245. *Organic Compounds of Multivalent Iodine. Part I. Infrared Spectra.*

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The infrared spectra of typical iodoxy-, iodoso-, and iodonium compounds have been recorded. Iodoxy-compounds show three characteristic bands between 700 and 800 cm.$^{-1}$; in solution the spectra change largely. No characteristic absorption is found in the spectra of iodoso-compounds. Acyloxy-derivatives of iodoso-compounds show low carbonyl frequencies which are attributed to partially ionic structures. The iodosobenzoic acids show abnormalities and are best represented as zwitterionic (*meta, para*) or cyclic (*ortho*); *o*-iodoxybenzoic acid is similarly cyclic. Iodonium salts show no characteristic bands.

OXIDATION of aromatic iodo-compounds can lead to organic derivatives of multivalent iodine. Such compounds were first prepared by Willgerodt [1] and by Meyer and Wachter [2] and were extensively studied by Willgerodt and his collaborators.[3] The compounds may be separated into three groups: iodoxy-compounds, $Ar{\cdot}IO_2$; iodoso-compounds, $Ar{\cdot}IO$, and their derivatives, $Ar{\cdot}IX_2$ (X = *e.g.*, Cl, OAc); iodonium salts, $Ar_2I^+X^-$. Infrared spectra of representative compounds of each class have been examined.

Iodoxy-compounds.—These compounds are colourless, non-volatile, infusible solids insoluble in all but highly polar solvents. The spectra of the solids (prepared as mulls with Nujol or as discs with potassium bromide) revealed a close similarity to those of the parent iodo-compounds except in the region 700—800 cm.$^{-1}$. A group of strong bands (Table 1) appears here in the spectra of all the iodoxy-compounds examined. Strong absorption in this region is shown by inorganic iodates,[4] iodic acid, and iodine pentoxide, and has been previously reported [5] for a few iodoxy-compounds. It may accordingly be attributed to the iodine-oxygen system. By using carefully purified materials it was possible to resolve the absorption of the iodoxy-compounds into three bands: 720 ± 5, 745 ± 5, and 765 ± 5 cm.$^{-1}$. Of the compounds examined, two, *viz.*, *o*-iodoxynitrobenzene and *o*-iodoxybenzoic acid, fail to show these characteristic bands. In both cases models indicate that the proximity of the two bulky substituents must lead to strong interactions. With *o*-iodoxynitrobenzene this shifts the iodoxy-bands to higher frequencies,

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[1] Willgerodt, *J. prakt. Chem.*, 1886, **33**, 154; *Ber.*, 1892, **25**, 3494.

[2] Meyer and Wachter, *Ber.*, 1892, **25**, 2632.

[3] Willgerodt, " Die Organischen Verbindungen mit mehrwertigem Iod," Enke, Stuttgart, 1914.

[4] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[5] Furlani and Sartori, *Ann. Chimica*, 1957, **47**, 124.

TABLE 1. *Infrared spectra* (700—800 *cm.*$^{-1}$) *of iodoxy- and iodo-compounds.*

	Absorption bands (in cm.$^{-1}$) *							
Probable assignment	—	IO_2	C–H	NO_2	IO_2	C–H	IO_2	—	C–H
Iodobenzene	—	—	730s	—	—	—	—	—	—
Iodoxybenzene	—	715s	730s	—	[740]w	—	765s	—	—
o-Iodonitrobenzene	—	—	—	730m	— 745s	780m	— 793s	—	—
o-Iodoxynitrobenzene	—	—	—	735m	755m	770s	800s	—	—
m-Iodonitrobenzene	715m	—	—	730m	—	—	—	—	800m
m-Iodoxynitrobenzene	710m	715m	—	732m	740w	—	760m	—	800w
p-Iodonitrobenzene	—	—	—	730m	—	—	—	—	833m
p-Iodoxynitrobenzene	704w	725m	—	735s	748w	—	774s	—	837s
o-Iodotoluene	—	—	745s	—	—	—	—	796w	—
o-Iodoxytoluene	—	723s	740s	—	[748]w	—	765s	794w	—
m-Iodotoluene	—	—	—	—	—	768s	—	801w	—
m-Iodoxytoluene	—	720s	—	—	740m	—	765s	804w	—
p-Iodotoluene	—	—	—	—	—	—	—	790m	800s
p-Iodoxytoluene	—	715s	—	—	742w	—	765s	—	793m
o-Iodoanisole	707w	—	750s	—	—	—	—	790m	—
o-Iodoxyanisole	—	723s	755s	—	748w	—	762s	795m	—
p-Iodoanisole	—	—	—	—	—	—	—	783w	805s
p-Iodoxyanisole	—	725s	—	—	745m	—	770s	800w	805w
o-Iodobenzoic acid	—	—	740s	—	—	—	—	—	—
o-Iodoxybenzoic acid	—	—	750m	—	—	—	785s	—	—
m-Iodobenzoic acid	—	—	—	—	—	750m	—	—	—
m-Iodoxybenzoic acid	—	720s	—	—	738m	750s	765s	—	—

* Letters indicate the relative intensity of the bands: s, strong; m, medium; w, weak. Square brackets indicate points of inflexion.

TABLE 2. *Characteristic bands in the spectra of iodoso-esters.*[1]

	Carbonyl stretching frequency (cm.$^{-1}$)		C–O single-bond stretching frequency (cm.$^{-1}$)						Other characteristic frequencies (cm.$^{-1}$)			
	Solid [2]	Soln.[3]		Solid [2]		Soln.[3]			Solid [2]	Soln.[3]	Solid [2]	Soln.[3]
(1) Iodosobenzene diacetate	1625m 1640s	1660s [a]	—	1275s	—	1230ms [a]	1263s [a]	—	1296s	1284s [a]	672ms	665m [a]
(2) Iodosobenzene dipropionate	1615m 1650s	1650s [a,b]	1180mw	1220s	—	1180m [a,b]	1212s [a,b]	—	1290ms	1284m [a,b]	[680] *	678 * m [b]
(3) Iodosobenzene di-isobutyrate	1655 s	1650s [a,b]	1170ms	1212s	—	1190m [a,b]	1207s [a,b]	—	1288m	1286m [a,b]	685 * m	680 * m [b]
(4) Iodosobenzene dibenzoate	1612ms 1650ms	1645s [b,c]	1174m	1277s	1325s	1175m [b]	1270s [b]	1320s [b]	1309ms	1287s [b]	680ms	680 * ms [b]
(5) Iodosobenzene di-(*p*-nitrobenzoate)	1605ms 1653ms	1603ms [d] 1650m	—	—	1315s	—	—	1304s [d]	1304s	1285s [d]	678 * m	—
(6) *p*-Iodosoanisole diacetate	1650ms	1650ms [b]	1258s	1276m	—	1236m [b] 1255s	1265s [b]	—	1295s	1285s [b]	672m	665m [b]
(7) *p*-Iodosonitrobenzene diacetate	1645s	1650s [b]	—	1276s	—	1232m [b]	1265s [b]	—	1295s	1282s [b]	670ms	665m [b]
(8) *m*-Iodosotoluene diacetate	1645s	1655s [b]	—	1275s	—	1240s [b]	1269s [b]	—	1300m	1286s [b]	672m	668ms [b]
(9) *p*-Iodosotoluene diacetate	1650s	1655s [b]	—	1270s	—	1240ms [b]	1269s [b]	—	1291s	1286s [b]	667s	668m [b]
[(10) Benzylidene diacetate	—	1755s [e]	—	—	—	1200s [e]	1243s [e]	—	—	—	—	—
(11) *p*-Methylbenzylidene diacetate]	1735s 1755s	1755s [b]	1208s	1242s	—	1200s [b]	1235s [b]	—	—	—	—	—

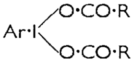
[1] Letters indicate the relative intensity of the bands. [2] In Nujol. [3] Alphabetical superscripts indicate the following solvents: *a*, CCl_4; *b*, CS_2; *c*, CH_2Cl_2; *d*, $CHCl_3$; *e*, liquid.

* Overlaps aromatic C–H deformation band.

together with a similar shift (found also in the parent iodo-compound) of the out-of-plane C–H deformation band. In the spectrum of *o*-iodoxybenzoic acid only one band derived from the iodoxy-group is recognised; it seems probable that chemical interaction of the two neighbouring groups has occurred: this will be discussed more fully below with the iodosobenzoic acids.

The physical properties of the iodoxy-compounds show the existence of strong lattice forces. That these are largely effective between neighbouring iodoxy-groups is indicated by the decomposition temperatures of the known iodoxy-compounds which are grouped between the limits 150° and 250° and lie in Gaussian distribution about 202°. Crystallographic examination[6] of *p*-chloroiodoxybenzene has shown that the iodine–oxygen distance between adjacent molecules is small, *i.e.*, 2·72 Å, significantly less than the sum of the van der Waals radii (3·15 Å). It is therefore particularly desirable to determine the spectra of the iodoxy-compounds in a dispersed phase. Although they are insoluble in the conventional spectroscopic solvents, iodoxy-compounds dissolve sufficiently in dimethylformamide for spectroscopic purposes; the window in this solvent, at 750—825 cm.$^{-1}$, permits the examination of part of the interesting 700—800 cm.$^{-1}$ range. The spectra of the compounds examined show considerable changes in solution. Two strong bands separated by *ca.* 20 cm.$^{-1}$ appear near 800 cm.$^{-1}$: iodoxybenzene, 782, 803; *o*-nitro-, 795, 813; *p*-nitro-, 787, 805; *p*-methyl-, 803; and *p*-methoxy-iodoxybenzene, 785, 805 cm.$^{-1}$ (these bands are additional to any due to the skeleton of the parent iodo-compound). The magnitude of these shifts shows it to be of doubtful propriety to attempt to assign precisely the bands in the spectra of the solid iodoxy-compounds. Although the data available are limited and there exists the possibility of strong solvent–solute interaction in dimethylformamide, the two bands found in the solution spectra may be tentatively assigned to the symmetrical and antisymmetrical iodine–oxygen stretching frequencies. An extension of the range of solution spectra is being examined.

Iodoso-compounds.—The physical properties of these compounds closely resemble those of the iodoxy-compounds: they are colourless or pale yellow solids, insoluble or soluble with decomposition in the common solvents. Their spectra were examined as mulls in Nujol; no characteristic bands could be detected. (We were not able to confirm the presence of a weak band near 740 cm.$^{-1}$ previously reported[5] for several iodoso-compounds: it seems probable that these bands were due to the presence of small amounts of iodoxy-compounds.) If the bands in the spectra of iodoxy-compounds between 700 and 800 cm.$^{-1}$ are correctly assigned to an iodine–oxygen stretching frequency, it follows that similar I–O bonding is not present in the iodoso-compounds; it seems possible that these have a polymeric structure. When specimens were prepared as discs by grinding and pressing with potassium bromide, a strong band appeared at 765 cm.$^{-1}$. The well-known disproportionation, to iodoxy- and iodo-compounds, probably occurs under these conditions; a more detailed examination of the ground and pressed material is being undertaken. Attempts to obtain solution spectra of iodoso-compounds have not been successful.

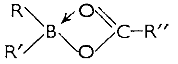


$\mathrm{Ar{\cdot}I}\begin{cases}\mathrm{O{\cdot}CO{\cdot}R}\\ \mathrm{O{\cdot}CO{\cdot}R}\end{cases}$

(I)

$p\text{-}\mathrm{C_6H_4R{\cdot}CH(OAc)_2}$

(II)



(III)

Iodoso-compounds react with carboxylic acids to give compounds formulated as diesters (I). These are tractable solids, readily soluble in organic solvents. An examination of their spectra (Table 2) revealed several points of interest. The carbonyl stretching band is displaced to values *ca.* 100 cm.$^{-1}$ less than those expected for the corresponding carbon compounds. The model compounds, benzylidene diacetate and *p*-methylbenzylidene diacetate (II; R = H, Me), show normal carbonyl bands. Correspondingly, the

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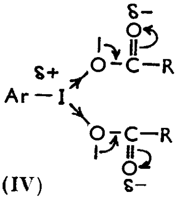
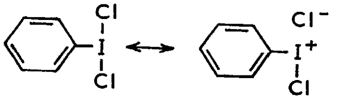
[6] Archer, *Acta Cryst.*, 1948, **1**, 64.

carbon–oxygen single-bond stretching frequency, normal in the two model esters, moves to higher values. A similarly low value for the carbonyl frequency has recently been reported [7] for certain acyloxy-derivatives of boron (III) and explained by chelation of the ester carbonyl group to the electron-deficient boron. There is, however, no evidence to suggest that tervalent iodine is electron-deficient, and it seems improbable that a similar effect is operating here. An alternative explanation may be found in the combination of the high polarisability of iodine with the inefficiency of the overlap between the oxygen $2p$- and the iodine $4d$- or $5sp$-orbitals. The consequent shift of electrons towards the more electronegative oxygen will lead to weakening of the carbonyl bond and to strengthening of the carbon–oxygen single bond and give a partially zwitterionic structure (IV). A similar structure (V) has been suggested [8] for iodosobenzene dichloride.



(IV)



(V)

The spectra of the esters are further characterised by bands near 1290 and 670 cm.$^{-1}$. These bands are not present in the parent iodo- or iodoso-compounds or in the benzylidene model compounds, and they may accordingly be attributed to the iodine ester system. The band near 670 cm.$^{-1}$ has been tentatively assigned to the iodine–oxygen single-bond stretching frequency in the I–O–(C) group; it is possible that the second band is a combination band of this and the carboxylic ester band [9] at 600 cm.$^{-1}$.

o-Iodosobenzoic acid has long been recognised as atypical. The absence of the usual " iodoso " smell and its stability to further oxidation led to its formulation [2,10] as the cyclic half-ester (VI). The presence of an –I–O–CO– system in this structure led us to expect a low value for the carbonyl stretching band. This was confirmed (Table 3); additionally, the absence of the hydrogen-bonded hydroxyl bands characteristic of carboxylic acids and the appearance of a weak hydroxyl band at 3340 cm.$^{-1}$ confirm the correctness of the cyclic structure (VI). However, *m*- and *p*-iodosobenzoic acid also had low carbonyl bands (Table 3) and weak hydroxyl bands, suggesting that their structures also involved proton transfer to the iodoso-group. No intramolecularly cyclised structures can be written for these acids, and formulation as linear, polymeric half esters does not appear to explain the extremely low values for the carbonyl stretching frequency (cf. Table 2). The carboxylate ion absorbs [11] in the region 1550—1610 cm.$^{-1}$, and an alternative representation of these compounds as zwitterions (*e.g.*, VII) appears to accommodate the

TABLE 3. *Carbonyl stretching bands in the spectra of iodo-, iodoso-, and iodoxy-benzoic acids.*

	Absorption bands (in cm.$^{-1}$)					
Subst. orientn.	Iodo-	Iodoso-	Iodoxy-	Iodoso- (Na salt)	Iodoso-acetate	Iodoso-chloride
ortho	1680	1620	1640	1595	[1640] 1660	1695
meta	1695	1605	1695	1595	—	1705
para	1690	1625	—	—	—	—

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[7] Duncanson, Gerrard, Lappert, Pyszora, and Shaffeman, *J.*, 1958, 3652.

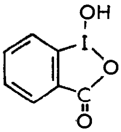
[8] Guryanova and Syrkin, *Acta Physicochim. U.R.S.S.*, 1939, **11**, 657.

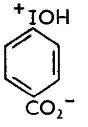
[9] Thompson and Torkington, *J.*, 1945, 64.

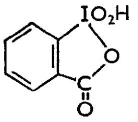
[10] Askenasy and Meyer, *Ber.*, 1893, **26**, 1354.

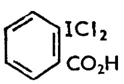
[11] Bellamy, " The Infra-Red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, p. 174.

evidence satisfactorily. Models of *o*-iodosobenzoic acid indicate that, owing to the proximity of the two large groups, there can be no useful distinction between the cyclic structure and a necessarily perturbed zwitterionic form. Comparison of the spectra of *o*- and *m*-iodosobenzoic acid with their sodium salts slows that the carbonyl band is similar both in position and shape. The zwitterionic structure assigned to the acids may be regarded in part as a limit of the tendency already expressed in the structure of the iodoso-esters assisted internally by the increased strength of the acid grouping: the basic nature of the iodoso-group and its ability to form salts with inorganic acids are well established. Additionally, external forces arising from packing considerations may well play some part in the apparently high basicity of the iodoso-group in the benzoic acids. It is of interest that the carbonyl band of several iodoso-esters is split in the solid state (Table 2); in each case the low-frequency band could arise from a carboxylate ion. No spectroscopically useful solvent for the iodosobenzoic acids has yet been found.


(VI)


(VII)


(VIII)


(IX)

The abnormality of the spectrum of *o*-iodoxybenzoic acid in the 700—800 cm.$^{-1}$ region has already been noted. Its spectrum shows no typical carboxylic acid hydroxyl absorption, and its carbonyl band appears at a low value (Table 3). A model indicates that the neighbouring iodine and carboxyl groups must interact strongly, but, that the low carbonyl band is not due solely to this, is shown by the normal position of the band in the iodo-acid. It seems probable that the slight basicity of the iodoxy-group [12] coupled with the proximity effect has resulted in the transfer of the proton from the carbonyl group with the formation of a cyclic system (VIII). *m*-Iodoxybenzoic acid shows normal hydroxyl, carbonyl, and iodoxy-bands.

Attempts to determine the iodine–chlorine stretching frequencies of the aryliodosochlorides, Ar•ICl$_2$, were not successful; the low stability of these compounds led to substantial decomposition during their examination. Slightly more stable is the dichloride of *o*-iodosobenzoic acid; this showed a normal carbonyl band and is correctly represented as the non-cyclic compound (IX).

Iodonium Salts.—No characteristic frequencies were observed in the spectra of these salts. A strong carbon–iodine stretching band appeared near 452 cm.$^{-1}$, a value similar to that of the parent iodo-compounds (445—450 cm.$^{-1}$).

EXPERIMENTAL

Iodo-compounds were obtained commercially or prepared by the Sandmeyer reaction and purified by crystallisation. Iodoso-compounds were prepared by hydrolysis of the dichlorides [13] with 5% sodium hydroxide solution; *o*-, *m*-, and *p*-iodosobenzoic acid were obtained by cautious neutralisation of the hydrolysis mixture.[3] Iodoxy-compounds were prepared by oxidation of the iodoso-chlorides with sodium hypochlorite [14] and purified by repeated crystallisation from water; purity was estimated iodometrically and was in all cases better than 98%.

Preparation of Iodoso-esters.—(*a*) Iodosobenzene (2 g.) was warmed with acetic acid (6 ml.); excess of acid was evaporated *in vacuo*; the residual iodosobenzene diacetate, crystallised from light petroleum–benzene, had m. p. 157—158°. Iodosobenzene dipropionate had m. p. 62°, and *iodosobenzene di-isobutyrate* m. p. 101—102° (from light petroleum) (Found: C, 44·3; H, 5·1. $C_{14}H_{19}O_4I$ requires C, 44·5; H, 5·1%). (*b*) *p*-Iodosoanisole diacetate, m. p. 82—83°, was obtained from the dichloride (1·9 g.) by the action of lead acetate (2·6 g.) in warm acetic acid

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[12] Masson, Race, and Pounder, *J.*, 1935, 1669.

[13] Lucas and Kennedy, *Org. Synth.*, Coll. Vol. III, p. 482.

[14] Formo and Johnson, *Org. Synth.*, Coll. Vol. III, p. 486.

(10 ml.).[15] After 1 hr. the mixture was filtered and evaporated *in vacuo*, and the residual ester crystallised from light petroleum. *p*-Iodosonitrobenzene diacetate, m. p. 167—168°, *m*- and *p*-iodosotoluene diacetate, m. p. 104—105° and 153—155°, respectively, were prepared similarly. (*c*) Iodosobenzene dibenzoate, m. p. 162°, was prepared by the action of ethereal benzoic acid on the acetate.[16] Iodosobenzene di-(*p*-nitrobenzoate), m. p. 209° (from chloroform), was prepared similarly.

Spectral Measurements.—Spectra were measured on a Perkin–Elmer Model 21 spectrophotometer with sodium chloride optics and on a Grubb-Parsons single-beam spectrophotometer with potassium bromide optics. Solids were examined as mulls with Nujol and Fluorolub and as discs with potassium bromide. Solutions were examined in 1 mm. matched cells; dimethylformamide was Eastman Kodak " Spectro " grade.

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[15] Neu, *Ber.*, 1939, **72**, 1505.

[16] Karelsky and Pausacker, *Austral. J. Chem.*, 1958, **11**, 39.