unknown classes of compounds of iodine, is submitted as a contribution to the organic chemistry of oxidised iodine and so to the problems of the valency of this element.

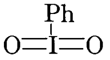
Two simple properties of iodoxybenzene which deserve notice are that, although it can be heated as much as to 230°, it neither melts nor vaporises, and that while it is slightly soluble in water (see Experimental Data, *a*), it is still less so in chemically inert organic solvents. These refractory qualities are shared by all the iodoxy-compounds, of which some seventy are described in Willgerodt's monograph of 1914 ("Die Organischen Verbindungen mit Mehrwehrtigem Jod," Enke, Stuttgart), and so they are characteristic of the group IO_2. They are not the result of unresolvable polymerisation, for we find iodoxybenzene to be monomeric in its aqueous solution (*b*). Internal polarity then suggests itself. This is, however, not ionic in nature : *i.e.*, iodoxybenzene is not diphenyliodonium periodate (which would have the empirical composition and the aqueous molecular weight of $C_6H_5{\cdot}IO_2$), as we showed by preparing this salt and examining its behaviour (*c*). $C_6H_5{\cdot}IO_2$ is thus acceptable as the true molecular formula, and any high polarity of the compound will have its source within the IO_2 group. Of the three structures, that which we find most easily applicable to the reactions hereafter described is (II). In this


$O\leftarrow\overset{\overset{\text{Ph}}{|}}{I}\rightarrow O$

(I.)

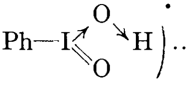

$O{=}\overset{\overset{\text{Ph}}{|}}{I}\rightarrow O$

(II.)


$O{=}\overset{\overset{\text{Ph}}{|}}{I}{=}O$

(III.)

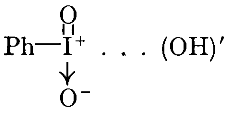
there is an opportunity for resonance (as in the nitro-group), which could, *inter alia*, contribute to the invariably greater stability of iodoxy- than of iodoso-compounds. The chemical evidence needs to be supplemented with *X*-ray and other electronic evidence before a final choice between these structures can be made for the substance; direct measurements of dipole moment and of parachor cannot well be expected, because of the physical properties of the iodoxy-compounds.

Iodoxybenzene is generally supposed to be a neutral compound; it is explicitly stated by Willgerodt (*op. cit.*, p. 35) to form salts neither with acids nor with bases, and its aqueous solution is neutral to indicators and is almost devoid of conductivity unless kept hot. But we find that it forms stable, though hydrolysable, crystalline salts on suitable treatment with several of the more powerful inorganic acids, and that it freely forms salts with aqueous alkalis. It is thus in fact amphoteric. As regards the salts with acids (*d*), the sulphate $PhIO_2,H_2SO_4$ (m. p. 127°) was analysed and examined, and among others a perchlorate was obtained; the existence of the latter proves that the iodoxybenzene here plays a cationic part, and suggests a structure (IV),  $\left(\text{Ph}{-}I\begin{smallmatrix}\nearrow O\searrow\\ \searrow O\end{smallmatrix}H\right)^{\bullet}\cdots\cdots\cdots X'$, in which univalent hydrogen is associated with the resonance between the two oxygen linkages. The basic character of iodoxybenzene is markedly greater than that of nitrobenzene, for $PhIO_2,H_2SO_4$ is formed in an acid sufficiently dilute to hydrolyse $PhNO_2,H_2SO_4$ completely; also the latter salt melts near 12° (cf. Masson, J., 1931, 3200). The compound described as $C_6H_5IOF_2$ by Weinland and Stille, who made it by acting on iodoxybenzene with hot concentrated hydrofluoric acid (*Ber.*, 1901, **34**, 2631), would represent a second stage of our reaction, a molecule of water having been eliminated; while hydrochloric acid goes still further and is oxidised, eliminating a second molecule of water in forming chlorine and iodobenzene dichloride (Willgerodt, *Ber.*, 1893, **26**, 1310).

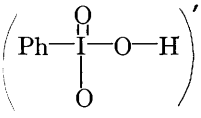
As regards the salts with alkalis, these have not been obtained as solids; their existence is transient; but we have been able by a combination of rapid measurements of solubility, conductivity, and freezing point to establish their formation and prove their formulæ. They are colourless. The acidity of iodoxybenzene can scarcely be supposed due to any cationic replacement or tautomerism of the hydrogen atoms of its phenyl group; and with this proviso the data (*e*) prove that the reaction is :

$$PhIO_2 + OH' \rightleftharpoons PhIO_2{\cdot}OH'.$$

The extent of the reversibility of the reaction is such that a twofold proportion of dilute alkali is ordinarily needed to prevent reversal, and indicates that iodoxybenzene behaves as if it were a monobasic acid with a dissociation constant of the order 10^{-11}, *i.e.*, about the same as that of phenol (*f*); the slight conductance measured for pure aqueous iodoxybenzene agrees with this, giving an apparent $K = 10^{-10{\cdot}4}$. It is not possible to dissect this magnitude into its two component equilibrium-constants, namely, that relating OH′ and $PhIO_2$ with $PhIO_3H'$, and that relating $PhIO_3H'$ and $H^{\cdot}$ with a hydrated iodoxybenzene solute. The numerical facts suggest, however, that the monomeric solute molecules of iodoxybenzene in pure water may be mostly hydrated (though the undissolved solid is not), the hydration occurring by way of the reaction with OH′, formulated above. There is no detectable *aci*-form with a higher acidity. We term these salts "phenyliodoxylates." They are formally analogous with the salts of aryl phosphinic and arsinic acids. It should, incidentally, be noted that the opinion expressed by Willgerodt in 1896 (*Ber.*, **29**, 2008) as to the possible formation of " Jodonate " by iodoxybenzene in barium hydroxide, although he contradicted it in 1914 in his monograph by the statements on the neutrality of iodoxybenzene, is justified by what we have proved. We regard the formation, the ready dissociation, and the later behaviour of iodoxylates as sufficiently explained by a local electrovalency joining the exceptionally large, positive donor iodine atom of the dipole I→O with the small anion OH′ (see V); while the sodium or other cation is shown by the evidence of freezing points to remain ionically free. In the analogous molecule of diarylsulphones, for example, which do not act upon alkali, the corresponding donor atom of sulphur is too thoroughly screened to permit this anionic access; and so also with the very small nitrogen atom in a *purely* aromatic nitro-compound. We have found no evidence to justify a supposition that in iodoxylates this linkage (V) can become covalent (VI) :

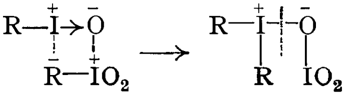
(V.) 

$$\mathrm{Ph{-}\overset{\overset{O}{\parallel}}{\underset{\underset{O^-}{\downarrow}}{I^+}}\ .\ .\ .\ (OH)'}$$

 (VI.)

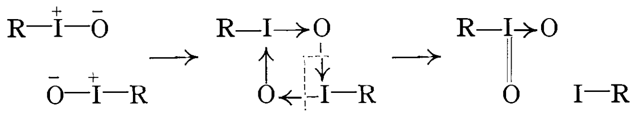
$$\left(\mathrm{Ph{-}\overset{\overset{O}{\parallel}}{\underset{\underset{O}{|}}{I}}{-}O{-}H}\right)'$$

It is to be noted that in one respect iodoxylates are close counterparts of the acidic salts of iodoxybenzene as represented in (IV) : in the latter, one end of the dipole $\overset{+}{I}\rightarrow\overset{-}{O}$ has co-ordinated $H^{\cdot}$, the anion of the acid remaining as such, while in iodoxylates the other end of the same dipole has made a union with OH′, the cation of the alkali remaining as such. The simultaneous accessibility of both ends of the iodyl dipole is, in our view, responsible for the remarkable general reaction of Victor Meyer and Hartmann whereby iodonium compounds are usually made (*Ber.*, 1894, **27**, 504) by the interaction of iodoso- and iodoxy-compounds in presence of wet silver oxide : this, which may be written $RIO + RIO_2 \xrightarrow[(OH)]{} R_2I^{\cdot} + IO'_3$, is easily understood as a dipole addition :



$$\begin{array}{c}\mathrm{R{-}\overset{+}{I}{\rightarrow}\overset{-}{O}}\\ \vdots\quad\ \vdots\\ \mathrm{\overset{-}{R}{-}\overset{+}{I}O_2}\end{array}\longrightarrow\begin{array}{c}\mathrm{R{-}\overset{+}{I}{-}\overset{-}{O}}\\ |\quad\ \ |\\ \mathrm{R\quad IO_2}\end{array}$$

The detailed steps of this process seem to be closely akin to those of the benzil–benzilic acid change. We do not here prejudge the question whether the iodoso-group contains a double bond or a single co-ordinate link, or whether the former is polarised into the latter by the reagent prior to its final conversion into an electrovalency. Other reactions of iodoso-compounds point to the vulnerability of their I—O link to addition; *e.g.*, their union with acid anhydrides to form covalent compounds $RI(OAc)_2$, and their spontaneous self-oxidation-reduction (Willgerodt, *Ber.*, 1892, **25**, 3500; 1893, **26**, 358, 1307; Askenasy and V. Meyer, *Ber.*, 1893, **26**, 1356), the course of which we take to be



$$\begin{array}{c} R-\overset{+}{I}-\overset{-}{O} \\ \overset{-}{O}-\overset{+}{I}-R \end{array} \longrightarrow \begin{array}{c} R-I\rightarrow O \\ \uparrow \quad \downarrow \\ O\leftarrow I-R \end{array} \longrightarrow \begin{array}{c} R-I\rightarrow O \\ \| \\ O \qquad I-R \end{array}$$

The " labile " nature of the iodoxy-group, which is the other factor in our theory of Meyer and Hartmann's reaction, will also be apparent in what follows.

Iodoxylates very rapidly change, irreversibly and quantitatively, soon after their formation in cold dilute aqueous alkali, into another and more stable new class of compound, according to the equation

$$2PhIO_3H' \rightrightarrows Ph_2IO{\cdot}OH + IO'_3 + OH',$$

or, more strictly, since the product is present as a dissolved salt of sodium, barium, etc.,

$$2PhIO_3H' = Ph_2IO{\cdot}O' + IO_3' + H_2O.$$

The general theory of this change is undoubtedly that it is an addition of the same kind as that just put forward for Meyer and Hartmann's reaction, and was, indeed, before us in the somewhat complex task of elucidating the facts (*g*). To the I→O dipole of one iodoxybenzene molecule are added the Ph and the IO_2 of another. The total change undergone by iodoxybenzene in the two consecutive reactions in cold dilute alkali (iodoxylate-formation being the first) is:

$$2PhIO_2 + OH' = Ph_2IO{\cdot}OH + IO_3'.$$

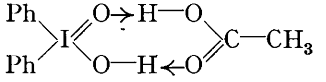
The new compound, diphenyliodyl hydroxide, is a stronger oxidising agent than the parent substances (for details, see Data, *g*, and Methods), and it is readily reduced by sulphur dioxide, by hydrogen peroxide, by neutral or acidic aqueous iodides, and even by dilute hydrochloric acid, to salts of diphenyliodonium hydroxide. A typical equation is:

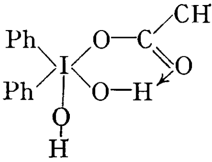
$$Ph_2IO{\cdot}OH + 3HI = Ph_2I{\cdot}I + I_2 + 2H_2O.$$

This is the origin of the iodonium salts familiarly obtainable from (but, as is now seen, not as such present in) alkaline solutions containing iodoxy-compounds, on treatment with any of the reagents just named; and it explains the qualitative results found by Willgerodt (1896, *loc. cit.*) in the action of iodoxybenzene with barium hydroxide or with boiling aqueous potassium iodide. With the latter reagent the alkali needed to form an iodyl compound is, of course, initially furnished by a part of the material undergoing the ordinary reaction $PhIO_2 + 2KI + H_2O = PhI + I_2 + 2KOH$, and the sequence of changes just described then proceeds.

Diphenyliodyl hydroxide is amphoteric (like its formal analogues the phosphinic and arsinic acids). It dissolves in alkali, and behaves as an acid to phenolphthalein, not so to methyl-orange; and it has been isolated as an impure, not very stable, amorphous solid, which forms a moderately stable, amorphous carbonate and a stable, well-crystallised acetate (*g*, iii); its salts with the stronger acids seem to be less stable. The last fact, which at first sight seems anomalous in an amphoteric substance, is because the " salts " with acetic and carbonic acids are actually not ionic, but are co-ordinated ring-compounds such as Sidgwick (cf. *Ann. Reports*, 1933, 114) has shown various carboxylic compounds to be; whereas the radicals of more powerful acids, being strongly anionic, do not so readily undergo chelation or, in Werner's sense, co-ordination, and their diphenyliodyl salts are therefore exposed to hydrolysis with consequent decomposition of the unstable hydroxide. The relative stabilities of the "salts," due to the ring-formation, may be illustrated by the fact that the carbonate is only slowly affected by cold 5*N*-sulphuric acid, whereas it effervesces briskly with cold *N*-acetic acid, liberating all its carbon dioxide as it forms the still more stably co-ordinated acetate. Again, although the active oxygen of the diphenyliodyl radical releases iodine from an added iodide even in a borax medium, this reduction is especially slow when the acetate is tested. The composition and the physical and chemical properties of the acetate (*g*, iii) are well represented by the formation and structure shown in (VII); the alternative unsymmetrical structure (VIII), while it cannot on present evidence be dismissed, is open to obvious criticisms. We propose to report other work on these compounds in a separate communication.

(VII.)





(VIII.)

The prolonged action of cold dilute alkali upon iodoxybenzene, or the rapid action of *N*-alkali at 100°, leads most notably to a hydrolysis which forms iodate and benzene (*h*). Whilst we have reason to think that this hydrolysis occurs by way of the formation and subsequent decomposition of iodyl compounds, so that its products are accompanied by other substances, it can ultimately be expressed

$$C_6H_5{\cdot}IO_2 + NaOH = NaIO_3 + C_6H_6.$$

The literature shows several other iodoxy-compounds whose alkaline hydrolysis has been examined, and all of them yield IO_3' and RH; for examples, *o*-iodoxybenzoic acid (Hartmann and V. Meyer, *Ber.*, 1893, **26**, 1727), *p*-iodoxynitrobenzene (Vorländer and Büchner, *Ber.*, 1925, **58**, 1291), iodoxychloroethylene (Thiele and Haakh, *Annalen*, 1909, **369**, 132). In these cases the neighbourhood of other substituents might have been supposed to loosen the iodoxy-group; no such factor enters with iodoxybenzene, and it is therefore apparent that the iodoxy-group is "labile" in alkali and that its iodine atom is positive towards the organic residue. This is fully in harmony with the reactions already discussed, and with the fact, shown by Victor Meyer and Hartmann, that *o*-iodoxybenzoic acid is a powerful acid. That the corresponding iodoso-acid is extremely feeble was ascribed by Meyer to internal ring-formation, with which view Willgerodt agreed. That it yields salicylate and not benzoate when boiled with alcoholic sodium hydroxide (Askenasy and V. Meyer, *loc. cit.*, p. 1363) appears *prima facie* at variance with the polarity of the I—O group as shown by our work, until it is realised that iodyl compounds, even when the iodyl group is in a chelate ring, are easily reduced by hot alcohol to the iodo-compounds; that *o*-iodobenzoic acid is capable of alkaline hydrolysis to salicylic acid (Hans Meyer, Beer, and Lasch, *Monatsh.*, 1913, **34**, 1669); and that Askenasy and V. Meyer actually noted the presence of aldehyde and of iodobenzoic acid in their experiment. In the absence of alcohol no such hydrolysis was found by these authors.

The hydrolysis of an iodoxy-compound to iodate and hydrocarbon—a type of reversed nitration—is to be connected with the fact that an iodite ion IO_2' is not stable, whereas the iodate ion IO_3' is, and so can separate from a hydrated diphenyliodylate ion, $Ph_2IO(OH)_2'$, leaving the components of benzene. The same instability of the anion X′ and stability of the anion XO′ may also be seen to determine the kindred hydrolyses $RX + OH' = XO' + RH$ which occur in alkaline fusions where $X = HSO_2$, $PhSO_2$, $P(OH)_2$, PO_2, RPO_2H, $B(OH)_2$ (Beilstein; Ainley and Challenger, J., 1930, 2171; and especially Ingold and Jessop, *ibid.*, p. 708). The same type of hydrolysis can also occur even where X′ is a stable anion as well as XO′, given suitable media; examples are shown where $X = SO_3H$ (steam and sulphuric acid on benzenesulphonic acid), halogen ("positive bromine," *e.g.*, in bromogallic acid, as Dr. G. H. Christie informs us, and in other cases), CO_2H in the ordinary alkaline fusion of carboxylates, and AsO_3H_2 in the alkaline fusion of arsanilic acid. When, however, a hydrolysis of RX can produce a simple anion X′, and consequently a phenol ROH, this tends to be the preferred alternative; it seems to be the sole mode of hydrolysis with $X = NO_2$, and occurs in alkalis with $X = SO_3H$, halogen, and (when $R = C_6H_5$) with AsO_3H_2. For $X = CO_2H$, this type of hydrolysis has to be sought outside the aromatic series, and occurs where $R = Ar_3C$, Ar_2RC (for references cf. Houben-Weyl, " Methoden," 1923, III, 60—61) and R·CO, including also oxalic acid; the hydrolytic medium being in each case concentrated sulphuric acid, the free anion CO_2H' is represented by carbon monoxide. In general, the question whether hydrolysis of RX eliminates the anion XO′, leaving RH, or eliminates the anion X′, leaving ROH—and, it may be added, the converse question whether the acid HOX can " nitrate " RH to RX—all depend upon how far (*a*) the medium, helped or restrained by (*b*) the organic radical R, can bring out in the atom or group X a positive (kationoid) character; and these correlations may be considered in the light of the work of Lapworth, Robinson, Ingold, and their associates.

All the facts so far stated concerning the iodoxy-group show it as very strongly kationoid (or, in Lapworth's term, acylous). This in turn suggests, according to the principle of Vorländer and the theory of the authors just named, that the iodoxy-group should be *meta*-orienting to a new substituent. The hitherto unexceptionable empirical rule of Hammick and Illingworth (J., 1930, 2358) would, on the contrary, predict it as *ortho-para*-orienting, since iodine is in a later Periodic Group than oxygen; the case is thus a crucial one for this rule. No substitution had hitherto been directly effected in any iodoxy-compound, despite attempts by Willgerodt, Vorländer, and others, and the compounds are well known to be unaffected by the free halogens often used in their preparation—facts which suggest rather the sluggishness caused by *meta*-directing groups than the reactivity caused by most *ortho-para*-directing groups. The peculiar ease with which *p*-iodoxynitrobenzene is hydrolysed (Vorländer, 1925, *loc. cit.*) is also significant, but cannot be stressed, since we have observed qualitatively that the *m*-isomeride also very easily yields nitrobenzene and iodate. We have succeeded in nitrating iodoxybenzene, mainly by choosing an acid indicated as appropriate by our work on the nitration of nitrobenzene (J., 1933, 105; 1934, 1352), and by guarding against the presence of nitrous acid, which reduces iodoxy- to iodo-compounds and so gives misleading orientations. We find that not less than 98·6% of the substance undergoes mononitration, and the product is about 99·5% *meta-* (*j*). Under the same conditions nitrobenzene yields about 9% of *o*- and *p*-isomerides, 91% of *m*-; and iodobenzene yields a mixture of *p*-iodonitrobenzene with some iododinitrobenzene (probably 1 : 2 : 4), but no appreciable *m*-iodonitrobenzene.

These results show that the *meta*-directing influence of the iodoxy-group (in acid media) is on a par with that of free aromatic ammonium and similar cations. It is also seen that the principle of Vorländer and the theory of Lapworth and Robinson and Ingold have led to the correct prediction. The rule of Hammick and Illingworth, however, as to the directive effect of groups XY is valid only so far as it may correctly imply which elements, X, in the Periodic Classification are positive to which other elements Y; it fails when, as in the case of $— XY = — IO_2$, X can be said to gain more of positive character from being in a later Period than of negative character from being in a later Group.

The very strongly dipolar character of the iodoxy-group IO_2, which is inferred from and underlies every reaction here discussed, and which appears to place it at the head of the kationoid groups, is the natural consequence of the fact that iodine has a higher atomic volume and a higher atomic number than any other non-metallic element.

EXPERIMENTAL.

Data.—(*a*) The solubilities of iodoxybenzene in water are :

Temp.	0°	14°	40°	61°	83°	99°
Millimols./litre	10·1	11·6	18·3	27·8	40·0	49·7

(The last two values have been corrected by about a unit for a slight gradual decomposition at high temperature, detectable by the conductivity and assumed to be of the kind which occurs in alkali.) No change of solid phase was observed throughout the temperature range, and the curve is smooth.

The solubility of iodosobenzene in water at 15·7° is 3·7 millimols./litre.

(*b*) A saturated solution of iodoxybenzene in water comes to equilibrium with the solid and pure ice together at $-0{\cdot}017° \pm 0{\cdot}001°$, its concentration (see *a*) being 0·010 molar. The technique needed for the measurements is described under " Methods." The only previous measurement of the molecular weight of iodoxybenzene is that of Mascarelli and Martinelli, using anhydrous formic acid (*Atti R. Accad. Lincei*, 1907, **16**, i, 183); low values were obtained, evidently due to salt formation—cf. (*d*) below.

(*c*) *Diphenyliodonium periodate* was obtained by mixing equivalent aqueous solutions of its free base and its free acid, the former made from the iodide and silver oxide, the latter from dilute sulphuric acid and barium periodate, which in turn was made by igniting barium iodate (Rammelsberg, *Ber.*, 1869, **2**, 1869). The compound forms large tabular crystals, nearly colourless, m. p. 129° (decomp.); its molar solubility at room temperature is several times that of iodoxybenzene. Our preparation, fully analysed, had the composition and the quantitative reactions of $(C_6H_5)_2I{\cdot}IO_4$ 91·3 mols., with possibly an orthoperiodate R_5IO_6 3·6 mols., and with iodate $(C_6H_5)_2I{\cdot}IO_3$ 5·0 mols. (the last-named being derived from the original barium iodate). Its liberation of iodine from an added iodide in saturated aqueous borax (characteristic of periodates) is alone enough to differentiate it from iodoxybenzene; also, it dissolves quietly in concentrated sulphuric acid, in which iodoxybenzene explodes; and it is not unstable in dilute alkali solution.

(*d*) The solubility of iodoxybenzene in quite dilute sulphuric acid differs little from that in water at the same temperature, but when iodoxybenzene is treated with acid of composition $H_2SO_4,2H_2O$ a visible change occurs, without evident dissolution. Under the microscope, each needle is seen to waste and then suddenly to sprout into brushes of other needles. Several grams of the product were freed from adherent acid with a porous tile or by washing it with dry ether; and analyses gave $PhIO_2 : H_2SO_4 = 1 : 0{\cdot}93$, $1 : 0{\cdot}90$ mols.; undetermined (moisture), 1·9 and 3·0% by wt. The compound is colourless; it has m. p. 127° (decomp.), is insoluble in ether, chloroform, or benzene, and in water it is resolved into its components. In sulphuric acid slightly more concentrated than $H_2SO_4,2H_2O$ it decomposes during 2—3 days at 0°, forming a little of (apparently) an iodophenyliodonium sulphate and some resinous matter; in still more concentrated acid it chars, and explodes in concentrated sulphuric acid.

Treated under the microscope with perchloric acid of constant b. p. (approx. $HClO_4,2H_2O$), iodoxybenzene shows the same striking change, though the crystals differ from those formed in $H_2SO_4,2H_2O$; the same is found with nitric acid (approx. $HNO_3,2H_2O$); syrupy phosphoric acid gave slight indications, while acetic acid did not seem to cause this change, nor did its anhydride. Hydrochloric acid cannot be tested, as it reduces iodoxybenzene. About a gram of the perchlorate was easily isolated, but it detonated with extreme violence while being spread, still damp, on a porous tile, causing personal injury, and so was not analysed.

(*e*) Iodoxybenzene, in contrast with iodosobenzene, is much more readily soluble in aqueous alkali than in water. Eventually this is connected with the irreversible changes described in (*g*); but in the first place it is due to a reversible salt-formation. The results now described are obtainable *only* by completing the tests within a few minutes of the dissolution of iodoxybenzene in alkali, at 0—12°; they are not true of any later tests.

(i) Dilute alkali dissolves readily about 1 mol. of iodoxybenzene for every 2 equivs. of alkali. With 0·1*N*-sodium hydroxide, for example, this means a solubility five times that in pure water; with *N*-sodium hydroxide, the ratio exceeds 50 : 1. The solutions are colourless, with a very faint turbidity. The solute can, like iodoxybenzene itself, be reduced to iodobenzene by sulphur dioxide or by acidified sodium iodide solution; and the iodonium and iodate radicals are absent, or else barely detectable. Neutralisation by carbon dioxide causes a slow but nearly quantitative precipitation of crystals which, when dried, prove to be pure iodoxybenzene. From their first deposition to their final desiccation individual crystals show no change microscopically, hence they were not hydrated when wet. These various observations prove the initial reversibility of the dissolution.

(ii) When the fresh alkaline solutions are titrated with acid, no loss of alkalinity is found, either with methyl-orange as indicator or with phenolphthalein. But rapid measurements of electrical conductivity in solutions from 0·1*N*- to 0·025*N*-sodium hydroxide show a marked fall from the values for the aqueous alkali alone. From these measurements, the mean mobility at 18° of all the anions present, in solutions made with $2NaOH : 1PhIO_2$, is found to be close to 100 units (assuming the only cation present to be $Na^{\bullet}$). It is known that the mobility of OH'

is about 160 and that those of any other possible anions are 30—40 units. It follows, since 100 is the mean of 160 and 40, that about one-half, and not less, of the original hydroxyl ions are still present as such. Hence, since practically all the iodoxybenzene owes its dissolution to the alkali, one OH', and only one, unites with each formula-weight of iodoxybenzene to form the new anion. The double proportion of alkali needed for the dissolution of iodoxybenzene must therefore act in virtue of its suppressing a reversal of the action.

(iii) While these conductivities establish the ratio $OH' : PhIO_2$ in the new anion, they cannot decide whether this ion is simple and univalent or is polymerised and multivalent; this question, which bears upon structural problems, was settled by measurements of freezing point. These, done with a Beckmann technique, and repeated more than once, prove that the freezing point of 2 mols. of 0·098*N*-sodium hydroxide is scarcely altered when 1 mol. of iodoxybenzene is freshly dissolved in it (Found: − 0·312° before dissolution, − 0·305° after dissolution; the small difference, 0·007°, is only about one-eighth of that which a doubly polymerised anion would give). Hence, with a possible reservation as to a small fraction, each newly-formed anion takes the place of only one hydroxyl ion; and since it has also been shown to contain $1PhIO_2$ per OH', it is unpolymerised and univalent.

The initial reaction is thus proved to be $PhIO_2 + OH' \rightleftharpoons (PhIO_2{\cdot}OH)'$.

(*f*) A detailed scrutiny of the mobilities already mentioned shows that with increasingly dilute solutions containing $2NaOH : PhIO_2$ the mean anionic mobility increases (95, 98, 102 units in 0·1*N*-, 0·07*N*-, 0·05*N*-sodium hydroxide). This implies an increasing reverse decomposition of the phenyliodoxylate ion, when the known mobilities of OH' are taken into account; and adopting, as is legitimate, probable values for the mobilities of the phenyliodoxylate ion, the simple principles of mass action show that the above data would approximately correspond with a salt of an acid of ionisation constant not far from $K = 10^{-11}$. It was found that when a freshly made iodoxylate solution in *N*/10-alkali was saturated with carbon dioxide, the conductivity of the liquid, measured before any iodoxybenzene had time to recrystallise, was not appreciably different from that of the sodium bicarbonate solution formed. Hence there appears to be no salt of any more strongly acidic *aci*-form of (hydrated) iodoxybenzene as a transient product of neutralisation. It was also found, by Mr. D. Dickinson of this laboratory, that at 25° a saturated solution (0·014*M*) of very pure iodoxybenzene, washed to constancy with purified water, had a specific conductivity exceeding that of the water by not more than $0{\cdot}9(\pm 0{\cdot}2) \times 10^{-5}$ ohm^{-1}. Disregarding any further corrections, this value gives an apparent molecular conductivity of 0·6 unit, which would be that of a monobasic acid of $K = 10^{-10{\cdot}4}$.

(*g*) (i) In aqueous sodium or barium hydroxide of concentrations from 0·025*N* upwards, the initial iodoxylate wholly decomposes within a few hours at 0—15°, the change being quicker in the more concentrated alkali solutions. The alkalinity to phenolphthalein (but not that to methyl-orange) falls, towards a steady value; iodoxylate or iodoxybenzene can no longer be found, the solution contains iodate, and the addition of sodium iodide precipitates $Ph_2I{\cdot}I$, and sets free iodine. Moreover, a liberation of iodine from sodium iodide occurs not only on acidification but also after neutralisation and saturation with borax—an oxidation which IO_3', iodoxybenzene, and iodoxylates will, as we have proved, not perform. Methods of analysis having first been worked out and tested (see Methods), a number of systematic series of tests, with samples taken at intervals, were made at 25° with a range of dilute alkali concentrations up to 0·2*N*; in each sample were independently measured OH' (with methyl-orange), $PhIO_2{\cdot}OH'$, IO_3', $Ph_2I^{\bullet}$, the iodine-liberating oxygen both in acid and in saturated borax, and free PhI (if any). For each time-interval in each series a " balance-sheet " was made for the atoms or radicals and for the presumed cations and anions. The data and the studies subordinate to them fill too much space to be quoted here; they may be focused into the statement that, of 2 mols. of initial iodoxybenzene, between 90% and 100% is, after a few hours in dilute alkali, analytically represented by 1 mol. of diphenyliodonium iodate, together with 1 atom of oxygen which sets free iodine in a borax medium. (In later stages the yields of $Ph_2I^{\bullet}$ and O diminish, and more rapidly do so in concentrations of OH' above 0·2*N*.) A summary equation at this point is therefore $2PhIO_2 = IO_3' + Ph_2I^{\bullet} + O^*$. The analytical data, however, always showed an excess of $Na^{\bullet} + Ph_2I^{\bullet}$ over OH' (to methyl-orange) $+ IO_3'$; also the decrease of alkalinity towards phenolphthalein, discovered afterwards, is not explained by the equation, though this is true as far as it goes. The supposition was made that the substances determined as $Ph_2I^{\bullet}$ were being converted into it only during the analysis, not before; and the whole of the facts fell into line quantitatively when the nature of the borax-active oxygen, marked O* in the equation, was independently followed up.

(ii) The proof of the source of the " active oxygen," which obviously forms part of some molecule or ionic radical, was lengthy, but must be sketched, as being essential evidence. Apart from hypothesis, the known substances which could *a priori* be present and which would satisfy the test of oxidising iodides in water saturated with borax are iodosobenzene (a frequent precursor of $Ph_2I^{\cdot}$), periodates, iodites (if they exist), hypoiodites, ozone (a known product of the decomposition of periodates), and possibly some peroxides, or a " peroxyiodate." Of these, each in turn has been proved by direct experiment to be absent; briefly as follows.

The active oxygen is not that of iodosobenzene, for on reduction of the liquor with added sodium iodide, no iodobenzene is formed. This was proved by benzene-extraction of the reduced liquor, followed by a Stepanow analysis of the extract, and by controls which showed that when iodosobenzene in the required amount is put into the liquor, the method duly discovers at any rate 90% of it. Periodate (whose production would satisfy the summary equation) is absent; for excess of barium hydroxide added to the alkaline liquor, or excess of barium acetate added to the neutralised liquor, precipitated only barium iodate, which was analysed. (When, in control experiments, periodate, KIO_4, is put in, it is duly precipitated fully as barium periodate in this treatment.) The filtrate from the barium iodate contained all the borax-active oxygen, and set free practically the same amount of iodine from added sodium iodide in a borax medium as it did in an acidic medium. (The latter fact excludes the possibility that a soluble barium periodate might be present.) Iodites and hypoiodites are absent, for the original liquor did not form free iodine on being acidified. This evidence cannot be discounted by presuming the countervailing presence of phenol (*e.g.*, from the alkaline decomposition of iodonium salts); for phenol, as we verified quantitatively, takes up no iodine in acidic media, whilst had it been present it would have wholly prevented the iodometric detection of the active oxygen in a borax medium. Direct search for it gave negative results; and again, the iodine " balance sheet " left no room for iodophenols. Ozone is absent; it cannot be smelt in the liquors; and the aspiration of pure air through them for many hours did not carry off any gas that set free iodine on passing through Geissler bulbs containing sodium iodide solution, nor did it appreciably diminish the titre of active oxygen in the liquor. That ozone, if present, would have been carried off in the air-stream is shown by converse tests in which we passed ozonised air through a solution of sodium iodate and analysed the resulting liquor; this had retained only traces of active oxygen from the ozone passed through it, and even these traces were present in the form of ordinary periodate, precipitable with $Ba^{\cdot\cdot}$ and duly determined. Finally, saline peroxides of $Na^{\cdot}$, $Ba^{\cdot\cdot}$, $Ph_2I^{\cdot}$, or $H^{\cdot}$ are absent, as also any such compound as a peroxidised iodate; for titanium sulphate (of measured sensitivity to hydrogen peroxide) produced not the slightest tint when added to the acidified solution, whether before or after the IO_3' had been precipitated as barium iodate.

The exclusion of all the known possibilities by these experiments left as the only explanation that the active oxygen atom belongs to a compound of new type; namely, one which yields the iodonium radical when reduced, by the addition of the sodium iodide used to precipitate $Ph_2I{\cdot}I$ from the solutions : in short, a substance $Ph_2IO{\cdot}OH$ or its hydrate $Ph_2I(OH)_3$. This was finally proved true, by the eventual isolation and study of the substance and its derivatives (see below); and the equation given in the text expresses all the analytical data.

(iii) Finely sieved iodoxybenzene (1 mol.) is dissolved at 0° in *N*-sodium hydroxide (2 mols.); after 1½ hours at 0° the precipitate of sodium iodate is filtered off and the filtrate, still kept at 0°, is saturated with carbon dioxide; a creamy solid then forms, *diphenyliodyl carbonate*, the weight of which, after it has been washed with ice-cold carbonic acid and dried in a vacuum, is one-half that of the initial iodoxybenzene. The washed precipitate may alternatively be treated, without being dried in a vacuum (during which process it tends to decompose slightly), with glacial acetic acid, whence on dilution *diphenyliodyl acetate* crystallises; this can further be recrystallised from benzene, forming orthorhombic prisms. The use of other concentrations of sodium hydroxide, or of potassium or barium hydroxide, or the use of other neutralising agents than carbon dioxide, has given us poor yields or none at all.

The acetate has the composition $(C_6H_5)_2I(OH)_2O{\cdot}CO{\cdot}CH_3$, as shown by :

	Found, %.	Calc., %.		Found, %.	Calc., %.
$Ph_2I^{\cdot}$	75·2, 74·3	75·1	C	*45·2, 44·7*	44·92
Active O	4·21, 4·28	4·28	H	*4·66, 4·36*	4·04
$CH_3{\cdot}CO$	12·5, 12·15, *11·45, 12·25*	11·50	I	34·0, 34·25, *33·0, 33·6*	33·93

(Figures in italics are of micro-analyses made by Dr. G. Weiler.)

It is not appreciably soluble in water, very sparingly in ether, moderately in cold benzene, chloroform, carbon tetrachloride and freely soluble in these at higher temperatures, soluble in glacial acetic acid, and soluble in but decomposed by alcohol or acetone. The m. p. (decomp.) is 114°, but is sensitive to slight impurities, 109° and even 100° being found in different preparations. The compound gives a weakly alkaline reaction to litmus paper owing to its reduction by the litmus. For its quantitative reduction to diphenyliodonium, see "Methods." Other reactions are given in the text and in (*h*) below.

(*h*) Iodoxybenzene is refluxed for an hour with excess of *N*-sodium hydroxide; an oil is then steam-distilled over, which on fractional distillation yields benzene, identified by its b. p. and by the m. p. of its dinitro-derivative both alone and mixed with *m*-dinitrobenzene. The active oxygen found iodometrically in the residue exceeds that of the original iodoxybenzene.

Similar results, qualitatively sufficient to account for these, are obtained if diphenyliodyl acetate is boiled with *N*-sodium hydroxide; and the active oxygen after the hydrolysis is 1·5 times its initial value, this increase being due to the production of iodate (independently determined by $Ba^{\bullet\bullet}$ precipitation). The formation of benzene and iodate is accompanied by less simple reactions, an account of which is postponed to a later note.

(*j*) *Nitration of iodoxybenzene.* The acid is H_2SO_4 60 mols. %, HNO_3 20, H_2O 20, the high sulphuric content of which minimises the formation of nitrous acid and at the same time promotes nitration in general. Before use, in order to remove initial nitrous acid, 0·1*N*-permanganate is added to the acid until the faintest pink persists (in our experiments, about 1 c.c. per 100 c.c. of acid). At room temperature, about 2 g. of iodoxybenzene in very small portions are ground with enough acid, fresh for each separate portion, to ensure instant immersion (otherwise flares occur) and complete dissolution (which takes 7—10 mins.); these requirements involve a considerable excess of the acid, in the aggregate about 50 c.c. for 2 g. of iodoxybenzene. The first effect of the addition is visibly to form salts of iodoxybenzene; and an alternative procedure is first to make and isolate the compound $PhIO_2,H_2SO_4$ as described in (*d*), and then to nitrate this. The results are the same, but the latter mode is better, as the material can be mixed fairly quickly with the nitrating acid and shaken until the liquid is clear. Diluted with 100 g. of pure ice, the liquid deposits crystals of *m*-nitroiodoxybenzene, which are washed wholly acid-free with water, and then with ether to extract a little *m*-iodonitrobenzene which is formed by the traces of nitrous acid unavoidably produced during the nitration. The liquors and aqueous washings (300—350 c.c.) are extracted with alcohol-free chloroform for the same purpose; they also contain dissolved nitroiodoxybenzene, which cannot be extracted but is determined iodometrically, and the reduction product so obtained, or alternatively with hydrogen peroxide, or with sodium iodide solution followed by barely enough dilute sulphurous acid to remove free iodine, is collected and, without recrystallisation, is identified by chemical and thermal analyses. A similar reduction, applied quantitatively to the main yield of iodoxy-compound, enables this also to be fully identified. The final and most exactly studied experiment gave, from 2·13 g. of iodoxybenzene:

Product.	Impurity, %.	G.	Equiv. $PhIO_2$, g.	Yield, %.
m-$IO_2{\cdot}C_6H_4{\cdot}NO_2$ cryst.	$< 0{\cdot}7$	2·03	1·70	80·0
,, in soln.	< 2	0·24	0·20	9·6
m-$I{\cdot}C_6H_4{\cdot}NO_2$ extracts	< 3	0·20	0·19	8·9
			2·09	98·5

Such reduction by nitrous acid as had occurred during the nitration had followed, not preceded, the act of nitration of iodoxybenzene; for had it taken effect upon this, forming iodobenzene, the nitration product of the latter would not have been 97% *m*-iodonitrobenzene but a very different mixture, of high m. p., of the *p*-isomeride with some iododinitro-compound; this we proved by nitrating iodobenzene under conditions exactly identical with those used for iodoxybenzene.

Thermal data. The iodonitrobenzenes melt at: *p*-, 173°; *o*-, 54°; *m*-, variously given from 38·5° (Caldwell and Werner) to 34·6° (Holleman), and there is a metastable form, m. p. 10° (Steinmetz). Our value is given below. The eutectics are: *po*-, *ca.* 46°, 5% *p*- (Holleman); *pm*-, 32·5°, *ca.* 4% *p*- (our value), each 1% of the *p*-compound lowering the m. p. of the *m*-compound by about 1·3° to the eutectic, and raising it steeply thereafter. 1 : 2 : 4-Iododinitrobenzene has m. p. 88·5° (Körner).

Our technique was essentially that described in J., 1934, 1357, all samples being internally stirred. The temperature first given is that at which the earliest signs of dampness (*i.e.*, of a eutectic) were seen, the next is that at which any marked liquidation set in, and the final temperature is the true m. p., when the last crystals liquefied.

1.	*m*-$I{\cdot}C_6H_4{\cdot}NO_2$ from *m*-nitroaniline, fractionally recryst.	33·0°—35·5°—37·0°
2.	(1) after sublimation at 100° and 3 mm.	36·6 —37·1 —37·9
3.	Reduction product of $IO_2{\cdot}C_6H_4{\cdot}NO_2$, main yield	35·0 —36·3 —37·2
4.	Mixture (1 : 1) of (2) and (3)	35·0 —36·6 —37·4
5.	Reduction product of $IO_2{\cdot}C_6H_4{\cdot}NO_2$ in soln. in liquors	33·0 —33·7 —34·4
6.	$I{\cdot}C_6H_4{\cdot}NO_2$ extracted from main yield with Et_2O	29·0 —32·5 —33·5
7.	Nitration product of PhI	27° ?—(47°)—84 —110 —153
8.	Mixtures of (2) or of (3) with (7), or with *o*-$I{\cdot}C_6H_4{\cdot}NO_2$, were oils at 15°	

Chemical analyses. The iodometric equivalent weight of nitroiodoxybenzene, the main yield, was 70·1 (calc., 70·25). Microchemical analyses by Dr. G. Weiler gave :

	C.	H.	I.	N.	
No. (3) above	28·4	1·72	50·75	5·74	= $C_6H_{4\cdot3}I_{1\cdot01}N_{1,04}(O_{2,1})$
Calc., $I{\cdot}C_6H_4{\cdot}NO_2$	28·9	1·62	50·98	5·63	
No. (7) above	29·0	1·71	51·39	6·30	= $C_6H_{4\cdot2}I_{1\cdot00}N_{1\cdot12}(O_{1\cdot8})$

Combustions of nitroiodoxybenzene itself were found to be affected by unavoidable explosions. It detonated at 213°.

Methods.—General. All stoppers and exposed joints must be of glass, and only sintered glass filters are used, so as to avoid decomposing the strong oxidising agents encountered. The use of oxidisable solvents and dehydrators such as alcohol, acetone, etc., has to be avoided except where reduction is actually intended. Most of the analytical and other reactions involve sparingly soluble substances; an aid indispensable for carrying them out properly is a bicycle wheel bracketed to a wall and turned over by a motor 20 or 40 times a minute; to its spokes the reaction-tubes, of 20—250 c.c. capacity, are clipped by rubber bands.

Materials.—Iodoxybenzene was at first made by Willgerodt's method *via* iodobenzene dichloride, alkaline hydrolysis to iodosobenzene, and oxidation of this with hypochlorous acid; this method was replaced by that of Bamberger and Hill (*Ber.*, 1900, **33**, 533), slightly modified, wherein Caro's acid converts iodobenzene almost quantitatively into iodoxybenzene. Both with this and with iodotoluene we found that the iodoso-compound is an intermediate product; hence excess of the titrated dilute Caro's acid is used, and the materials are ground once or twice during the operation. The product is boiled in water with free steam, which converts traces of iodosobenzene into iodoxy- and iodo-benzene and expels the latter. Our material was free from detectable impurities, including acid, and gave iodometric analyses showing it to be 99·9—100·0% pure.

Analytical. Iodoxy- and iodoso-benzene are each quantitatively reduced to iodobenzene in aqueous acid by added iodides, and the free iodine is titrated; this was Willgerodt's method, confirmed by Victor Meyer, and checked and used by us. With nitroiodoxybenzene, where the product of reduction is a solid, the addition of chloroform (freed from alcohol) near the end of the titration with thiosulphate ensures a sharp end-point by releasing mechanically engaged iodine. Iodosobenzene can be accurately determined in a mixture of iodoso- and iodoxybenzene by reduction at room temperature in water saturated with borax, the iodoso-compound alone being attacked, even during 24 hours; 2 hours on the wheel are required to complete this, and the free iodine is titrated with arsenite. (In saturated bicarbonate, iodoxybenzene is gradually attacked.) Other reducing agents, such as sulphite, are not reliable. As oxidising agents, iodoxy- and iodoso-benzene resemble respectively iodates and hypoiodites.

Unfortunately, iodide is also the only quantitative precipitant we have found for $Ph_2I^{\bullet}$—the beautifully crystalline *picrate*, m. p. 132°, is not sufficiently insoluble, the gelatinous *silicotungstate* is inconvenient—hence the foregoing iodometric reductions first produce free iodine and then, in presence of iodonium or iodyl radicals, precipitate a polyiodide; and in the ensuing titration this is not quickly convertible into the ordinary iodide, especially in acid media. Moreover, in presence of $Ph_2I^{\bullet}$, thiosulphate cannot very accurately be used owing to a decomposition of iodonium thiosulphate to aryl sulphide and other products.

The general method which has been arrived at to overcome these and other difficulties in mixed solutions such as we here encounter, is to measure the " B " oxygen—that available in a borax medium—by mixing the neutralised solution first with excess of borax and then with aqueous sodium iodide and a measured volume of 0·1*N*-arsenite in excess, after which the whole is " wheeled " over-night. If iodyl compounds have been present, a strong yellow tint persists in the precipitate until their reduction is complete. The unused arsenite is finally back-titrated with 0·1*N*-iodine. The "A" oxygen—that available in acid media—is measured by "wheeling" for 1—2 hours the solution to which aqueous sodium iodide has been added after acidification with sulphuric acid; the liquor, with its precipitate of $Ph_2I{\cdot}I_3$, is then saturated with sodium bicarbonate and titrated with arsenite. Some time on the wheel is usually needed to complete the decomposition of polyiodide. These methods are scarcely drastic enough for the complete reduction of diphenyliodyl acetate, to be later referred to.

To determine $Ph_2I^{\bullet}$, the solution is treated with sulphur dioxide and aqueous sodium iodide, and the precipitated iodide after some hours is filtered off, washed carefully with dilute sodium iodide solution and finally with acetone, dried in a vacuum without heating, and weighed. Water-washing is to be avoided, and acetone-washing to be minimised, owing to the solubility of the precipitate; it is much less soluble in sodium iodide solution than in water.

IO_3' was precipitated by barium acetate or nitrate as its barium salt, which was decomposed on the wheel with dilute sulphuric acid and the free iodic acid was then measured iodometrically.

The total iodine content of every organic compound was determined by Stepanow's method, which proved very reliable. Independent microchemical determinations by Dr. G. Weiler are recorded in the data. The anionic iodine of iodonium iodides was determined as silver iodide volumetrically or gravimetrically.

The analytical reduction of solid iodyl compounds is difficult to make quantitatively complete, owing to their chelation of the active oxygen atom; the sample must first be dissolved in dilute sodium hydroxide solution (0·05*N*) and then mixed with the iodide reagent, and so acidified or neutralised as the "A" or "B" analysis requires. The best reagent for determining accurately their available $Ph_2I^{\bullet}$ is a solution of hydrogen iodide and sulphur dioxide in ether, made by reducing iodine in wet ether with sulphur dioxide. The weighed solid iodyl compound in a tared glass filter is thus converted *in situ* into $Ph_2I{\cdot}I$, which is washed acid-free with dry ether and is vacuum-dried and weighed. For determining acetyl groups, no alcoholic reagent is permissible; *N*- or 5*N*-sodium hydroxide was used, followed by phosphoric acid as in Wenzel's method.

For the small depression of f. p. mentioned in (*a*), 350 c.c. of solution were contained in a light Dewar cylinder which bore a Beckmann thermometer and stirrer-guide in its rubber bung, and was set in a larger Dewar cylinder packed with ice; and it was essential to enclose the whole projecting stem of the thermometer in melting ice up to the readings. A suspension of iodoxybenzene being present, fragments of pure ice at 0° were added to the liquid at 0°, and the whole was briskly stirred vertically with a wire so coiled as to carry fragments of ice up and down with it, equilibrium being thereby readily set up and held within 0·001—0·002°. The same method was finally used for the measurements noted in (*e*, iii); in them, the iodoxybenzene was finely sieved, to help it to dissolve quickly. The electrical conductivities were measured in a cell with smooth platinum electrodes; and a portable "Megger" instrument made by Messrs. Evershed and Vignoles, which we had previously found very reliable and convenient, enabled the rapid changes occurring in the solutions to be easily followed with enough accuracy for the present purposes. The alternating current at the cell is of frequency 60, the heating effect is small in a quick reading, and the instrument reads directly in ohms. For the conductivity of pure aqueous iodoxybenzene the ordinary bridge-telephone method was used.

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