363. *Studies in Spectroscopy. Part III.* The Ultra-violet Absorption Spectra of Halogen-containing† Aliphatic Iodo-compounds, and the Relative Stability of Free Halogen-containing Alkyl Radicals.*

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The ultra-violet spectra of a variety of organic iodo-compounds of the type $\overset{\beta}{C}-\overset{\alpha}{C}\cdot I$ with various combinations of H, F, Cl, Br, and I substituted on the α, β, or γ carbon atom have been determined; the spectra of compounds of type $I\cdot[\overset{\vee}{C}-\overset{\vee}{C}]_n\cdot I$, and of some secondary and tertiary iodides have also been recorded. The position of the near ultra-violet maximum, which is very sensitive to structural change and to substitution on the β- and, particularly, on the α-carbon atom, varies from 257 mμ for a *n*-alkyl iodide to 346 mμ for CBr_3I, and can be used diagnostically for unknown iodo-compounds. Bathochromic shifts of the maxima increase in the order of substituents $H < F < Cl < Br < I$. Interaction between the carbon–iodine chromophores can be detected in $I\cdot[CH_2]_n\cdot I$ and $I\cdot[CF_2]_n\cdot I$ when $n = 2$, but not when $n \geqslant 3$. The auxochromic effect of halogen on the carbon–iodine chromophore is discussed.

The stabilisation of alkyl radicals by halogen substitution, and steric effects in molecules of type $-CX_2I$ and $-CX_2Br$, are considered and, by qualitative correlation of radical stability with position of the absorption maximum, relative stabilities for primary, secondary, and tertiary alkyl and halogenoalkyl radicals are proposed.

In connection with work on organic halogen compounds reported elsewhere, the ultra-violet spectra of a variety of iodo- and polyhalogeno-iodo-compounds† have been examined, and the position of the characteristic broad absorption maximum in the 250—350-mμ region has been correlated with structure.

The discussion below refers to solutions of the compounds in light petroleum or to vapour spectra, since the polyhalogeno-iodo-compounds show marked solvent effects (which will be discussed later); if the spectrum is only slightly affected by change of solvent from light petroleum to ethanol, values in both solvents are given.

Alkyl Iodides: $R\cdot[CH_2]_n\cdot I$, $R'R''CH\cdot[CH_2]_m\cdot I$, R_3CI, $I\cdot[CH_2]_x\cdot I$.—The values in Table 1(*a*) show that compounds $R\cdot[CH_2]_n\cdot I$ are characterised by a maximum at 257 mμ (ε 400—500), and a minimum at 210—215 mμ (ε <50). There is only a slight shift of wave-length (2—4 mμ) on change to ethanol, and the continuum is broad with a well-defined maximum.

For $R'R''CH\cdot[CH_2]_m\cdot I$ [Table 1(*b*)], chain branching has but little effect when $m \geqslant 1$, and the spectrum is identical with that of the corresponding compound $R\cdot[CH_2]_n\cdot I$. When $m = 0$, *i.e.*, when the iodine atom is attached to a secondary carbon atom, there is a bathochromic shift of 4 mμ and an increase in intensity of absorption (ε 550—600). *cyclo*Hexyl and *cyclo*pentyl iodide are included as special examples with $m = 0$; steric effects are apparently negligible.

A further bathochromic shift of 7—10 mμ is apparent with solutions of the tertiary iodides R_3CI [Table 1(*c*)], and ε increases to 600—650; a solvent effect of 2—3 mμ is observed on changing from light petroleum to ethanol.

It was difficult to obtain allyl iodide spectroscopically pure, but the spectrum of a freshly distilled sample [Table 1(*d*)] showed a marked increase in absorption relative to a primary alkyl iodide; the absorption maximum is at approximately the position for a tertiary iodide, but ε is enhanced (800—900).

The spectra of the di-iodides $I\cdot[CH_2]_x\cdot I$ [Table 1(*e*)] with $x \geqslant 3$ are very similar to those of $R\cdot[CH_2]_n\cdot I$, with the expected doubled extinction coefficient, and no interaction between the chromophores can be detected. When $x = 2$, however, a shift (3—4 mμ) of the

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* Part II, preceding paper.

† Used in this sense, halogen excludes iodine.

maximum to longer wave-length with increase in intensity of absorption is apparent, indicating chromophore interaction. When $x = 1$, *i.e.*, when two iodine atoms are attached to the same carbon atom, there is a marked change in spectrum, and a long wave-length maximum of high intensity ($\varepsilon > 1000$) appears at 291 mμ in addition to a band at 248 mμ (ε *ca.* 600). In $-\overset{\beta}{C}H_2\cdot\overset{\alpha}{C}H_2I$, replacement of hydrogen by iodine on the α-carbon atom thus has the greatest effect.

TABLE 1.

	Light petroleum solutions				Ethanol solutions			
	$\lambda_{\text{max.}}$	ε	λ_{min}	ε	$\lambda_{\text{max.}}$	ε	$\lambda_{\text{mix.}}$	ε
(*a*) $R\cdot[CH_2]_n\cdot I$.								
MeI ………………	257·5	365	216	30	254·5	360	215	34
	257 *	230	225	30				
EtI ………………	258	435	215	20	255	450	215	28
	258 *	310	215	22				
Pr^nI ………………	258	465	210	15	254·5	485	212	45
Bu^nI ………………	—	—	—	—	255	520	212	45
$CH_3\cdot[CH_2]_4\cdot I$ ……	257·5	500	212	27	255·5	500	212	22
$CH_3\cdot[CH_2]_6\cdot I$ ……	257	300	214	25	254	510	208	33
$CH_3\cdot[CH_2]_7\cdot I$ ……	—	—	—	—	255	500	208	46
$CH_3\cdot[CH_2]_9\cdot I$ ……	—	—	—	—	255	500	208	25
$CH_3\cdot[CH_2]_{11}\cdot I$ ……	—	—	—	—	255	510	209	25
$CH_3\cdot[CH_2]_{15}\cdot I$ ……	257·5	500	210	35	254·5	520	207	70
$Cl\cdot[CH_2]_3\cdot I$ ………	257·5	430	217	60	255	460	214	85
(*b*) $R'R''CH\cdot[CH_2]_m\cdot I$.								
$Me_2CH\cdot[CH_2]_2\cdot I$	257	520	216	27	255	515	217	40
$Me_2CH\cdot CH_2I$ ……	255·5	510	225	130	254	530	210	125
$CHMe_2I$ …………	261	550	219	24	261	565	227	38
CHMeEtI ………	261	555	219	24	260	570	220	26
$CH_3\cdot[CH_2]_5\cdot CHMeI$	—	—	—	—	260	580	223	47
cyclo-$C_6H_{11}I$ ……	260	675	222	68	259	710	223	62
cyclo-C_5H_9I ………	260	540	231	175	257	635	219	375
(*c*) R_3CI.								
Me_3CI ……………	270	590	229	34	268	630	240	150
Me_2EtCI …………	267	620	228	44	265·5	600	239	223
(*d*) *Allylic iodo-compound.*								
$CH_2{:}CH\cdot CH_2I$ ……	271	800	249·5	490	267	900	249·5	700
(*e*) $I\cdot[CH_2]_x\cdot I$.								
x								
1	291·5	1320	260	470	291	1320	260	510
	248	650	235	450	247	670	235	550
2	261	1900	232	725	259·5	1550	232	720
3	258·5	970	223	110	257	1000	224	170
4	257·5	990	217	85	255	1030	217	125
5	256	1020	212	85	255·5	1040	212	95

* Vapour spectra.

Fluorine-containing Organic Iodides containing the $-CH_2I$, $>CHI$, $-CH_2\cdot CHXI$, $-CHY\cdot CHXI$, $>CH\cdot CF_2I$, *or* $-CHF\cdot CF_2I$ group (X *and* Y = *Halogen*).—Fluorine substitution on the γ-carbon atom in $\overset{\gamma}{C}\cdot\overset{\beta}{C}\cdot\overset{\alpha}{C}\cdot I$ causes a well-defined shift of *ca.* 4 mμ, with decrease in intensity relative to a *n*-alkyl iodide [Table 2(*a*)].

Substitution of fluorine on only the β-carbon atom ($CF_3\cdot CH_2I$) causes a similar shift of 4 mμ, *i.e.*, fluorine has about the same influence on the spectrum in the β- or the γ-position. Substitution of bromine on the β-carbon atom produces a further shift to the red of 4—5 mμ [Table 2(*a*)]. The similarity in position of $\lambda_{\text{max.}}$ for vapour and light petroleum solution spectra show that solvent effects in light petroleum are low.

A secondary fluorine-containing alkyl iodide [Table 2(*b*)] shows a bathochromic shift for the $>CHI$ group of 5 mμ with increase in intensity relative to the primary fluorine-containing alkyl iodides of Table 2(*a*), *i.e.*, a structural effect on passing from a primary to a secondary fluorine-containing iodo-compound similar to that found in the alkyl iodide series. For a secondary iodide $\overset{\gamma}{C}{\cdot}\overset{\beta}{C}{\cdot}\overset{\alpha}{C}HMeI$, introduction of fluorine on the γ-carbon causes a distinct shift to the red (6 mμ; cf. MeEtCHI and $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$); further substitution of halogen in the methyl group gives an increasing order of bathochromic shifts $CH_2Cl < CF_3 < CF_2Cl$.

The fluoro-iodo-acids reveal the effect of conjugation of the carbon–iodine chromophore with the CO_2Me group [Table 2(*b*)]. Comparison of $CF_3{\cdot}CH_2{\cdot}CH_2I$ and $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CO_2Me$ shows a bathochromic shift of 23 mμ or, by comparison with a secondary iodide ($CF_3{\cdot}CH_2{\cdot}CHMeI$), a shift of 17 mμ. Comparison of the primary iodide, monoiodoacetic acid [Table 2(*b*)], with ethyl iodide reveals a similar shift to the red of 22 mμ.

TABLE 2.

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
(*a*) $-CH_2I$.					(*c*) $-CH_2{\cdot}CHXI$ (X = halogen).				
$CF_3{\cdot}CH_2{\cdot}CH_2I$	261	375	213	20	$CF_3{\cdot}CH_2{\cdot}CHFI$	262·5	350	218	30
$CF_3{\cdot}CH_2I$	262	265	—	—	$CF_3{\cdot}[CH_2{\cdot}CHF]_2{\cdot}I$	261	410	221	50
	262 *	125	215	5	$CF_3{\cdot}CH_2{\cdot}CHClI$	277·5	430	231	42
$CF_2Br{\cdot}CH_2I$	266	420	239	230					
	266 *	134	238	60	(*d*) $-CHY{\cdot}CHXI$ (X and Y = halogen).				
(*b*) $>CHI$.					$CF_3{\cdot}CHF{\cdot}CHClI$	280	400	229	56
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CF_2Cl$	272	320	227	48					
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CF_3$	270	290	224·5	26	(*e*) $>CH{\cdot}CF_2I$.				
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_2Cl$	267	440	216	80	$CF_3{\cdot}CHMe{\cdot}CF_2I$	270	330	238	120
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	267	430	218	25					
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CO_2Me$	284	370	252	210	(*f*) $-CHF{\cdot}CF_2I$.				
$CF_3{\cdot}[CH_2{\cdot}CH{\cdot}CO_2Me]_2{\cdot}I$	284	350	252	240	$CF_3{\cdot}CHF{\cdot}CF_2I$	269	255	223	50
$CH_2I{\cdot}CO_2H$	279	375	244	175		269 *	190	227	23

* For vapour spectra, otherwise in light petroleum solution.

The spectral properties of a carbon–iodine bond in $\overset{\beta}{C}{\cdot}\overset{\alpha}{C}{-}I$ are markedly affected by replacement of hydrogen on the α- or the β-carbon atom by halogen. Introduction of one fluorine atom on the α-carbon atom has little effect, since $CF_3{\cdot}CH_2{\cdot}CHFI$, $CF_3{\cdot}[CH_2{\cdot}CHF]_2{\cdot}I$, and $CF_3{\cdot}CH_2{\cdot}CH_2I$ have very similar spectra [Table 2(*c*)]. However, chlorine causes a shift to the red of 15 mμ when substituted on the α-carbon atom [Table 2(*c*)]; further introduction of fluorine on the β-carbon atom [$CF_3{\cdot}CHF{\cdot}CHClI$; Table 2(*d*)] then causes a further shift to the red of 2—3 mμ.

The only example yet studied of a compound with both α-hydrogen atoms replaced by fluorine but with no halogen substituent on the β-carbon atom [$CF_3{\cdot}CHMe{\cdot}CF_2I$; Table 2(*e*)] shows a bathochromic shift of 9 mμ relative to $CF_3{\cdot}CH_2{\cdot}CH_2I$ and of 15 mμ relative to *iso*butyl iodide. Replacement of the methyl group by fluorine [Table 2(*f*)] causes but little change.

Polyhalogeno-alkyl Iodides: $-CF_2{\cdot}CF_2I$, $I{\cdot}[CF_2]_n{\cdot}I$, $-CF_2{\cdot}CFClI$, CCl_3I, CBr_3I.—The spectra of a series of compounds containing the $-CF_2{\cdot}CF_2I$ group are shown in Table 3(*a*). Trifluoroiodomethane and pentafluoroiodoethane are too volatile for convenient spectral measurements in solution but the vapour spectra show a broad maximum at 268 mμ, *i.e.*, a bathochromic shift relative to methyl or ethyl iodide of 10 mμ. The spectrum of heptafluoroiodopropane is very similar when measured for the vapour or for the solution. The spectra of the series $CF_3{\cdot}[CF_2]_n{\cdot}I$ are closely similar when $n > 2$, although a slight shift to red is apparent as n changes through 0, 1, 2.

The bathochromic shift on changing from $CF_3{\cdot}CHF{\cdot}CF_2I$ to $CF_3{\cdot}CF_2{\cdot}CF_2I$ is only 2 mμ, and again shows that one or two atoms of hydrogen or fluorine can be interchanged on the β-carbon atom of the $CF_3{\cdot}C{\cdot}C{\cdot}I$ system without major influence on the spectrum.

The spectra of the perfluoro-alkyl di-iodides $I{\cdot}[CF_2]_n{\cdot}I$ with $n > 4$ [Table 3(*b*)] closely resemble those of the $CF_3{\cdot}[CF_2]_n{\cdot}I$ series and show that the chromophoric effects are additive and not transmitted by four or more CF_2 groups. When $n = 2$, however, appreciable interaction occurs, since there is a shift of the maximum to longer wavelength of 10 mμ, with substantial (*ca.* 50%) increase in intensity.

Examination of the series $CF_2X\cdot CF_2I$ [X = H, F, Cl, Br, Table 3(*a*); X = I, Table 3(*b*)] reveals the effect of auxochrome change on the β-carbon atom. The bathochromic shifts are given in Table 4 for vapour spectra, and the marked increase in intensity, particularly when X = I, is noteworthy.

TABLE 3.

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
(*a*) $-CF_2\cdot CF_2I$.				
CF_3I	267·5 *	155	—	—
C_2F_5I	268·5 *	165	224	105
n-C_3F_7I	271	240	215	13
	271 *	195	229	22
n-C_4F_9I	271	270	215	11
n-$C_5F_{11}I$	271	275	213	14
n-$C_6F_{13}I$	271	290	214	18
n-$C_7F_{15}I$	271·5	285	216	20
$CHF_2\cdot CF_2I$	266	255	215	14
	264 *	280	222	28
$CF_2Cl\cdot CF_2I$	272	295	215	17
	269 *	245	220	24
$CF_2Br\cdot CF_2I$	273	385	236	140
	269·5 *	343	237·5	125
(*d*) CX_3I.				
CCl_3I	324	—	—	—
CBr_3I	346	333	—	—

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
(*b*) $I\cdot[CF_2]_n\cdot I$.				
n				
2	282·5	1120	223	104
	280 *	—	228	—
4	272·5	690	220	95
6	272	670	219	55
8	272	690	220	65
(*c*) $-CF_2\cdot CFClI$.				
n in $CF_3\cdot[CF_2\cdot CFCl]_n\cdot I$				
1	286	300	229	28
2	291	345	234	35
3	292	375	244	120
4	292	340	243	100
5	292	390	242	145
$CF_2Cl\cdot CFClI$	283	315	229	26
$CF_2Br\cdot CFClI$	288	375	245	110

* For vapour spectra, otherwise light petroleum solutions.

TABLE 4.

X	H		F		Cl		Br		I
Δλ (mμ)		4		1		1		10	

The large shift to the red (14 mμ) for $-CF_2\cdot CF_2I$ relative to $-CH_2\cdot CH_2I$ was noted above. A further large shift of 15 mμ is obtained by replacement of one α-fluorine atom by chlorine to give $-CF_2\cdot CFClI$ [Table 3(*c*)]. Further changes can be detected when a β-fluorine atom is replaced by chlorine or bromine (cf. $CF_2Cl\cdot CFClI$, $CF_2Br\cdot CFClI$). The effect of increase in chain length on absorption is shown by the series $CF_3\cdot[CF_2\cdot CFCl]_n\cdot I$: change from $n = 1$ to $n = 2$ gives a distinct shift to red of 5 mμ, but further increase in n has little effect; the absorption of the maximum merges with the general absorption of the $CF_2\cdot CFCl$ chain as n increases, until when $n > 6$—10, only an inflection can be observed.

The two polyhalogeno-alkyl iodides containing at least two α-halogen atoms other than fluorine so far studied are trichloro- and tribromo-iodomethane. Very large bathochromic shifts are observed: 53 and 75 mμ respectively relative to a perfluoroalkyl iodide such as trifluoroiodomethane and heptafluoroiodopropane, or 67 and 89 mμ relative to methyl or ethyl iodide.

The changes in wave-length on replacement of α- or β-hydrogen in $-\overset{\beta}{CH_2}\cdot\overset{\alpha}{CH_2}I$ are summarised in Table 5. These large changes are very valuable in determination of constitution of unknown polyhalogeno-organic iodides.

TABLE 5.

α-Substituents	HH	HH	HF	HH	FF	FF	HCl	HCl	FCl
β-Substituents	HH	FF	HH	FBr	HF	FF	HH	HF	FF
$\lambda_{max.}$	258	262	262	266	269	271	278	280	286

DISCUSSION

The ultra-violet absorption spectra of non-halogen-substituted organic iodo-compounds have been studied. Mulliken (*J. Chem. Phys.*, 1940, **8**, 382; *Phys. Review*, 1935, **47**, 413) suggested that the ultra-violet continua of the hydrogen and alkyl halides are $N \longrightarrow Q$ transitions. In hydrogen iodide or methyl iodide the long-wave-length continuum extends at least far enough to indicate that at least a small fraction of the molecules dissociate to give a $^2P_{1\frac{1}{2}}$ iodine atom. Porret and Goodeve (*Proc. Roy. Soc.*, 1938, *A*, **165**, 31) concluded that for methyl iodide the *A* band leads to dissociation to give an excited $^2P_{\frac{1}{2}}$ iodine atom and a normal unexcited methyl free radical, whereas absorption of light in the *B* band gives products both of which are unexcited.

In considering the bathochromic shifts in the 250—350-mμ region outlined above, factors which may be involved are (*a*) the effect of the substituent halogen as an auxochrome, (*b*) the resonance stabilisation of a radical $C{-}C\cdot$ derived from $C{-}CI$, and (*c*) steric effects. These factors will be considered separately although clearly all three play a part, and are inter-related.

(a) *Auxochromic Effect of Halogen.*—A chromophore is usually defined as a covalently unsaturated centre containing π-electrons, but for purposes of discussion the iodine atom will be regarded as a chromophore, and the substituents as auxochromes. Auxochromes produce increases in $\lambda_{max.}$ and in $\varepsilon_{max.}$, and are most effective when they are covalently unsaturated or contain unshared electron pairs.

The ultra-violet spectra of trichlorofluoromethane and dichlorodifluoromethane lie at shorter wave-length than those of chloroform or methylene chloride respectively, so that replacement of hydrogen by fluorine here causes a shift of absorption to the blue (Lacher, Hummell, Bohmfalk, and Park, *J. Amer. Chem. Soc.*, 1950, **72**, 5486). In substituted ethylenes, however, replacement of hydrogen by fluorine causes a shift to the red, presumably by increase in resonance, with structures such as $CHCl{:}CHF \longleftrightarrow \overset{-}{C}HCl{\cdot}CH{:}\overset{+}{F}$ increasing with the number of halogens attached directly to the double bond.

Consider now the halogen-substituted organic iodides. The contribution of non-classical resonance forms in a molecule is commonly considered to be greater in the excited than in the ground state; decrease in their energy content decreases the energy of the excited state more than that of the ground state, and this produces a shift to the red of the wave-length concerned with the electronic transition. In the undissociated molecule of the iodo-compound, direct interaction between the unshared electron pairs of iodine and a substituent X on the α-, β- or γ-carbon atom is possible [*e.g.*, $RCX_2{\cdot}CX_2I \longleftrightarrow X^-\ RC({:}\overset{+}{X}){\cdot}CX({:}\overset{+}{I})\ X^-$], and hyperconjugation effects must also be considered (*e.g.*, $RCX_2{\cdot}CH_2I \longleftrightarrow X^-\ CRX{:}CHI\ H^+$; $CF_3{\cdot}CH_2{\cdot}CH_2I \longleftrightarrow F^-\ CF_2{:}CH{\cdot}CH_2I\ H^+ \longleftrightarrow F^-\ CF_2{:}\overset{H^+}{CH}{\cdot}\overset{H^+}{CH}{:}I^+$). If such effects played a *major* part in determining the very large shifts observed in the spectra, it would follow from the data that the auxochromic effect for a halogen, X, on the α-carbon atom increased in the order $X = H < F < Cl < Br < I$, *i.e.*, with descent of the Periodic Group, and increased availability of the lone pairs of X (cf. Ramart-Lucas and co-workers; references given by Braude, *J.*, 1949, 1902). The above effects are, however, considered to be less important than those discussed in (b) below.

Until relatively recently it was considered that the absorption due to chromophores separated by one or more CH_2 groups was additive, but there is increasing evidence that this is not completely valid (Ramart-Lucas *et al.*, *loc. cit.*; Braude, *loc. cit.*; Hillmer and Paersch, *Z. physikal. Chem.*, 1932, **161**, 46). Examination of the series $I{\cdot}[CF_2]_n{\cdot}I$ and $I{\cdot}[CH_2]_n{\cdot}I$ shows that interaction between the chromophores occurs when $n = 2$. The bathochromic shift is larger with the fluorine compound, and this can be attributed to the greater auxochromic effect of fluorine relative to hydrogen in the undissociated molecule, or to a difference in radical stability (see below).

(b) *Relative Stabilities of Radicals.*—If it is accepted that the absorption of light by the halogeno-alkyl iodide in the region of peak continuous absorption brings about dissociation of the molecule into a radical and an iodine atom $\cdot C{\cdot}C{\cdot}I \longrightarrow \cdot C{\cdot}C\cdot + \cdot I$, the change in position of absorption maximum can be correlated with the C–I bond dissociation energy, and with the relative stabilities of the $\cdot C{\cdot}C\cdot$ radicals. It is suggested that the stability of the $\cdot C{\cdot}C\cdot$ radical is the most important factor involved in determining the position of the absorption maximum; the more stable the radical, the further into the red will be the absorption maximum of its iodide.

In the alkyl iodides, RI, the bathochromic shifts run parallel to the ionisation potentials (I.P., ev) of the alkyl radical, the dissociation energy of the carbon–iodine bond, R–I (kcal./mole), the resonance energies of the hydrocarbon radicals (R.E., kcal./mole, calculated and observed), and the stabilisation energies (S.E., kcal./mole) of the radicals relative to the methyl radical. These values are shown in Table 6 and are taken from papers by Baughan, M. G. Evans, and Polanyi, Baughan and Polanyi, Butler and Polanyi, Butler, Mandel, and Polanyi, and by A. G. Evans (*Trans. Faraday Soc.*, 1941, **37**, 377; 1943, **39**, 19; 1944, **40**, 384; 1945, **41**, 298; 1946, **42**, 719); carbon–bromine and carbon–hydrogen bond dissociation energies are included.

TABLE 6.

	Me	Et	Pr^n	Pr^i	Bu^n	Bu^t	$CH_2{:}CH{\cdot}CH_2$
I.P.	13·60	10·07	8·67	7·77	—	7·19	—
R–I	54·0	52·0	50·0	46·5	49·0	45·0	39
R.E., calc.	0	7·05	8·6	14·1	—	21·1	—
obs.	0	7·2	8·1	12·6	—	16·7	—
S.E.	0	2	4	7·5	5	9	—
R–Br	68·5	67·0	64·5	61·0	63·5	60·0	—
R–H	102·5	97·5	95·0	89·0	94·0	86·0	—
$\lambda_{max.}$ (mμ)	257	258	258	261	—	270	271

Resonance stabilisation of alkyl radicals can occur by hyperconjugation [*e.g.*, $H{\cdot}CH_2{\cdot}\dot{C}Me_2 \longleftrightarrow H{\cdot}\ CH_2{:}CMe_2$], and in the *tert.*-butyl, *iso*propyl, and *n*-propyl radicals, for example, nine, six, and two C–H bonds respectively are available for this (Wheland, *J. Chem. Phys.*, 1934, **2**, 474). Radical stabilisation thus decreases in that order, and this is reflected in the spectra of the corresponding iodides. Resonance stabilisation of radicals substituted by halogen on the α- or β-carbon atom can be visualised *e.g.* :

$$\cdot CX_2{\cdot}\dot{C}X_2 \longleftrightarrow \cdot CX_2{\cdot}\overset{\cdot +}{C}X \quad X^- \longleftrightarrow \cdot CX_2{\cdot}\ddot{C}X \quad \dot{X}$$

$$\cdot CX_2{\cdot}\dot{C}X{-}\underset{\cdot\cdot}{\ddot{X}}{:} \longleftrightarrow \cdot CX_2{\cdot}\bar{C}X{-}\underset{\cdot\cdot}{\overset{\cdot +}{X}}{:} \qquad\qquad \cdot CX_2{\cdot}\dot{C}X_2 \longleftrightarrow \dot{X} \quad \cdot CX{:}CX_2$$

The importance of β-halogen in stabilising the radical is shown by the series $CF_2X{\cdot}CF_2I$ (X = H, F, Cl, Br, I) considered above.

The greater chromophore interaction in $ICX_2{\cdot}CX_2I$ when X = F than when X = H can thus be explained, since the $I{\cdot}CF_2{\cdot}CF_2{\cdot}$ radical will be more stable than the $I{\cdot}CH_2{\cdot}CH_2{\cdot}$ radical. Similarly the marked difference in the spectra of methylene iodide and ethylene di-iodide can be ascribed to the greater stability of the $\cdot CH_2I$ compared with the $CH_2I{\cdot}CH_2{\cdot}$ radical. The slight shift to red in the spectra of the series CF_3I, C_2F_5I, C_3F_7I can also be attributed to increased radical stabilisation by the β- or γ-fluorine atoms.

For halogen substitution on the α-carbon atom, the shifts to red increase in the order H < F < Cl < I and with the number of α-halogen atoms. A sequence of decreasing radical stability is thus obtained, shown in Table 7, reading down each column and following-on in columns from left to right.

TABLE 7. *Radicals of type* $\geqslant C{\cdot}C{\cdot}$.

$CBr_3{\cdot}$
$CCl_3{\cdot}$
$CF_3{\cdot}[CF_2{\cdot}CFCl]_{2-5}{\cdot}$
$CF_2Br{\cdot}CFCl{\cdot}$
$CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}$
$CF_2Cl{\cdot}CFCl{\cdot}$
$CF_3{\cdot}CHF{\cdot}CHCl{\cdot}$
$CF_3{\cdot}CH_2{\cdot}CHCl{\cdot}$
$CF_2Br{\cdot}CF_2{\cdot}$
$CF_2Cl{\cdot}CF_2{\cdot}$
$CF_3{\cdot}[CF_2]_n{\cdot}$
$CF_3{\cdot}CHF{\cdot}CF_2{\cdot}$
$CHF_2{\cdot}CF_2{\cdot}$
$CF_3{\cdot}CH_2{\cdot}CHF{\cdot}$

Stabilisation by β- or γ-halogen is shown in the secondary radicals $CF_3{\cdot}CH_2{\cdot}\dot{C}HMe$ and $CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2Cl$, $CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CF_3$, and $CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CF_2Cl$. Stabilisation of a secondary radical by CO_2Me is greater than that by a saturated alkyl or halogeno-alkyl group (cf. $CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me$ and $CF_3{\cdot}CH_2{\cdot}\dot{C}HMe$ etc.).

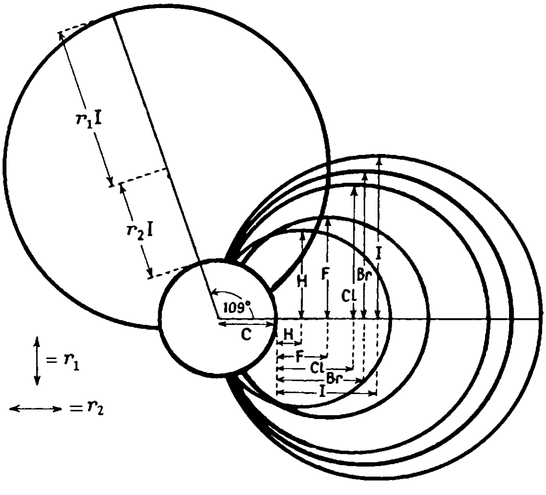
The sequence of decreasing stabilities for alkyl radicals substituted by halogen on the β- or γ-carbon atom is shown in Table 8.

The correlation between absorption maximum and radical stability is, of course, only qualitative, and assumes that the differences in the vibrational energies of the radicals are not of major importance and that changes in the absorption maximum are due mainly to changes in the resonance energies of the radicals. The relative stabilities of radicals estimated from the ultra-violet spectroscopic data run parallel, however, to the data on radical stability obtained from chemical evidence which is being presented in another series (Haszeldine, *J.*, 1952, 2504; Haszeldine and Steele, *Chem. and Ind.*, 1951, 684; *J.*, 1953, 1199 *et seq.*).

TABLE 8. *Relative radical stabilities when no halogen is present on the α-carbon atom.*

$\geqslant C{-}CH_2\cdot$	$(\geqslant C)_2CH\cdot$	$(\geqslant C)_3C\cdot$
$\cdot CH_2{\cdot}CO_2H$	$CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me$	$\cdot CMe_3$
$CH_2{:}CH{\cdot}CH_2\cdot$	$CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CF_2Cl$	$\cdot CMe_2Et$
$CF_2Br{\cdot}CH_2\cdot$	$CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CF_3$	
$CF_3{\cdot}CH_2\cdot$	$CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2Cl$	
$CF_3{\cdot}CH_2{\cdot}CH_2\cdot$	$\cdot CHMe_2$	
$CH_3{\cdot}[CH_2]_n\cdot$	$\cdot CHMeEt$	
	cyclo-$C_6H_{11}\cdot$	
	cyclo-$C_5H_9\cdot$	

In assessing the relative importance of the effects so far considered, the resonance effects in the *undissociated* molecule could often lead to an increase in carbon–iodine bond strength, and consequently could offset to some extent the decrease in bond strength caused by radical stability. That the effects on the undissociated molecule are of minor importance relatively to the stability of the radical R may be judged from the R–H dissociation energies (Table 6). The trend is the same as for the R–Br and R–I dissociation energies, yet only small resonance effects are to be expected in the C–H bond.



	H	F	Cl	Br	I	C
van der Waals radii (r_1)	1·2	1·35	1·80	1·95	2·15	—
Covalent radii (r_2)	0·3	0·64	0·99	1·14	1·33	0·77

(c) *Steric Effects.*—In substitution of halogen for hydrogen on the α-carbon atom, steric effects might be expected to play a part as the halogen atom increases in size, since some stabilisation of the radicals given in Table 7 will occur by the change from the tetrahedral angle of $-CX_2$ in the $-CX_2I$ molecule to the (presumably) planar $-CX_2\cdot$ radical, by virtue of the steric interaction between X and I when X = Cl, Br, I (see below), which will be lost during dissociation, with consequent decrease of the repulsion energy. The interaction between X and I in a substituted alkyl iodide can be seen from the Figure, where the van der Waals and covalent radii have been taken from Pauling (" Nature of the Chemical Bond," Cornell Univ. Press, 1945). When X in $-CHXI$ is hydrogen or fluorine, only slight overlap occurs with the iodine atom, but when X = Cl, Br, or I, the steric interaction is appreciable. For $-CX_2I$ or CX_3I the steric effect would be increased further.

If the steric effect were of major importance it might be expected that it would be detectable in the carbon–iodine bond lengths. Although little is yet known about the polyhalogeno-iodo-compounds discussed above, the carbon–iodine bond length in trifluoroiodomethane (2·16 Å; Sheridan and Gordy, *Phys. Review*, 1950, **77**, 292) is close to that in methyl iodide (2·13 Å), and since little variation is found in bond length in the series CH_3I, CH_2I_2 (2·12 Å), CHI_3 (2·12 Å) and CI_4 (2·12 Å) (Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46, give relevant references), it can be predicted that the carbon–iodine bond length will not vary greatly in compounds $-CX_2I$ ($X = F, Cl, Br, I$).

Butler, Mandel, and Polanyi (*loc. cit.*) noted a decrease in carbon–iodine bond strength when halogen is present on the α- or β-carbon atom. There is some doubt about the precise accuracy of these bond strengths: $CHCl_2I$, 42·4; $CHBr_2I$, 41·4; $CHI_2{-}I$, 37; $CH_2Cl{\cdot}CH_2I$, 45·9 kcal./mole (cf. alkyl iodides, Table 6), but the general trend is clear.

It is thus concluded that the resonance stabilisation of the radical is of greater importance and it can be predicted that the carbon–iodine bond dissociation energies of the compounds discussed in this paper will decrease in the orders given by radical stabilities shown in Tables 7 and 8.

Szwarc and Sehon (*J. Chem. Phys.*, 1951, **19**, 656) have shown by pyrolysis studies that the carbon–bromine bond dissociation energy decreases markedly in the several series, CH_3Br, CF_3Br; CH_2ClBr, $CHCl_2Br$, CCl_3Br; CH_2Br_2, $CHBr_3$, CBr_4, and point out that the available structural data do not reveal any significant change in carbon–bromine bond lengths. These facts, the decrease in bond dissociation energy on passing from $CH_3{-}H$ to $CCl_3{-}H$ (which can hardly be attributed to steric repulsion), the decrease in the carbon–carbon bond strength in chloral and bromal relative to acetaldehyde (Pritchard and Skinner, *J.*, 1950, 1928), and the difference in carbon–chlorine bond energies (10 kcal./mole) for methyl chloride and carbon tetrachloride, can also be correlated with the resonance stabilisation of the CX_3 radical.

The extent to which the assumptions made in the above correlations of radical stability and absorption spectra are justified will be seen only when further physical data (bond lengths and dissociation energies, ionisation potentials, etc.) are available. Until such a time the correlations give a means of estimating the relative stabilities of unknown free radicals, and their application in this connection will be described in another series.

EXPERIMENTAL

The alkyl iodides were commercial samples purified by distillation. The halogen-containing iodo-compounds were prepared in this laboratory by the author (*J.*, 1949, 2856 *et seq.*; *J.*, 1951, 584 *et seq.*; *J.*, 1952, 584 *et seq.*; *J.*, 1952, 4423), or by Mr. B. R. Steele (Haszeldine and Steele, *J.*, 1953, 1199), to whom due acknowledgment is made.

The spectra were usually determined in duplicate, maxima being read to 0·25 mμ, and average values are reported. Beckman DU and Unicam Spectrophotometers were used, with 1-, 4-, and 10-cm. silica cells for liquids and 4- and 10-cm. silica cells for vapours. The extinction coefficient (ε) for the vapour was calculated from $\varepsilon = 760 \times 22{\cdot}4 \times DT/273\,lp$ where D = optical density, T = temperature (K), l = cell length (cm.), and p = pressure of vapour (mm.), and is liable to appreciable error when pressures <10 mm. were required in a 4-cm. cell; pressures were read to $\pm 0{\cdot}5$ mm.

The light petroleum had b. p. 60—80° and was purified by treatment with fuming sulphuric acid and alkaline permanganate, and showed 43% transmission at 210 mμ. Ethanol was obtained by drying 95% ethanol, and showed 42% transmission at 210 mμ.

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