534. *Studies in Spectroscopy. Part V.* Molecular Compound Formation with Polyhalogeno-iodo-compounds.*

By R. N. HASZELDINE.

The ultra-violet spectrum of a polyfluoro-iodo-compound $R\cdot CF_2\cdot CF_2I$ is markedly dependent on the solvent used. The spectrum in light petroleum resembles that of the vapour, but in solvents such as Bu^nCl, Bu^tCl, $CH_3\cdot CO_2Et$, Et_2O, EtOH, or $Bu^n\cdot NH_2$, the absorption maximum moves up to 20 mμ towards the blue. For a particular solvent the shift in spectrum from that in light petroleum decreases in the series $R\cdot CF_2\cdot CF_2I$, $R\cdot CHF\cdot CF_2I$, $R\cdot CH_2\cdot CF_2I$, $R\cdot CF_2\cdot CH_2I$, $R\cdot CF_2\cdot CH_2\cdot CH_2I$, $R\cdot CH_2\cdot CH_2I$, *i.e.*, halogen substitution on both the α and the β carbon atom, but particularly on the former, is necessary for the maximum effect.

The shifts in spectra are compared with those for iodine in similar solvents. Molecular compound formation, (RI),B, between the neutral-molecule base B and the iodo-compound, RI (a weak Lewis acid), is suggested, with dative resonance structure of the type $(RI)^-$–$(B)^+$, and the implications of such complex formation on the reactivity of RI are discussed.

THE ultra-violet absorption spectra of a series of fluorine-containing iodo-compounds were recorded and discussed in Part III (*J.*, 1953, 1764). The solvent was light petroleum, and it was shown that the spectrum in this solvent differed only slightly from the spectrum of the vapour. It has now been found that the spectra of polyhalogenoiodoalkanes containing halogen (other than iodine) on the α carbon atom in $\overset{\beta}{C}\cdot\overset{\alpha}{C}\cdot I$ vary greatly with the solvent. With heptafluoro-*n*-propyl iodide as an example, relevant data are given in Table 1. It is apparent that shifts in the absorption maximum of up to 20 mμ occur on change of solvent, and these shifts are larger than the usual slight solvent effect observed for unsubstituted alkyl iodides (cf. Pr^nI, Table 3 : also the series of alkyl iodides in Part III, *loc. cit.*).

TABLE 1. *Ultra-violet spectrum of* C_3F_7I *in various solvents.*

Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
Vapour	271	195	229	22	$CH_3\cdot CO_2Et$	258—261	230	—	—
Petrol *	271	240	215	13	Et_2O	257	250	235	200
$CHCl_3$	269·5	250	—	—	Dioxan	Inflexion 253—260, ε, 275			
Bu^nCl	267	240	—	—	50% Aq. EtOH	254	200	220	100
Bu^tCl	265	230	232	130	MeOH	251	235	225	160
H_2SO_4 †	265	—	219	—	EtOH	250·5	230	225·5	150
$CH_3\cdot CO_2H$	261—263	225	—	—					

* Light petroleum, b. p. 60—80°. † Saturated solution in conc. H_2SO_4.

The maximum moves to shorter wave-length as the solvent changes from non-polar to polar in type, but this is not merely the effect of change in dielectric constant, since the maximum is at a longer wave-length in 50% aqueous ethanol than it is in anhydrous ethanol. The shift of the maximum is associated with solvents which contain an atom or atoms (*e.g.*, O, N) containing lone pairs of electrons, and if such a solvent is progressively diluted with petrol the maximum moves back to the longer wave-length. This is shown in Figs. 1 and 2, and in Table 2. For comparable *molar* dilutions, butylamine is more effective than ethanol, since the maximum almost disappears in the former solvent (Fig. 2). It should be noted that an isosbestic point is obtained in Figs. 1 and 2, and that double or abnormally broad maxima are not apparent in Fig. 1; the band envelope remains approximately the same in area and it is the position which is altered. The carbon–iodine bond in polyfluoroiodo-compounds undergoes homolytic fission readily but heterolytic fission only with difficulty (see papers in another series); true alkylammonium salt formation between, say, C_3F_7I, and a tertiary amine (*e.g.*, NMe_3) has not been achieved, although evidence other than that given below suggests that a weak complex can be formed.

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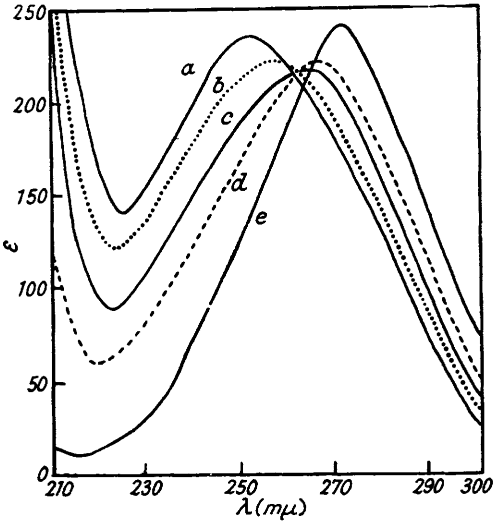
* Part IV, *J.*, 1953, 2525.

TABLE 2. *The effect of mixed solvents.*

Solvent *		$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
EtOH–petrol	100 : 1	250	230	226	160
	1 : 2	257	220	223	120
	1 : 5	264·5	220	222	90
	1 : 10	267	225	221	70
	1 : 100	271	240	215	15
$Bu^n\cdot NH_2$–petrol	1 : 50	Slight inflexion 262—265 mμ, ε, 250			
	1 : 150	Inflexion 262—265 mμ, ε, 250			
	1 : 250	268	225	244	160
	1 : 500	271	225	244	155
Tetrahydropyran–petrol	1 : 5	256	240	—	—
	1 : 10	263	235	—	—

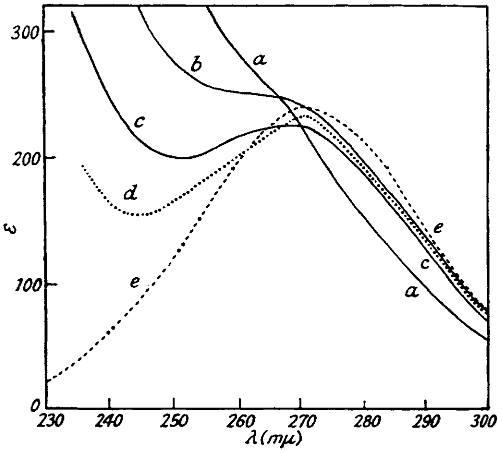
* Petrol = light petroleum, b. p. 60—80°.

FIG. 1. *Ultra-violet spectrum of heptafluoroiodopropane in ethanol–light petroleum.*



Solvents : *a*, Pure ethanol.
b, EtOH–petrol 1 : 2.
c, „ 1 : 5.
d, „ 1 : 10.
e, Light petroleum (100%).

FIG. 2. *Ultra-violet spectrum of heptafluoroiodopropane in* n-*butylamine–light petroleum.*



Solvents : *a*, $Bu^n\cdot NH_2$–petrol 1 : 50.
b, „ 1 : 150.
c, „ 1 : 250
d, „ 1 : 500.
e, Light petroleum (100%).

That the marked solvent effect depends on both α and β substitution in the iodo-compound $\overset{\beta}{C}\cdot\overset{\alpha}{C}\cdot I$ is shown in Table 3. These results may be analysed as follows :

Compounds of the type $R\cdot CH_2I$ (R = *alkyl, polyfluoroalkyl*). The solvent effect, Δ [$\lambda_{max.}$ (petrol) — $\lambda_{max.}$ (EtOH)], is very similar to that in propyl iodide (3—4 mμ) when R = $CF_3\cdot CH_2$ or CF_3; *i.e.*, if only hydrogen is present on the α carbon atom of the iodo-compound, β- and γ-substituents do not have a marked influence.

Compounds of the type $R\cdot CH_2\cdot CF_2I$ *or* $RR'CH\cdot CF_2I$ (R = H, *alkyl, or polyfluoroalkyl,* R = H *or alkyl, but not perfluoroalkyl*). When the compound has fluorine on the α-carbon atom but does not contain halogen on the β-carbon atom, the solvent effect is appreciably increased (5—8 mμ; see $CF_3\cdot CHMe\cdot CF_2I$, $CF_3\cdot CH_2\cdot CF_2I$, Table 3). Substitution of fluorine at the α-carbon atom thus determines the value of Δ more than does substitution at the β-carbon atom, but that β-substitution has an effect is shown below.

Compounds of the type $R\cdot CHF\cdot CF_2I$ (R = *fluorine or polyfluoroalkyl*). Here the solvent effect becomes large (10—12 mμ), but it is noteworthy that the highest value of Δ (20 mμ) is obtained when the β-carbon atom carries no hydrogen atom or alkyl group, but only fluorine or perfluoroalkyl groups (*e.g.*, C_3F_7I). The effect on Δ of replacement of the β-hydrogen atom in $CF_3\cdot CHF\cdot CF_2I$ by fluorine is much larger than might have been expected from comparison of the spectra of $CF_3\cdot CH_2\cdot CF_2I$ and $CF_3\cdot CHF\cdot CF_2I$.

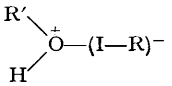
The effect of solvent on the absorption spectrum of the polyhalogenoiodo-compounds is very similar to that on the spectrum of iodine. It is well known that iodine vapour and iodine solutions in non-polar solvents (CCl_4, CS_2, light petroleum, etc.) have similar spectra, the solutions being violet ($\lambda_{max.}$ 495—540 mμ), whereas iodine solutions in ethers, alcohols, or water are brown ($\lambda_{max.}$ 460—480 mμ); iodine solutions in benzene and methylbenzenes are intermediate in colour ($\lambda_{max.}$ 490—500 mμ) (see Kleinberg and Davidson, *Chem. Reviews*, 1948, **42**, 601; Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703). Mulliken (*ibid.*, 1950, **72**, 600; 1952, **74**, 811) has discussed the spectra of iodine solutions on the basis of electron-donor and -acceptor interaction, and a similar concept is now applied to the spectra of the polyhalogenoiodo-compounds.

TABLE 3.

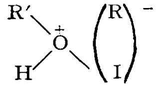
Compound	Solvent *	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	Δ
C_3F_7I	Petrol	271	240	215	13	20
	EtOH	250·5	230	225·5	150	
$CF_3\cdot CHF\cdot CF_2I$	Petrol	268	255	223	50	12
	EtOH	256	230	221	88	
$CHF_2\cdot CF_2I$	Petrol	265	255	215	14	10
	EtOH	255	255	222	120	
$CF_3\cdot CH_2\cdot CF_2I$	Petrol	271	290	219	25	8
	EtOH	263	280	219	70	
$CF_3\cdot CHMe\cdot CF_2I$	Petrol	270	330	238	80	5
	EtOH	265	300	233	100	
$CF_3\cdot CH_2I$	Petrol	262	265	—	—	4
	EtOH	258	255	214	30	
$CF_3\cdot CH_2\cdot CH_2I$	Petrol	261	370	213	20	3
	EtOH	258	350	209	25	
Pr^nI	Petrol	258	465	210	15	3
	EtOH	254·5	485	212	45	

* Petrol = light petroleum, b. p. 60—80°.

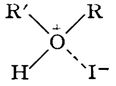
It is clear that the true spectra of the iodo-compounds are those obtained in light petroleum solution, since these closely resemble the spectra of the vapours; the valency structure of the C–I bond in the RI molecule must thus be changed appreciably when an oxygen- or nitrogen-containing solvent is used. It is suggested that in solution in a neutral-molecule ("onium") base B (NR'_3, OR'_2, R′OH, etc.) the iodo-compound RI forms a 1 : 1 (probably) or 1 : *n* molecular complex of the donor–acceptor type, the donated electron in the structure $\psi[B^+\text{–}(RI)^-]$ being derived from the lone pair of electrons in B. The wave-functions are mainly of the van der Waals [(RI)·(B)] structure such as (I) or (II) (the latter being of the type postulated for iodine by Mulliken); *i.e.*, transfer of an electron from B to RI with formation of a *weak* covalent bond between the odd electron of B^+ and $(RI)^-$, with resonance in the excited state involving structures for (II) such as (III) or (IV). An alcohol R′OH is taken as example of B.



(I)

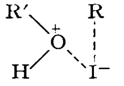


(II)



2 structures

(III)



2 structures

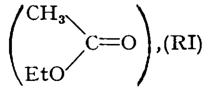
(IV)

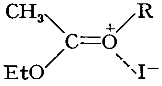
Table 3 shows that the shift in $\lambda_{max.}$ increases (for the particular pair of solvents studied) as the inductive effect of R in RI increases, *i.e.*, as the number of electronegative substituents on the α-carbon atom of RI increases. In a weak molecular complex of the type postulated above, the more positive the α-carbon atom in RI, the more positive will be the iodine atom, and the ease of charge transfer from the oxygen or nitrogen of the base should increase, *i.e.*, the more positive the iodine, the greater should be the shift in absorption spectrum. RI thus acts as a neutral-molecule Lewis acid by virtue of the incompletely satisfied electronegativity of its iodine atom. It is emphasised that there is only a slight shift in the spectrum (3—4 mμ) of an unsubstituted iodo-compound on change from light petroleum to ethanol (see Table 3 and Part III, *loc. cit.*).

From consideration of Table 1 it would appear that an alkyl chloride containing a lone chlorine atom can act as a Lewis base. The shift in absorption maximum of heptafluoroiodopropane from that in light petroleum is 4 mμ with *n*-butyl chloride and 6 mμ with *tert.*-butyl chloride. Loose complexes $(Bu^{n}Cl),(C_3F_7I)$ and $(Bu^{t}Cl),(C_3F_7I)$ involving the lone pair of electrons on the chlorine atom are indicated.

The solubility of heptafluoroiodopropane in concentrated sulphuric acid is limited, but a distinct shift in spectrum (6 mμ) is apparent. With acetic acid and ethyl acetate shifts of 9—10 and 12—13 mμ relatively to light petroleum are obtained. Here the complexes could be either of two types (or both): (*a*) complex formation involving the OH or OEt group of the acid or ester as discussed above for alcohols and ethers, and (*b*) complex formation involving the carbonyl group (*e.g.*, V or VI).

(V)





(VI)

Mulliken has pointed out that the ease of transfer of the non-bonding electron from the base B to the Lewis acid should depend on the ionisation potential of B, and the stability of the complex should vary accordingly. For water, ethyl chloride, ethanol, ethyl ether, and trimethylamine, the ionisation potentials are 12·61, 10·89, 10·7, 10·2, and 9·4 ev, respectively (Price, *Chem. Reviews*, 1947, **41**, 257) and one would expect base strength to increase in this order. Tables 1 and 2 show that the shifts in absorption spectra are in fact $Bu{\cdot}NH_2 > EtOH > 50\%\ EtOH > Et_2O > BuCl$. The amine is the most efficient of all in shifting the maximum to shorter wave-length and in fact the maximum almost disappears (Fig. 2); here, a relatively stable complex is formed whose bonding tends towards that of a tetra-alkylammonium iodide in type.

Table 1 and Figs. 1 and 2 show that there is little change in extinction coefficient on change of solvent; *i.e.*, if a spectral transition corresponding to *intermolecular charge transfer* in the molecular complex occurs in the 215—350-mμ region studied it does not lead to high-intensity absorption of the type observed near 300 mμ for the iodine–aromatic solvent complexes.

In Part III (*loc. cit.*) the absorption of a polyfluoroiodo-compound in light petroleum was shown to lie at much longer wave-length than that of the corresponding unsubstituted compound and this was interpreted as indicating a decrease in carbon–iodine bond dissociation energy caused by increase in stability of the free radical R. The present study has shown that in a basic solvent such as ethanol the carbon–iodine absorption is very similar to that of an unsubstituted primary alkyl iodide in *either* alcohol *or* light petroleum. If in the basic solvent the fluoro-iodide is part of a complex, it is suggested that by use of such a complex, where the carbon–iodine bond approaches more to that in, say, ethyl iodide, in character, it might be possible to effect synthetic reactions involving ionic intermediates which are difficult, if not impossible, to effect with polyfluoroiodo-compounds in solvents where complex formation cannot occur. Experiments to test this hypothesis are in progress, but there is already some evidence from published work that this might be so. In another series (*J.*, 1952, 3423 *et seq.*) the preparation of the Grignard compound $C_3F_7{\cdot}MgI$ was shown to be possible in ethyl ether and triethylamine, but impossible in the non-basic solvents $(C_4F_9)_2O$ or $N(C_3F_7)_3$; further, the yield of the Grignard compound was increased if the more basic solvent tetrahydropyran were used; *i.e.*, possibly complex formation first occurs and makes the fluoro-iodide more susceptible to reaction with magnesium.

The evidence presented above thus shows that a polyfluoroalkyl group R in an iodo-compound RI acts like a pseudohalogen, and that solutions of RI in basic solvents yield molecular compounds of the type which have long been known to exist between halogen molecules and organic compounds and between the Ag^+ ion and aromatic or unsaturated compounds.

EXPERIMENTAL

Compounds.—The iodo-compounds were prepared in this laboratory, and the methods used and the physical properties have been, or will be, reported in other series (Haszeldine, *J.*, 1949, 2856 *et seq.*; 1951, 584 *et seq.*; 1952, 1504 *et seq.*). The compounds $CF_3{\cdot}CHF{\cdot}CF_2I$, $CHF_2{\cdot}CF_2I$, $CF_3{\cdot}CH_2{\cdot}CF_2I$, and $CF_3{\cdot}CH_2I$ were kindly prepared by Mr. B. R. Steele.

Apparatus.—A Beckman Model DU and a Unicam Spectrophotometer were used, with 1-, 2-, or 10-cm. cells as required. The spectra were usually determined in duplicate, and average values are reported. The wave-length was measured to 0·25 mμ in the maximum, minimum, or inflexion areas.

Solvents.—Light petroleum (b. p. 60—80°) was purified by treatment with fuming sulphuric acid and alkaline permanganate. It showed 43% transmission at 210 mμ. Ethanol (95%; benzene-free) was dried by distillation from calcium oxide and then showed 42% transmission at 210 mμ.

Other solvents were thoroughly dried and purified by conventional methods. The following transmissions were shown: $CHCl_3$, 265 mμ, 95%; 255 mμ, 70%. H_2SO_4, 250 mμ, 70%; 210 mμ, 55%. Bu^nCl, 250 mμ, 90%; 235 mμ, 70%. Bu^tCl, 270 mμ, 80%; 250 mμ, 62%. $CH_3{\cdot}CO_2H$, 260 mμ, 80%; 250 mμ, 30%. $CH_3{\cdot}CO_2Et$, 270 mμ, 65%; 260 mμ, 60%. Et_2O, 220 mμ, 65%; 210 mμ, 45%. Dioxan, 270 mμ, 90%; 250 mμ, 60%. MeOH, 250 mμ, 90%; 220 mμ, 50%. $Bu^n{\cdot}NH_2$–light petroleum, 1 : 50, 250 mμ, 50%; 242 mμ, 40%. 1 : 150, 250 mμ, 96%; 240 mμ, 55%. 1 : 250, 250 mμ, 100%; 240 mμ, 75%. 1 : 500, 240 mμ, 95%; 234 mμ, 45%. Tetrahydropyran–light petroleum, 1 : 5, 260 mμ, 65%; 242 mμ, 40%. 1 : 10, 260 mμ, 81%; 240 mμ, 60%.

Pure butylamine and tetrahydropyran do not transmit sufficient light in the 250—280-mμ region to make them suitable as solvents, and dilution with light petroleum in the *volume* ratio shown above was therefore used (Table 2; Figs. 1 and 2).

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[*Received, March 23rd,* 1953.]