780. *Chemistry of Positive Iodine. Part II.*[1] *Reactions of Iodobenzene Dichloride with Silver Salts.*

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The reactions of iodobenzene dichloride with a wide variety of silver salts are reported. The esters iodosobenzene diacetate and iodosobenzene ditrifluoroacetate, as well as iodosobenzene dinitrate (contaminated with silver nitrate), have been prepared by this method. The preparation of μ-oxodi-bisulphatodiphenyldi-iodine and the formation, under certain conditions, of μ-oxodi-trifluoroacetatodiphenyldi-iodine is also reported. With many silver salts the iodosobenzene esters, if formed, decompose; with some silver salts they yield iodosobenzene and the acid anhydride, with others they give iodobenzene and an oxidised product.

Esters of iodosobenzene were first prepared by Willgerodt.[2] He treated iodosobenzene with acetic acid to obtain the diacetate, and either iodosobenzene or iodobenzene diacetate with other dilute acids to obtain the corresponding esters. His method was not very successful, and he claimed only to have isolated the nitrate and chromate esters as crystalline compounds; several other esters were apparently difficult to characterise as they separated as oils. It seems possible, in view of the known hygroscopic nature of the parent positive iodine derivatives, that the water produced in the reaction, or already present, interfered. This water cannot be eliminated from the reaction. Dasent and Waddington[3] have shown that the compound Willgerodt claimed to be the dinitrate was in fact μ-oxodinitratodiphenyldi-iodine, $Ph{\cdot}I(O{\cdot}NO_2){\cdot}O{\cdot}(O{\cdot}NO_2)I{\cdot}Ph$. This can be considered as the half-hydrolysis product of iodobenzene dinitrate:

$$2PhI(NO_3)_2 + H_2O = (PhINO_3)_2O + 2HNO_3$$

The true dinitrate could not be prepared by either of Willgerodt's methods.

The only other method used to prepare these compounds has been that used for an isolated synthesis of the diacetate by Neu, from the reaction of iodobenzene dichloride with lead acetate.[4] The reaction of iodobenzene dichloride with silver salts offers an alternative method, with very few limitations (as almost all acids give stable silver salts), which can be carried out under rigorously anhydrous conditions. This is an improvement on Neu's method, because both the lattice energy and insolubility of silver chloride are greater than for lead chloride, and silver salts are often more readily prepared than lead salts. This paper contains an account of the reactions of silver salts with iodobenzene dichloride. Acetonitrile was used as a solvent throughout as it complexes strongly with silver salts, which are therefore more soluble in it than in most non-aqueous solvents, and it is not attacked either by iodobenzene dichloride or by the products of reaction.

Silver salts behave in three different ways: some do not react at all, some react to give comparatively stable esters, and some do not give stable esters at all. Some of these salts probably fail to react because of their insolubility in acetonitrile. Silver borofluoride and perchlorate are however readily soluble, but do not react; this lack of reaction indicates that neither of the following reactions is thermodynamically favourable.

$$PhICl_2 + 2AgBF_4 \longrightarrow PhI^{2+} + 2BF_4^- + 2AgCl\downarrow$$

$$PhICl_2 + AgBF_4 \longrightarrow PhICl^+ + BF_4^- + AgCl\downarrow$$

Attempts to prepare new esters by this method were only partly successful. Table 1 lists the products from those silver salts that did react.

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[1] Part I, Alcock and Waddington, *J.*, 1962, 2510.
[2] Willgerodt, " Organische Verbindungen mit mehrwertigem Jod," Enke, Stuttgart, 1914.
[3] Dasent and Waddington (*a*) *Proc. Chem. Soc.*, 1960, 71; (*b*) *J.*, 1960, 3350.
[4] Neu, *Ber.*, 1939, **72**, 1505; Bell and Morgan, *J.*, 1960, 1209.

TABLE 1.

Silver salt	Product	Remarks	Silver salt	Product	Remarks
Acetate	$PhI(CO_2CH_3)_2$		Oxalate	$PhI + CO_2$	Ester formed and decomposes
Trifluoroacetate	$PhI(CO_2CF_3)_2$				
Nitrate	$PhI(NO_3)_2$	Complexed	Azide	$PhI + N_2$	Immediate decomposition
Chromate	$PhICrO_4$	Probably rapid decomposition	Cyanide	$(CN)_2$	
			Cyanate	$(OCN)_x$	
Sulphate	$PhISO_4$	Very hygroscopic $2PhISO_4,H_2O$ isolated	Thiocyanate	$(SCN)_x$	
			Bromide	Br_2	
Hyponitrite	$PhIO + N_2O$	Immediate decomposition	Iodide	I_2	
Nitrite	$NO + NO_2$		Cyanamide	Complex	See text
Carbonate	CO_2				
Oxide	—				

With silver acetate and silver trifluoroacetate the products were, respectively, iodobenzene diacetate and iodobenzene di-trifluoroacetate, though with the latter it was difficult to remove the last traces of unchanged silver salt.

Silver nitrate reacted immediately but incompletely. The reaction ratio ($AgNO_3 : PhICl_2$) at room temperature, measured by the amount of unchanged silver nitrate, was intermediate between 1 : 1 and 2 : 1. At —22° the reaction ratio, measured conductometrically, was 1 : 1. The product at this ratio must be either a complex, $PhICl_2,PhI(NO_3)_2$ or $PhICl(NO_3)$. At ratios intermediate between 1 : 1 and 2 : 1, presumably $PhI(NO_3)_2$ was formed as well.

The reaction of silver chromate with iodobenzene dichloride gave red crystals that decomposed rapidly. Willgerodt reported that the reaction of chromic acid, in acetic acid, with iodosobenzene gave red crystals, but made no mention of any decomposition. However repetition [5] of his preparation gave red crystals that did decompose rapidly, so that the two methods probably give the same compound. Silver sulphate appeared to give, primarily, iodobenzene sulphate, $PhISO_4$. This compound is, however, extraordinarily hygroscopic, so that only the yellow half-hydrate, which we formulate as μ-oxodibisulphatodiphenyldi-iodine, $Ph{\cdot}I(O{\cdot}SO_3H){\cdot}O{\cdot}(O{\cdot}SO_3H)I{\cdot}Ph$, could be isolated. Willgerodt only succeeded in preparing an oil from the reaction of sulphuric acid and iodosobenzene.[2]

When heated, iodobenzene bistrifluoroacetate formed an unstable yellow μ-oxo-derivative similar to μ-oxodinitratodiphenyldi-iodine, but heating of iodobenzene diacetate yielded only iodosobenzene and acetic anhydride. Thus there is a progression from the strongly electron-attracting nitrate group, for which the μ-oxo-compound is the stable species under ordinary conditions, through the trifluoroacetate, for which both types of compound exist but the di-ester is the more stable, to the weakest electron-attracting group, acetate, for which only the di-ester is known.

This behaviour of the phenyl-substituted tervalent compounds of iodine enables us to understand more clearly the behaviour of the unsubstituted compounds. All these appear, from their physical and chemical properties, to be polymerised. The intermolecular bridges can be formed either through the anion or directly by –I–O–I–O–I– bridges. IX_3 compounds are of the first type while iodosyl compounds, IOX, are of the second.

Among these parent compounds iodine triacetate,[6] $I(OAc)_3$, is unbridged, while, from the rather confused literature,[7] iodine(III) nitrate appears to exist both as $I(NO_3)_3$ and $IO(NO_3)$. Iodine(III) perchlorate is claimed to be $I(ClO_4)_3,2H_2O$, for which either structure would be possible.[8] Iodosyl sulphate and selenate, $(IO)_2SO_4$ and $(IO)_2SeO_4$, respectively, are bridged.[3b] Iodine phosphate, IPO_4, from its formula, is unbridged.[9] The iodine(III)

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[5] Dasent, unpublished work.

[6] Foque, *Chem.-Ztg.*, 1914, **38**, 680.

[7] Kappler, *Ber.*, 1911, **44**, 3496; Kikindai, *Compt. rend.*, 1954, **238**, 1229; Schmeisser, Fink, and Bandle, *Angew. Chem.*, 1957, **69**, 780.

[8] Fichter and Kappeler, *Z. anorg. Chem.*, 1915, **91**, 134.

[9] Fichter and Stern, *Helv. Chim. Acta*, 1928, **11**, 1256.

iodates are particularly interesting. I_2O_4 is $IO(IO_3)$, the bridged compound; the less stable I_4O_9 can be formulated as $I(IO_3)_3$, without bridges between the tervalent iodine atoms but polymerised through the iodate groups.

In both the substituted and unsubstituted series the criterion of bridge formation is the electron-attracting strength of the acid group. This can itself be explained in simpler terms. Iodine attracts electrons strongly, and so its compounds are most stable when the groups around the iodine attract electrons least strongly. The difference between the environment of unbridged and bridged iodine atoms is that an acid group in the former is replaced by an $-I-O-$ group in the latter. Thus the relative stabilities of the bridged and unbridged compounds enable one to arrange the electron-attracting abilities of the various groups relative to I–O–I in the following order: $-O\cdot SO_3$, $-O\cdot SeO_3 > -O-I-$; $-O\cdot NO_2 > -O-I-$; $-O\cdot IO_2 \approx -O\cdot I-$; $-O\cdot CO\cdot CF_3 \leqslant -O-I-$; $-O\cdot CO\cdot CH_3 < -O-I-$. As would be expected, $-O-I-$ has about the same strength as $-O-IO_3^-$, but the latter, with more oxygen atoms, is a slightly stronger electron acceptor and thus $I(IO_3)_3$ is less stable than $IO(IO_3)$.

Table 1 shows that the reaction of many silver salts with iodobenzene dichloride did not lead to the formation of stable esters. The final products from these reactions fell into two groups. In the first group the products were iodosobenzene and the acid anhydride. In the second group, neither iodosobenzene nor an acid anhydride could be formed from most of the silver salts, as they contain no oxygen. Instead iodobenzene was formed, and from the halides and pseudohalides the free halogens and pseudohalogens, respectively, were produced, if they were capable of existence, and in the case of the azide, nitrogen was evolved (the decomposition product of the hypothetical N_6). The reaction of silver cyanamide was consistent with a similar reaction scheme, in the amount of nitrogen given off:

$$2PhICl_2 + 2Ag_2CN_2 = 4AgCl + 2PhI + (CN_2)_2$$
$$(CN_2)_2 = (CN)_2 + N_2$$

However it is certainly a complex reaction and no further products could be positively identified.

The reaction with silver oxalate was of the second type; an ester was probably formed transiently, as gas was only evolved on warming:

$$PhICl_2 + Ag_2C_2O_4 = 2AgCl + PhIC_2O_4 = PhI + 2CO_2$$

The expected iodosobenzene and mixed carbon dioxide and monoxide were not produced. The oxalate was oxidised by the iodobenzene dichloride, although the nitrite and hyponitrite were not. This agrees with the order of the oxidation potentials in aqueous alkali, *i.e.*, for the ions, though not with those in acid, *i.e.*, for the undissociated acids. These oxidation potentials[10] are given in Table 2; they do not reflect the relative rates of oxidation of the ions, as the rate of oxidation of oxalate is generally very slow.

TABLE 2.

Reaction	E_0 acid	E_0 alkaline
$N_2O_2^{2-} \longrightarrow 2NO$	$+0{\cdot}71$	$-0{\cdot}18$
$2NO_2^- \longrightarrow N_2O_4$	$-1{\cdot}07$	$-1{\cdot}76$
$C_2O_4^{2-} \longrightarrow 2CO_2$	$+0{\cdot}49$	$+0{\cdot}71$ (calc. from ΔF_0 values)

The results of the reaction of iodobenzene dichloride with the silver pseudohalides showed that the iodobenzene dipseudohalides, if formed at all, were only transiently stable. Now both iodobenzene dichloride and iodobenzene diacetate are more stable, respectively, than iodine trichloride and iodine triacetate. Thus the non-existence of iodobenzene dicyanate and dithiocyanate should mean that iodine tricyanate and trithiocyanate do not exist either, and one must view with suspicion the reported preparation of these compounds.[11]

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[10] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952.

[11] Cornog, Horrabin, and Karges, *J. Amer. Chem. Soc.*, 1938, **60**, 429.

EXPERIMENTAL

Infrared spectra of the esters were taken as Nujol mulls between sheets of Polythene (0·001 in. thick), with compensation sheets, also with Nujol, in the reference beam. The Polythene was held between metal sheets having a hole cut in the centre, to allow passage of the beam; no other support was needed.[12] The above method served the double purpose of protecting the sample from moisture and preventing reaction of the esters with alkali halides. The spectra were recorded with a Perkin-Elmer model 21 double-beam recording spectrophotometer with sodium chloride, potassium bromide, or cæsium bromide optics. For some identification spectra Perkin-Elmer Infracord instruments, with sodium chloride or potassium bromide optics, were used. Raman spectra were recorded with a Hilger E612 spectrometer, using the mercury 4358 Å line and saturated potassium nitrite as a filter to remove lines of shorter wavelength. The solutions were centrifuged for 15 min. at 3000 r.p.m. to obtain a clear sample. Conductivities were measured with a Philips type 9500 conductivity bridge. *X*-Ray powder photographs were taken by using a De Wolff-type monochromating camera manufactured by Nonius; specimens were held between Sellotape, and hygroscopic or air-sensitive specimens were first mulled in Apiezon M grease, which was considered to provide sufficient protection.

Apparatus and Methods.—For those reactions which were expected to produce gases, acetonitrile was condensed on to iodobenzene dichloride, under a vacuum, and the silver salt added by rotating a bent tube which was held above the mixture. The mixture was then allowed to warm while being stirred; if a gas was evolved the solution was cooled to −45°, at which temperature the vapour pressure of acetonitrile is low, and the gas identified by its infrared absorption spectrum. The acetonitrile was then pumped off, and the infrared spectrum of the residue measured. The characteristic strong peaks of iodobenzene at 1575, 1059, and 997 cm.$^{-1}$, of iodosobenzene at 685 cm.$^{-1}$, and of iodobenzene dichloride at 675 cm.$^{-1}$, enabled these compounds to be readily identified.

Reactions between silver salts, soluble in acetonitrile, and iodobenzene dichloride were performed in a dry-box; the solution of the silver salt was mixed with either solid or dissolved iodobenzene dichloride, the precipitated silver chloride filtered or centrifuged off, and the remaining solution freeze-dried. Reactions with insoluble silver salts were performed similarly, the mixtures being either shaken or stirred, after which they were filtered and the solution freeze-dried. Analyses for carbon, hydrogen, and nitrogen were carried out by standard microchemical methods. Chlorine was determined gravimetrically as silver chloride and sulphur as barium sulphate, after Parr bomb fusion with sodium peroxide. Chromium was determined colorimetrically as chromate, in 2N-sodium hydroxide; complete oxidation to chromate was effected by fusion with sodium peroxide in a Parr bomb, followed by acidification and boiling with potassium persulphate and silver nitrate.[13]

Materials.—All hygroscopic materials were handled in a dry-box containing phosphorus pentoxide and a molecular sieve. Acetonitrile was fractionally distilled from phosphorus pentoxide or molecular sieve on to molecular sieve. Silver perchlorate, nitrate, and trifluoroacetate were dried at 110° *in vacuo* over phosphorus pentoxide. Silver borofluoride was a commercial sample from the Ozark Mahoning Co. Silver aurichloride, azide, bromate, bromide, chromate, cyanamide, cyanate, cyanide, hyponitrite, iodate, iodide, molybdate, oxalate, sulphide, and sulphite were prepared by standard metathetical reactions and dried by washing with acetone and ether. Silver vanadate (Ag_3VO_4) was made from sodium orthovanadate, prepared by heating the stoicheiometric quantities of sodium metavanadate and sodium carbonate in a nickel crucible.

Iodobenzene dichloride was prepared, as described by Mann and Saunders,[14] by passage of chlorine into iodobenzene in chloroform; the final washing was carried out with petroleum (b. p. 60—80°), rather than with chloroform. The iodobenzene dichloride was then pumped for 1—2 hr. and stored under a vacuum, in liquid nitrogen, to avoid the slow decomposition to *p*-chloroiodobenzene and hydrogen chloride.

Iodosobenzene was prepared by the method given by Mann and Saunders; [14] hydrolysis with pyridine gave a product which could be dried more easily.

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[12] Lawson and Purdie, *Chem. and Ind.*, 1961, 508.

[13] Hildebrand *et al.*, " Applied Inorganic Analysis," 2nd edn., Wiley, New York, 1953, p. 530.

[14] Mann and Saunders, " Practical Organic Chemistry," Longmans, Green, London, 3rd edn., 1952, pp. 143, 144.

Results.—Silver borofluoride or perchlorate, in solution, did not react with iodobenzene dichloride in acetonitrile—neither did solid silver aurichloride, bromate, iodate, molybdate, sulphide, sulphite, or vanadate; filtration followed by freeze-drying gave only the starting materials.

An incomplete reaction appeared to have taken place after silver fluoride (0·830 g., 6·5 mmoles) had been stirred at $-15°$ for 24 hr. with iodobenzene dichloride (0·901 g., 3·28 mmoles). Freeze-drying of the solution produced yellow crystals mixed with a yellow oil which solidified overnight. Both components appeared to have the same infrared spectrum, but this contained no peaks attributable to I–F; it showed a peak at about 775 cm.$^{-1}$, possibly C–Cl, and another at 1095 cm.$^{-1}$, possibly C–F. The spectrum also indicated that the solid mixture contained unchanged iodobenzene dichloride (Found: C, 26·4; H, 2·0. PhF_2I requires C, 29·7; H, 2·1; and $PhCl_2I$ requires C, 26·1; H, 1·8%). This must indicate either decomposition or the occurrence of secondary reactions.

Iodobenzene diacetate.—Silver acetate (2·03 g., 12·3 mmoles), was stirred with iodobenzene dichloride (1·49 g., 5·43 mmoles); reaction was fairly rapid, and was followed by filtration and removal of solvent. The product was recrystallised from benzene (Found: C, 36·6; H, 3·5. Calc. for $C_{10}H_{11}IO_4$: C, 36·7; H, 3·4%); it had an infrared spectrum identical with that of an authentic specimen of iodobenzene diacetate.[14]

Iodobenzene di-trifluoroacetate.—Iodobenzene dichloride (1·485 g., 5·41 mmoles) was added to a solution of silver trifluoroacetate (2·39 g., 10·8 mmoles) in acetonitrile (17 ml.). After filtration and freeze-drying of the resultant solution the product still contained traces of silver trifluoroacetate. The infrared spectrum was identical with that of *iodobenzene di-trifluoroacetate* prepared by an independent method; redistilled trifluoroacetic acid (4 ml.) and iodosobenzene (2 g.) were heated for 45 min. on a steam-bath, and then poured into ether (50 ml.). On partial evaporation of the ether yellow-white crystals were deposited; washing with a small amount of ether removed the colour. The crystals were *iodobenzene di-trifluoroacetate*; $PhI(CO_2CF_3)_2$ [Found: C, 28·3; H, 1·7%; *M* (cryoscopy in dioxan), 433. $C_{10}H_5F_3IO_4$ requires C, 27·8; H, 1·2%; *M*, 430], $\nu_{max.}$ (infrared) 2940, 1740s, 1700s, 1560, 1477, 1455, 1392, 1365, 1225—1125s, 1015, 992, 855, 835, 801, 775, 735, 725, 672, 655, 605, 515, 495, and 455 cm.$^{-1}$.

The yellow ethereal solution gave a yellow gum on evaporation. This changed fairly rapidly into iodosobenzene and iodobenzene di-trifluoroacetate, and for this reason no pure compound could be isolated. The colour is almost certainly due to μ-oxodi-trifluoroacetatodiphenyldi-iodine. A yellow colour was also produced on heating iodobenzene di-trifluoroacetate to about 70° either in petroleum solution, or alone (*e.g.*, after a lengthy scan in the infrared spectrometer), or on heating iodobenzene di-trifluoroacetate with iodosobenzene. Presumably reactions (1) and (2) take place.

$$2PhI(CO_2{\cdot}CF_3)_2 \longrightarrow (PhI)_2O(CO_2{\cdot}CF_3)_2 + O(CO{\cdot}CF_3)_2 \tag{1}$$

$$PhI(CO_2{\cdot}CF_3)_2 + PhIO \longrightarrow (PhI)_2O(CO_2{\cdot}CF_3)_2 \tag{2}$$

The infrared spectrum of this yellow compound is very similar to that of iodobenzene di-trifluoroacetate, except that the 1740 and 1700 cm.$^{-1}$ peak become 1660s, 1705sh, and 1740sh cm.$^{-1}$.

The reaction of silver nitrate and iodobenzene dichloride is complex, and does not go to completion; iodobenzene dichloride (2·645 g., 9·6 mmoles) reacted with silver nitrate (3·395 g., 20 mmoles) in acetonitrile (20·1 ml.) at room temperature; 2 ml. of this solution was treated with water, dilute nitric acid, and sodium chloride and gave 0·0636 g. of silver chloride. This corresponds to a reaction ratio ($AgNO_3 : PhICl_2$) of 1·61 : 1·0. Conductometric titration at $-22°$ gave an end-point at $AgNO_3 : PhICl_2 = 1 : 1$.

Freeze-drying of a solution containing more than 1·5 moles of silver nitrate per mole of iodobenzene dichloride gave a colourless, or sometimes slightly yellow oil. Extraction of this oil with ether left a white solid which with water gave the yellow colour associated with μ-oxodinitratodiphenyldi-iodine but gave no chloride ions. Hence the white solid must contain iodobenzene dinitrate, as well as the unchanged silver nitrate which could not be removed. The ether extract was yellow, and contained largely iodobenzene dichloride.

When the reaction was carried out with less than 1·5 moles of silver nitrate per mole of iodobenzene dichloride a solid was produced, on freeze-drying, which rapidly decomposed to give yellow oil and fumes of nitrogen dioxide.

Raman spectra of acetonitrile solutions, with a reaction ratio between 1·5 : 1 and 2 : 1, and infrared spectra of the oil, produced on freeze-drying of these solutions, were taken; $\nu_{max.}$ (infrared) 2970, 1660, 1580—1540, 1442, 1325, 1270, 1175, 1160, 1085, 1060, 1045, 1005, 985, 925, 860—850, 800w, 773, 730, 710, 675, 655sh, 575s, 515vw, 455, 397, 383, 351, 342 (328, 324, 303, 299, 282 cm.$^{-1}$ structure of a large strong band); $\nu_{max.}$ (Raman) 1674, 1570, 1473?, 1412, 1377, 1332, 1280, 1056?, 1016, 992, 955, 875?, 719, 640?, 343?, 308vs, 258, 169 cm.$^{-1}$.

Silver chromate reacts rapidly with iodobenzene dichloride, the colour of the solution changing almost immediately to red; equivalent quantities were stirred overnight at −15° to produce a red solution which gave red crystals on removal of the solvent. These crystals decomposed rapidly, and no infrared spectrum could be taken. Analysis was carried out as soon as possible after separation, but still on material that was probably partly decomposed (Found: C, 20·7; H, 1·4; Cr, 8·9. $C_6H_5CrIO_4$ requires C, 22·5; H, 1·6; Cr, 16·2%). Willgerodt,[15] analysing his material for acidic properties alone, obtained only 11·5% of acid rather than the expected 16·2%. The decomposition product was a black gum which crystallised after some time (Found: C, 10·0; H, 0·7; Cr. 20·3%). This does not correspond to any reasonable formulation and the infrared spectrum of the gum has only a few weak peaks and several broad absorptions. The above results indicate that it is a partially oxidised product.

Silver sulphate and a solution of $PhICl_2$ were stirred overnight at −15°, after which the solution had become almost colourless. Removal of the solvent left a pale yellow gum; this very readily became more yellow, even in the dry-box, although its colour could be partly removed again by further pumping. This probably represents slight partial hydrolysis which is reversible, as the sulphate is dibasic, and could give a half-ester first:

$$2PhISO_4 + H_2O \longrightarrow PhI(O{\cdot}SO_3H){\cdot}O{\cdot}(O{\cdot}SO_3H)IPh.$$

One sample, prepared with an excess of silver sulphate, crystallised after some months; it was only faintly yellow. However, analysis and an *X*-ray powder photograph showed that it contained some free silver sulphate, which must have been sufficiently soluble to provide contamination.

Another sample, prepared from a 1 : 1 mixture, was much more yellow and was almost certainly the half hydrate, *μ-oxodi-bisulphatodiphenyldi-iodine* (Found: C, 22·4; H, 1·8; S, 9·0. $C_{12}H_{12}I_2O_4S_2$ requires C, 23·3; H, 2·0; S, 9·5%). The above mentioned crystalline material was so hygroscopic that mulling even with sodium-dried Nujol gave an intractable gum; a mull could only be obtained by using Nujol that had been carefully dried with a molecular sieve. The infrared spectrum was rather ill-defined, showing broad bands in the SO_4 (1000—1200 and 625 cm.$^{-1}$) and C–I regions (450 cm.$^{-1}$). The non-crystalline material could not be mulled at all. A poor spectrum was obtained after pressing it between Polythene sheets; it was similar to that of the first material.

Silver nitrite reacted with iodobenzene dichloride at low temperature, giving a blue solution of dinitrogen trioxide. On warming to room temperature nitric oxide and nitrogen dioxide were given off.

Silver hyponitrite reacted at low temperature to give nitrous oxide, together with traces of nitric oxide and nitrogen dioxide (probably arising from some contamination of the hyponitrite with nitrite).

Silver carbonate reacted at room temperature giving carbon dioxide. These three compounds gave iodosobenzene and silver chloride as the other reaction products. Silver oxide reacted to give iodosobenzene and silver chloride alone.

Silver oxalate appeared to react at low temperature; on allowing the solution to warm up carbon dioxide was evolved but no carbon monoxide was formed (*M* for CO_2, 44·0. Found for the gas: *M*, 44·2). The other products were iodobenzene and silver chloride.

Silver azide reacted immediately at room temperature. There was a transient brown colour formed in the solution, which immediately faded, followed by rapid evolution of gas (not further identified; it can only be nitrogen).

Silver cyanide reacted very slowly at room temperature. The solid became yellowish and there was a smell of cyanide, consistent with a slow production of cyanogen.

Silver cyanate reacted immediately to give a transient red colour, which immediately faded leaving a colourless solution; no gas evolution was observed.

Silver thiocyanate reacted immediately; there was no visible gas evolution. After some

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[15] Willgerodt, *Ber.*, 1893, **26**, 1309.

time the solution and precipitate assumed an orange-red or orange-yellow colour. The infra-red spectrum of the precipitate then showed the broad band between 1600 and 1000 cm.$^{-1}$ associated with the polythiocyanogens; the behaviour of the solution was identical with that of solutions of thiocyanogen.[16]

Reactions with these four pseudohalogens were performed on a small scale; in each case the final solution contained iodobenzene as the major product.

Silver bromide reacted rapidly, and silver iodide rather more slowly, with solutions of iodobenzene dichloride; both gave brown solutions of the respective halogens.

Silver cyanamide reacted rapidly to give a red solution, with evolution of a gas. Silver cyanamide (0·713 g., 2·80 mmoles) and iodobenzene dichloride (0·772 g., 2·80 mmoles) reacted to give 1·15 mmoles of a gas (*M*, 31). As it had no infrared spectrum it must have been nitrogen, possibly with traces of higher molecular-weight species, such as cyanogen. The precipitate was buff, and washing with acetonitrile again gave a red solution. Freeze-drying of the original solution left a dark red solid (Found: C, 22·9; H, 1·9; N, 27·3. $C_5H_5IN_5$ requires C, 22·9; H, 1·9; N, 26·8%).

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[16] Söderbäck, *Annalen*, 1919, **419**, 217.