

LXXXIV.—*Studies of Valency. Part VI. General and Selective Absorption of Halogen Derivatives of Methane. The Origin of General Absorption.*

By THOMAS MARTIN LOWRY and ROSE RACHEL SASS.

1. *Purpose of the Experiments.*

(a) THE observations described in the preceding paper created the impression that, just as the selective absorption of the ketones can be attributed to some form of polar activation or incipient ionisation of the *double* bond of the carbonyl group, so their general absorption might be attributed to the activation or incipient ionisation of a *single* bond, *e.g.*, between carbon and hydrogen or between carbon and a halogen. In camphor itself, the single bonds appear to be so strong that they can only be activated by, and can therefore only absorb, light of very high frequency; the corresponding maximum of "general" absorption is therefore so remote that even the foot of the band cannot be detected at a wave-length of 2400 Å.U. On the other hand, in $\alpha\alpha'$ -dibromocamphor (where the bonds between carbon and bromine are so weak that the compound acts as an oxidising agent) the general absorption is so strong that it almost covers up the selective absorption. The increase of absorptive power is indeed so rapid as to indicate that it must reach a maximum at a wave-length not far beyond the limits of our experiments. We therefore formed the opinion that, just as the double bond of the carbonyl group produces a characteristic absorption at about 2700 Å.U., so the single bond between carbon and bromine might have a characteristic absorption at some shorter wave-length; and that just as the maximum of the ketonic band of camphor can be shifted to the extent of some 350 Å.U. under the influence of contigu-

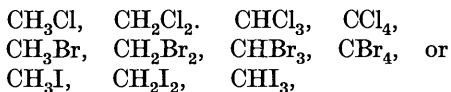
ous negative atoms, so the band of general absorption might be shifted through some hundreds of Ångström units in the direction of longer wave-lengths, as a result of the weakening of the single bond under the influence of contiguous negative atoms. This view, which served to explain the close analogy between the influence of the halogens on the selective and on the general absorption of the halogen derivatives of camphor, had the advantage that it could be tested by direct experiments on a much simpler series of compounds, and in this way it led to the experiments on the general and selective absorption of the halogen derivatives of methane, which form the subject of the present paper.

(b) In the experiments on general absorption advantage was taken of the fact that the introduction, first of the sector-photometer and then of the ultra-violet spectrophotometer, has made it possible to measure the molecular extinction coefficients of a solution in the ultra-violet region, and so to make an exact quantitative comparison of the general absorptions of a series of substances. Previous observations, in which the older qualitative methods were used (Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1183; Massol and Faucon, *Compt. rend.*, 1917, **164**, 813), had given numerical values only for the characteristic wave-lengths of the iodo-compounds, which are the only ones to show a selective absorption in the accessible ultra-violet region.

(c) On the supposition that a marked general absorption could be produced by the incipient ionisation of a weak single bond between carbon and a halogen we anticipated :

(i) That the general absorption would increase progressively in the series CH_3F , CH_3Cl , CH_3Br , CH_3I , since the bond between carbon and fluorine is known to be extremely strong, whilst the bond between carbon and iodine is so weak that it can be ionised quite readily, *e.g.*, in the formation of a methiodide from an alkyl iodide and a nitrogenous base, or in the interaction between methyl iodide and silver nitrate in the Zeisel method of estimating methoxyl groups.

(ii) That the general absorption would increase in series such as :



since the accumulation of negative atoms would tend to weaken the bond between the carbon and the halogen, and so bring the crest of the band nearer to the accessible ultra-violet region. These anticipations have been fulfilled, as can be seen from the following summary of the experimental results.

2. Summary of Experimental Results.

The experimental data in reference to the halogen derivatives of methane are shown in Fig. 1, and are summarised in Table I.

TABLE I.

Absorption Spectra of Alcoholic Solutions of Halogen Derivatives of Methane.

Formula of substance.	Wave-lengths for integral values of $\log \epsilon$.				
	$\log \epsilon = 0.0$.	1.0.	2.0.	3.0.	4.0.
CHCl ₃	2320				
CCl ₄	2700	2500	2360		
CH ₃ Br	2640	2360			
CH ₂ Br ₂	2900	2700	2560	2300	
CHBr ₃	—	3000	2900	2400	
CBr ₄	—	3600	3300	2600	
CH ₃ I	—	3000	2900		
CH ₂ I ₂	3900	3720	3600	3200	
CHI ₃	—	—	4500	3900	2200

Position of maxima.

	(a) Lowry and Sass. Å.U.	(b) Crymble, Stewart, and Wright.	(c) Massol and Faucon.
I ₂	$\left. \begin{array}{l} \log \epsilon = 2.7 \text{ at } 4770 \\ \log \epsilon = 3.3 \text{ at } 2900 \end{array} \right\}$	4800 — 3030 —	4700 3500 2880 —
CH ₃ I	$\log \epsilon = 2.7 \text{ at } 2600$	— — — 2570	— — — 2500
CH ₂ I ₂	$\log \epsilon = 3.1 \text{ at } 2960$	— — — 3030 —	— — — 2880 —
CHI ₃	$\log \epsilon = 3.5 \text{ at } 3450, 2940$	— 3570 3030 —	— 3350 2880 —
Cl ₄			— 3450 2880 —
KI ₃	$\log \epsilon = 3.9 \text{ at } 3550, 2900$	— 3570 3030 —	

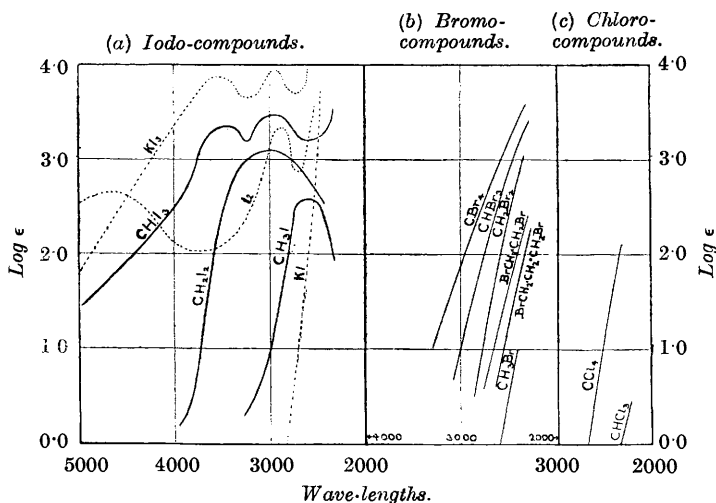
(i) The data recorded above show that the absorptive power of the chlorine compounds is very slight. Thus even chloroform only produces a measurable absorption at high concentrations and short wave-lengths, *e.g.*, the value of $\log \epsilon$ at 2400 Å.U. is only -1.0. Carbon tetrachloride, however, develops a marked absorptive power at 2700 Å.U., where $\log \epsilon = 0.0$, and gives rise to a well-defined curve of general absorption (Fig. 1, *c*).

(ii) Just as $\alpha\alpha'$ -dibromocamphor gives rise to a much greater general absorption than $\alpha\alpha'$ -dichlorocamphor, so the bromo-derivatives of methane are much more absorptive than the corresponding chloro-compounds. Thus methyl bromide is nearly as absorptive as carbon tetrachloride; and the general absorption becomes increasingly strong in the series CH₃Br, CH₂Br₂, CHBr₃, CBr₄ (Fig. 1, *b*), until in the last compound the foot of the band begins to approach the violet end of the visible spectrum. It is noteworthy that the general absorption of β -bromocamphor, where the distance between the bromine atom and the oxygen of the ketonic group is sufficiently great to prevent the two negative radicals from influencing each other to any large extent, is very similar to that of methyl

bromide; thus the molecular extinction coefficient, which rises to $\log \epsilon = 1.1$ at 2500 Å.U. in β -bromocamphor, reaches the same value at 2400 Å.U. in methyl bromide. This result is in harmony with the view that in both cases the weak bond which gives rise to the general absorption is the bond between carbon and bromine.

(iii) Conclusive evidence that the general absorption of the halogen derivatives of methane is due to a band of short wave-length, and that this wave-length can be increased by weakening the bond which links the halogen to the carbon, was obtained from the study of the iodides of the series CH_3I , CH_2I_2 , CHI_3 . In this series, although we only expected to find an enhanced "general absorption,"

FIG. 1.



Absorption spectra of halogen derivatives of methane.

definite bands are in fact developed (Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1183; Massol and Faucon, *Compt. rend.*, 1917, **164**, 813). Up to a certain point the extinction coefficients of methyl iodide are almost identical with those of bromoform, *viz.*, $\log \epsilon = 1.0$ at 3000 Å.U. and 2.0 at 2800 Å.U.; but the curve for the iodide, instead of rising progressively to $\log \epsilon = 3.0$ at 2400 Å.U., reaches a maximum, $\log \epsilon = 2.6$ at 2600 Å.U., and then falls again to $\log \epsilon = 2.0$ at 2327 Å.U. (Fig. 1, a).

(iv) The absorption band, which thus makes its appearance for the first time in methyl iodide, develops progressively in the series CH_3I , CH_2I_2 , CHI_3 , until, in the case of iodoform, the foot of the band extends half-way across the visible spectrum. The visible colour of this compound, however, unlike that of *p*-benzo-

quinone, is still due to a selective absorption in the ultra-violet. The appearance of a general absorption beyond the band is a novel feature, which was seen for the first time in iodoform ; but no great significance appears to attach to it, since it merely suggests the existence of a reserve of bands of shorter wave-length, which can be shifted towards the accessible ultra violet region by the accumulation of negative atoms.

(v) The most interesting feature of the iodoform curve is the division of the crest of the band into two maxima, $\log \epsilon = 3.5$ at 3450 and 2940 Å.U., separated by a shallow minimum. It is not certain, however, whether even this should be regarded as an entirely abrupt development, since the band becomes progressively wider on passing from methyl iodide to methylene iodide and then to iodoform, although a careful examination failed to reveal any similar subdivision of the crest of the band in methylene iodide. The general form and position of the curves certainly suggest that we are dealing with the same band throughout, and that, although the second and third atoms of iodine may reinforce and develop the band, they are not needed in order to initiate it. It is, however, equally clear that the striking development of the band in methylene iodide and in iodoform reveals the influence of certain novel factors, which are not present in the simple alkyl iodides and are sufficiently important to form the subject of a separate discussion.

3. *Absorption Spectra of Iodine, Potassium Iodide, and Potassium Tri-iodide.*

In view of the qualitative comparisons which earlier workers have made between the absorption spectra of the iodo-derivatives of methane and those of solutions of iodine in alcohol and in aqueous potassium iodide, we have thought it desirable to include these solutions in our series of quantitative measurements. The results are shown in Fig. 1, *a*, together with a curve of general absorption of potassium iodide. They have also been included in Table 1. The general conclusions are as follows :

(a) Although visible colour is developed more readily in compounds of iodine than in those of the other halogens, so many colourless compounds of iodine are known that one must suppose its chromophoric properties to be like those of oxygen, which depend on the mode of combination of the element, rather than like those of chromium or cobalt, where the elements seem to be almost incapable of yielding colourless derivatives. It is, therefore, very doubtful whether Massol and Faucon were justified, after recording the existence of three bands at 4700, 3500, and 2880 Å.U. in an alcoholic solution of iodine, in identifying these same bands in the

absorption spectra of the iodo-derivatives of methane. A theoretical objection to this method of treatment is found in the fact that, according to the conventional view, the atoms of iodine in an alcoholic solution are linked only by iodine-iodine bonds, whilst in the iodo-derivatives of methane all the atoms of iodine are held by carbon-iodine bonds. There is, therefore, no obvious basis for an identity of characteristic frequency, unless it arises from the inherent properties of the iodine atom or molecule; and the former alternative at least is ruled out by the fact that the frequency of the band in methyl iodide (2600 Å.U.) is so far different from that of the iodine bands that Massol and Faucon did not attempt any identification in this case. On the experimental side, this identification is limited by the fact that the band at 4800 Å.U., which imparts a visible colour to the alcoholic solution of iodine, is not reproduced in any of the derivatives, the colour of which is invariably due to the extension into the visible spectrum of the foot of an ultra-violet band. The second band at 3500 Å.U. can also be omitted from the discussion, since it is not recorded by Crymble, Stewart, and Wright, and no trace of it can be found on the quantitative curves which we have plotted in Fig. 1, *a*. It is therefore only the third band, at 2900 Å.U., that is available for the purpose of identification.

A band at 2900 Å.U. occurs in the absorption spectrum of iodine in aqueous potassium iodide, as well as of iodine in alcohol; but it is accompanied by a second band at 3500 Å.U., which is of much shorter wave-length than the visible band at 4770 Å.U. of the alcoholic solution. It is, therefore, impossible to attribute the selective absorption at 2900 Å.U. to the presence of free iodine in the aqueous iodide solution. If, therefore, the band is really the same in the two cases, it must be ascribed to some identical type of bond between the atoms of iodine, a conclusion against which no theoretical objection can be urged.

We have already seen that the wave-length of the band in methyl iodide is less than in elementary iodine; but in methylene iodide it is approximately equal to it. Since ethylene iodide gives a band of the same frequency as methyl iodide, although of rather greater intensity, Crymble, Stewart, and Wright attribute the methylene iodide band to the juxtaposition of two atoms of iodine in the same molecule, *i.e.*, they suggest that $\text{I}-\overset{\text{I}}{\underset{|}{\text{C}}}-\text{I}$ gives the same band as $\text{I}-\text{I}$, but that $\text{I}-\overset{\text{I}}{\underset{|}{\text{C}}}-\overset{\text{I}}{\underset{|}{\text{C}}}-\text{I}$ behaves like $-\overset{\text{I}}{\underset{|}{\text{C}}}-\text{I}$. Our own measurements indicate, however, that the band in methylene iodide reaches a maximum at 2960 Å.U., and is definitely of lower frequency than the iodine band at 2900 Å.U. It is, moreover, quite different in appearance, and could only be identified with the iodine band on the

assumption that it was really a double band, of which one component was identical with one of the bands of elementary iodine. It is therefore only in iodoform that any real identification is possible.*

(b) Whilst Massol and Faucon attempt (perhaps somewhat unreasonably) to identify the bands of elementary iodine with those of its derivatives, Crymble, Stewart, and Wright associate together the spectra of potassium tri-iodide and iodoform. This identification appeared at first sight to be at least equally unreasonable, since the colour of the tri-iodide is always attributed to the negative ion I_3^- , which (like iodine itself) can only contain iodine-iodine bonds, whilst in iodoform the three atoms of iodine have always been regarded as linked independently to a central atom of carbon. Before accepting so remote an identification, therefore, we regarded it as essential to plot quantitative absorption curves for the two substances. The result has been to establish a degree of resemblance which is even closer than that shown by the qualitative curves. Thus (i) each spectrum includes two bands, and only two, in the accessible range of the spectrum.

(ii) The foot of the band of longer wave-length extends in each case into the visible spectrum and gives rise to visible colour.

(iii) In the same way, the band of shorter wave-length is followed almost immediately by a strong general absorption.

(iv) The persistence of the band of shorter wave-length is thereby limited to about 0.25 in both compounds.

(v) The two crests are of similar wave-length, namely, 3500 and 2900 Å.U. for potassium tri-iodide and 3450 and 2940 for iodoform.

(vi) In both cases the two crests are of equal intensity.

(vii) They are also separated by a shallow minimum which limits the persistence of the band of longer wave-length to about 0.25 in both cases.

(viii) Finally, the intensities of the bands on the absolute scale, although not identical, are almost the same in the two cases, namely $\log \epsilon = 3.5$ for iodoform and 3.9 for potassium tri-iodide.

These eight points of agreement, which appear to us to be far beyond the possibilities of a mere coincidence, point to the existence of some definite similarity of structure between the two compounds. No such similarity is indicated, however, by any of the conventional formulæ. Thus, the most plausible formula for the I_3^- ion is perhaps

* Carbon tetraiodide is so unstable in alcoholic solution that it was not investigated by Crymble, Stewart, and Wright, nor by ourselves; we cannot therefore say what weight should be attached to the statement of Massol and Faucon that it gives the same bands as iodoform.

one which represents it as the analogue of the HF_2^- ion, *e.g.*, $\overset{+}{\text{K}}[\overset{-}{\text{I}}\overset{+}{\text{I}}\overset{-}{\text{I}}]$ (compare $\overset{+}{\text{K}}[\overset{-}{\text{F}}\overset{+}{\text{F}}\overset{-}{\text{F}}]$); but the formula of iodoform cannot be made to conform to this pattern, since it has always been assumed that the three atoms of iodine are linked directly to carbon and not to one another. The stricter rules of the electronic theory of valency forbid, in an even more emphatic manner than before, any tampering with these formulæ, *e.g.*, by assigning a higher covalency to iodine, and thus superposing a ring structure on the traditional tetrahedron. We can therefore only conclude that our present theories of valency are inadequate to express certain features of molecular structure which may become of predominant importance in cases such as that now under consideration. It appears, indeed, as if both molecules were dominated by a cluster or ring of three contiguous iodine atoms, just as (according to W. L. Bragg's recent determinations) the crystal structure of most of the oxy-salts and of many of the metallic oxides is dominated by clusters of contiguous oxygen atoms, leaving the co-ordinating atom to occupy a mere cavity between the oxygens. This picture, from which all traces of the bonds between the atoms have been erased, is admittedly unconventional, but it appears to be the only one which gives any clue to the origin of the amazing similarity of the two absorption spectra.

4. Summary and Conclusions.

(a) The general absorption of the chloro- and bromo-derivatives of methane increases progressively from chloroform to carbon tetrabromide. Methyl iodide, however, produces a band which becomes more intense and of longer wave-length on passing to methylene iodide and to iodoform, where the crest of the band is finally resolved into two maxima.

(b) The ultra-violet absorption band of methyl iodide cannot be explained by any of the older theories of colour, but finds a simple explanation in the relative weakness of the bond between carbon and iodine, and the consequent smallness of the quanta of energy that are required to activate it. The suggestion is therefore made that the general absorption of the halogen derivatives of camphor and of methane, and the intensification of the general absorption by an accumulation of contiguous negative atoms, is due to the activation or incipient ionisation of a single bond, just as the ketonic band of camphor may be attributed to the activation or incipient ionisation of the double bond of the carbonyl group.

(c) There is a close resemblance between the absorption spectra of iodoform and of potassium tri-iodide, which is not accounted for by the formulæ commonly assigned to these compounds, and appears

to be beyond the scope of our present theories of valency. It may, however, be due to the presence of three contiguous atoms of iodine in the space models of the two compounds.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[*Received, November 19th, 1925.*]
