LXXXIII.—*Studies of Valency. Part V. Absorption Spectra of Halogen and Sulphonic Derivatives of Camphor: Origin of the Ketonic Absorption Band.*

By Thomas Martin Lowry and Glyn Owen.

1. *Scope of the Work.*

The preceding paper on absorption spectra (Lowry and French, "Studies of Valency," Part IV, J., 1924, **125**, 1921) dealt with the selective absorption of camphor and of some of its conjugated derivatives. Its principal feature was an experimental proof of the existence in camphorquinone and in methylenecamphor of two different types of conjugation, corresponding perhaps with the presence of "crossed" and of "concordant" polarities in these two compounds. In the present paper, these experiments have been extended to a series of halogen derivatives of camphor, for which data were required in connexion with measurements of rotatory dispersion (J., 1925, **127**, 1260). The absorption spectra of some of these compounds had been plotted previously by one of us (Lowry and Desch, J., 1909, **95**, 807), but only by the old qualitative method of recording the last line transmitted through a given thickness of solution in sufficient intensity to leave a record on the photographic plate. These observations were therefore not sufficiently exact for a quantitative comparison, the ultimate result of which was to reveal the existence of a small discrepancy between the characteristic frequencies deduced from measurements of rotatory dispersion and those obtained by recording directly the maximum value of the molecular extinction coefficient.

The original purpose of the experiments demanded only a knowledge of the characteristic frequency of the band of selective absorption; but the data in Table I have an interest of their own, which exceeds that of the approximate coincidence of the frequencies deduced by the two methods referred to above. Thus, not only have we been able to draw more exact conclusions as to the effect of halogens on the familiar absorption band of the ketone, but the " general absorption " of the compounds, which can now be investigated just as accurately as their " selective absorption," has been found to present striking characteristics, especially with regard to the mutual influence of negative radicals (compare Part VII, following paper). In this way the observations have provided important clues as to the origin and significance of selective and general absorption in carbon compounds generally.

2. *Experimental Methods.*

Camphor-β-sulphonic acid, and four camphorsulphonates containing a halogen atom, were examined in aqueous solutions. The fifteen other halogen derivatives were all examined in *cyclo*hexane. This solvent was selected in order to conform as closely as possible to the conditions under which the rotatory dispersions of many of these compounds had been measured in benzene (J., 1925, **127**, 807). The choice of *cyclo*hexane as an alternative to benzene (which was not sufficiently transparent for measurements of absorption) was justified by the fact that some of its physical properties approximate very closely to those of benzene (Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, **104**, 430) and in particular that the wave-length of maximum absorption for a solution of camphor in *cyclo*hexane had been found to be the same as for a thin film of camphor in benzene (Lowry and French, J., 1924, **125**, 1924). Apart from these considerations, however, *cyclo*hexane has proved to be a good solvent for measurements of absorption, since, although unpurified specimens are not very transparent, and may even exhibit an absorption band, the material can be purified readily by repeated shaking with 100% sulphuric acid on a mechanical shaker. When washed with water and distilled, it was then found to be transparent to about 2200 Å.U., which is approximately the limit of transmission of the calcite of the ultra-violet spectrophotometer.

The fifteen halogen derivatives of camphor and the five sulphonates had all been purified by crystallisation, and in most cases the samples had already been used for measurements of rotatory dispersion.

The methods of measurement were the same as in Part IV of this series of papers, absolute values being recorded for the " molecular extinction coefficients " at different wave-lengths up to the limit of transparency of the solution. As a rule, about 60 measurements were made with each compound, at concentrations ranging from $M/4$ to $M/400$; but the experimental points were too numerous to be inserted in the figures, except in one case (Fig. 7), where the range of wave-lengths and intensities made it possible to plot the data on a larger scale.

3. *Summary of Experimental Results.*

The present series of observations has proved that, whilst the presence of a halogen influences both the selective and the general absorption of the compounds, and affects these two properties in a somewhat similar manner, the two influences are sufficiently independent to produce large variations in the " persistence " of the band,* *i.e.*, in the relative separation of the accessible band of " selective " absorption and the inaccessible band of " general absorption " as measured by the depth of the trough between them. The experimental results, which are summarised in Table I, may therefore be discussed most conveniently under these two headings.

(*a*) *Selective Absorption.*—The principal results are as follows :

(i) The general proposition, that the position of the ketonic band is largely independent of the nature of the ketone, is confirmed, since the wave-length of maximum absorption ranges only from 2880 Å.U. in camphor to 3230 in $\alpha\alpha'$-dibromocamphor. The intensities also cover only a small range from $\log \varepsilon = 1{\cdot}4$ to $2{\cdot}0$. This is in marked contrast with the conjugated systems examined in Part IV, where the value of $\log \varepsilon$ rose from 1·4 in camphor to 4·3 in benzylidenecamphor.

(ii) A halogen in the α-position produces a marked " intensification " of the selective absorption, since it increases both the wave-length and the maximum extinction coefficient of the ultra-

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* It is therefore unlikely that the general absorption of these compounds is a mere harmonic of the selective absorption.

TABLE I.

Selective and General Absorption of Halogen and Sulphonic Derivatives of Camphor.

No. of curve.	Substance.	Selective absorption.				Persistence $\log \epsilon$ (max.). $-\log \epsilon$ (min.).	General absorption	
		Maximum.		Minimum.				
		λ max.	$\log \epsilon$ (max.).	λ min.	$\log \epsilon$ (min.).		λ for $\log \epsilon = 1·5$.	$\log \epsilon$ for $\lambda = 2500$.
	(a) *In* cyclo*hexane.*							
I.	Camphor.	2880	1·45	<2327	<−0·26	<1·72	None at 2400 Å.U.	
II.	α-Chlorocamphor.	3050	1·72	2510	0·67	1·05	<2300*	0·68
	α′-Chlorocamphor.	3060	1·75	2550	0·94	0·81	<2300*	0·97
III.	α-Bromocamphor.	3100	1·95	2700	1·20	0·75	2590	1·83
	α′-Bromocamphor.	3120	1·95	2720	1·26	0·69	2530	1·96
IV.	β-Bromocamphor.	2930	1·39	2750	0·98	0·41	2370	1·12
V.	αα′-Dichlorocamphor.	3100	1·82	2570	0·22	1·60	2400	0·40
VI.	αα′-Bromochlorocamphor.	3150	1·84	2840	1·57	0·27	†	2·45
VII.	αα′-Dibromocamphor.	3230	1·88	2970	1·74	0·14	†	2·86
VIII.	α-Chloro-β-bromocamphor.	3060	1·67	2600	0·73	0·94	2400	1·3
IX.	α-Bromo-β-chlorocamphor.	3080	1·87	2690	1·40	0·47	2630	1·9
X.	αβ-Dibromocamphor.	3080	2·03	2700	1·46	0·57	2680	2·5
XI.	απ-Dichlorocamphor.	3080	1·68	2590	0·40	1·68	2370	0·5
XII.	α-Bromo-π-chlorocamphor.	3150	2·01	2610	0·59	1·42	2490	1·45
XIII.	απ-Dibromocamphor.	3120	2·05	2670	1·09	0·96	2590	1·83
	α′π-Dibromocamphor.	3090	2·02	2680	0·80	1·22	2560	1·85
	(b) *In water.*							
XIV.	Camphor-β-sulphonic acid.	2850	1·54	2390	0·50	1·04	2300	‡
XV.	Potassium α-chlorocamphor-β-sulphonate.	3000	1·59	2510	0·50	1·09	2300	0·51
XVI.	Potassium α-bromocamphor-β-sulphonate.	3030	1·93	2640	1·39	0·54	2600	1·90
XVII.	Ammonium α-chlorocamphor-π-sulphonate.	3030	1·85	2660	1·00	0·85	2500	1·50
XVIII.	Ammonium α-bromocamphor-π-sulphonate.	3020	2·09	2630	1·50	0·59	2630	1·90

* In these compounds, the general absorption is very weak and $\log \epsilon$ does not rise to 1·5 within the limits of our experiments; the value of λ corresponding to $\log \epsilon = 1·5$ could therefore only be deduced by extrapolation.

† In these two compounds, where the general absorption is very strong, the molecular extinction coefficient falls to a minimum (at $\log \epsilon = 1·6$ and 1·75 respectively), and then begins to rise again towards the crest of the band of selective absorption, but it never falls as low as $\log \epsilon = 1·5$.

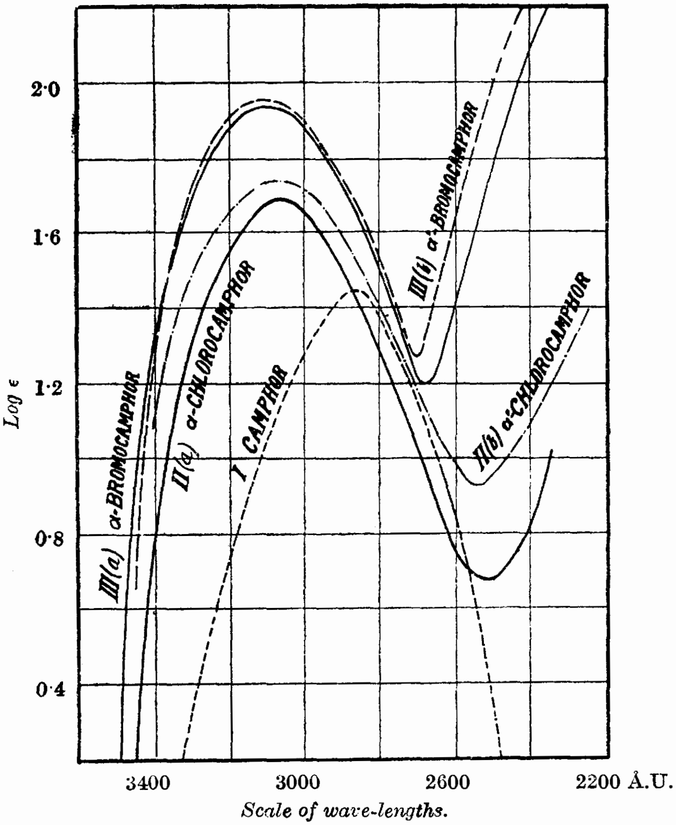
‡ In this compound, where the general absorption is very weak, the band of selective absorption extends to a minimum at about 2400 Å.U.; the general absorption does not begin, therefore, until the wave-length is already less than 2500 Å.U.

violet band (Fig. 1). The influence of an atom of bromine in the β-position is, however, almost negligible, since an insignificant increase of wave-length is balanced by an equally unimportant diminution in the maximum extinction coefficient (Fig. 7). The conclusion reached in an earlier paper (J., 1909, **95**, 817) that, whilst a halogen atom in a α-position produces an "intensification" of the band, an atom of bromine in the β- or π-position has a "repressive action," is therefore no longer valid when applied to the selective absorption alone instead of to the "persistence" of the band.

(iii) The data for the αβ- and απ-derivatives (Figs. 3 and 4) confirm the conclusion that an atom of bromine in the β- or π-position produces only negligible changes in the wave-length and penetration of the band, and certainly has no "repressive" action.

(iv) The most striking intensification of the selective absorption is seen in the αα′-dihalogen derivatives (Fig. 2). In this group of compounds the progressive replacement of chlorine by bromine is accompanied by a progressive increase in the wave-length of the band, whilst the maximum extinction coefficient remains practically constant at a value midway between those recorded for a single atom of chlorine or bromine in the α-position. On the other hand, a similar replacement of chlorine by bromine in the αβ-series (Fig. 3) produces a progressive increase in the value of the maximum

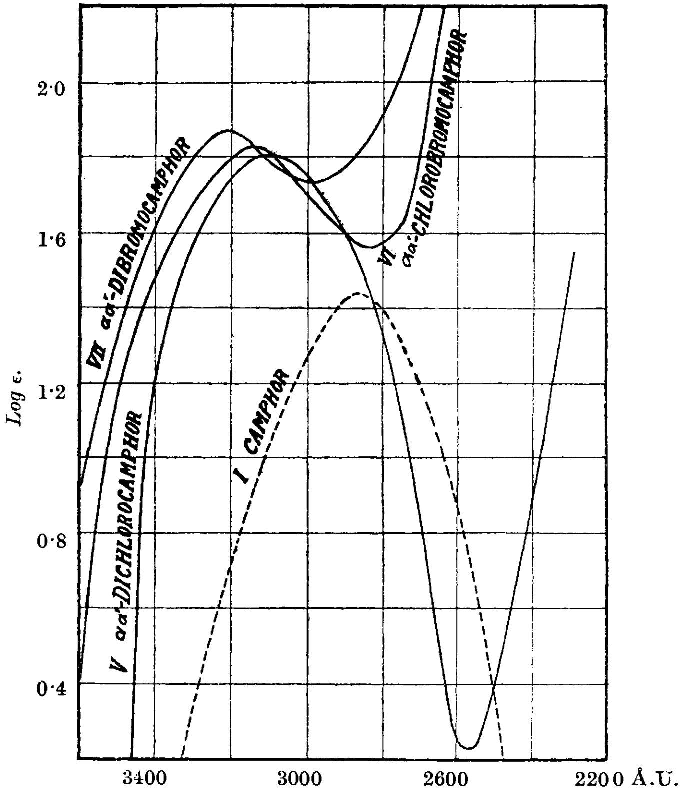
FIG. 1.



Molecular extinction coefficients of I *camphor,* II(*a*) *α-chlorocamphor,* II(*b*) *α′-chlorocamphor,* III(*a*) *α-bromocamphor,* III(*b*) *α′-bromocamphor in* cyclo*hexane.*

extinction coefficient, which is not accompanied by any marked change of wave-length. These two figures therefore recall, but in a much less striking form, the contrast between the optical effect of the two types of conjugation recorded in Part IV. In the απ-series (Fig. 4), the principal contrast is between the α-chloro- and the α-bromo-compounds. Thus απ-dichlorocamphor gives a band in very much the same position as in α-chlorocamphor itself; and in the same way απ- and α′π-dibromocamphor (which give almost identical curves) and π-chloro-α-bromocamphor resemble α-bromocamphor very closely, although the introduction of a halogen atom in the π-position appears to produce a minute increase both in the wave-length and in the maximum value of the extinction coefficient of the bromo-compounds.

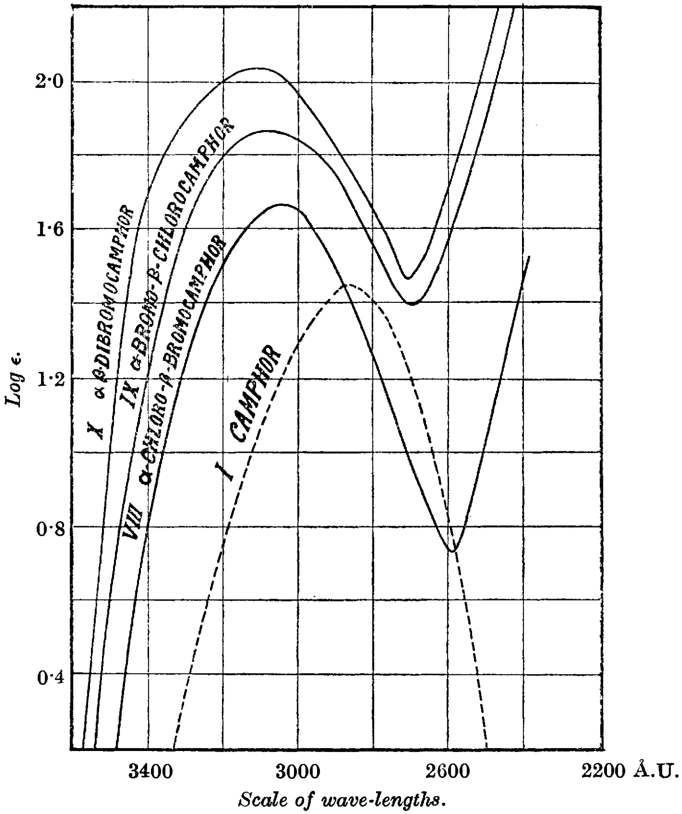
FIG. 2.



Molecular extinction coefficients of I *camphor,* V *aa′-dichlorocamphor,* VI *aa′-chlorobromocamphor,* VII *aa′-dibromocamphor in* cyclo*hexane.*

(v) The influence of a sulphonic group in the β- or π-position is almost negligible, like that of a halogen atom in either of these positions. Thus in Reychler's camphor-β-sulphonic acid (Fig. 5) a small increase of intensity is balanced by a small decrease of wave-length, just as in β-bromocamphor (Fig. 7) a small decrease of intensity was balanced by a small increase of wave-length. Similar statements apply to the αβ- and απ-chloro- and bromo-sulphonates, where the introduction of the sulphonic group produces only small changes in the wave-length and intensity of the band of α-chloro- and α-bromocamphor.

FIG. 3.



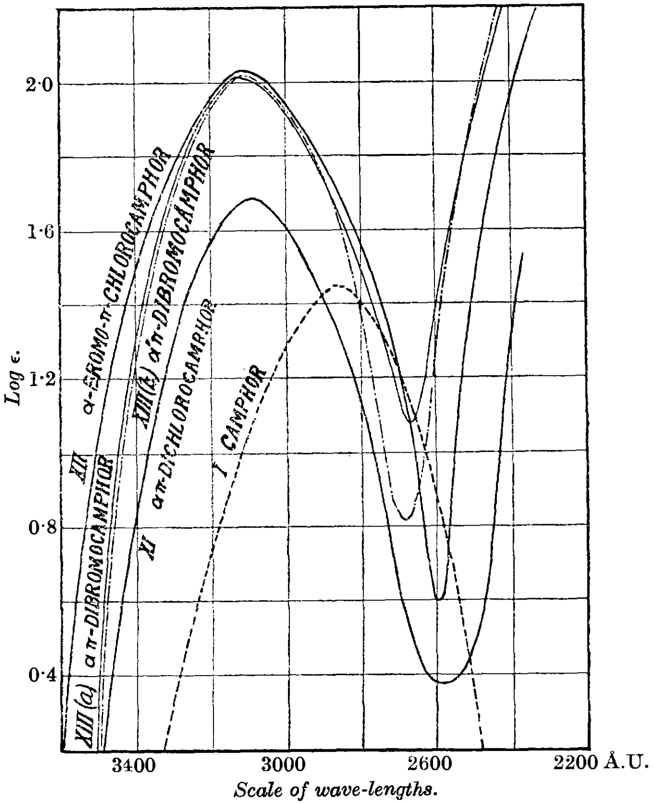
Molecular extinction coefficients of I *camphor,* VIII *α-chloro-β-bromocamphor,* IX *α-bromo-β-chlorocamphor,* X *αβ-dibromocamphor in* cyclo*hexane.*

(*b*) *General Absorption.* For the purpose of comparing general absorptions, we have chosen, quite arbitrarily, a standard wave-length, λ = 2500 Å.U., and a standard absorptive power, log ε =

1·5, and have recorded in Table I the wave-length at which the standard absorptive power is attained, and the absorptive power at the standard wave-length. The principal experimental results are as follows :—

(i) We have obtained complete confirmation of the recent observation of Lowry and French (J., 1924, **125**, 1924) that a solution of camphor in *cyclo*hexane shows no general absorption up to the limits of our present methods of measurement. It is therefore impossible to record the persistence of the band, except by stating that it must be greater than 1·7.* It is indeed a noteworthy fact that, whereas

FIG. 4.



Molecular extinction coefficients of I *camphor,* XI *απ-dichlorocamphor,* XII *α-bromo-π-chlorocamphor,* XIII (*a*) *απ-dibromocamphor,* XIII (*b*) *α'π-dibromocamphor in* cyclo*hexane.*

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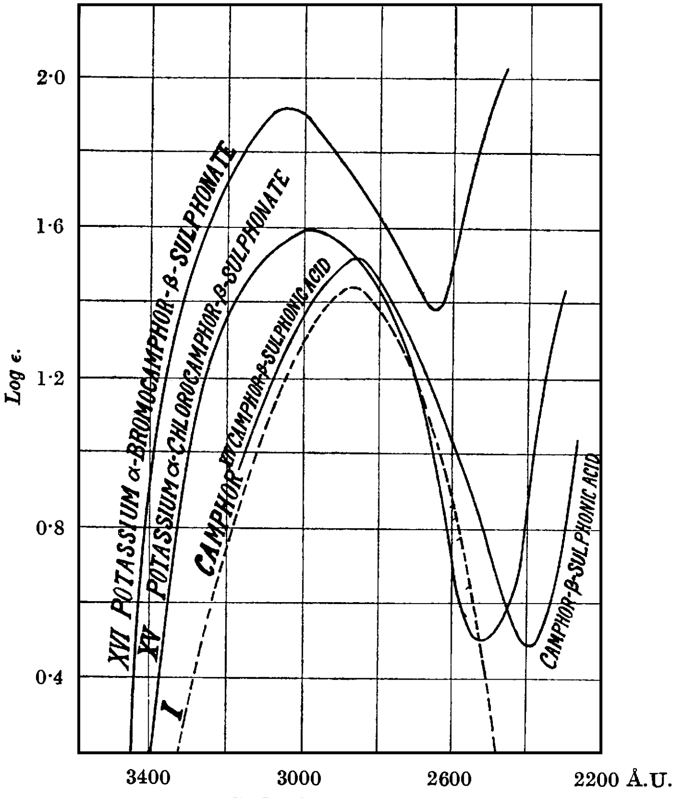
* In the same way, V. Henri found (*Ber.*, 1913, **36**, 3627) that acetone shows no general absorption up to 2144 Å.U., although the band had already persisted through a range of 2·0 in log ε, *i.e.*, over a range of intensities of 100 : 1.

the earlier methods of measurement always indicated the existence of a real or fictitious general absorption in every solution that was examined, we have failed completely in our attempts to detect by the quantitative method any trace of a general absorption in camphor itself when dissolved in *cyclo*hexane, although we have been able to reach the end of the band of selective absorption in all the twenty derivatives which were examined in the course of the present research, as well as in camphor itself when dissolved in alcohol (Lowry and French, *loc. cit.*). From the experimental point of view, it is a remarkable experience to find that a relatively strong solution of camphor, containing about 8 grams in 100 c.c., which extinguishes almost the whole of the ultra-violet spectrum from

FIG. 5.



Molecular extinction coefficients of I *camphor* (*in* cyclo*hexane*), XIV *camphor-β-sulphonic acid* (*in water*), XV *potassium α-chlorocamphor-β-sulphonate* (*in water*), XVI *potassium α-bromocamphor-β-sulphonate* (*in water*).

3400 Å.U. onwards, becomes transparent again at about 2400 Å.U., and transmits with equal intensity all the remaining lines of the iron arc to 2327 Å.U.*

(ii) After camphor, the smallest general absorption was observed in camphor-β-sulphonic acid (Curve XIV), but, as the acid was examined in aqueous solution, the general absorption was easily observed, by reason of the exceptional transparency of the solvent. The minimum lies just beyond 2400 Å.U., but is followed by a very rapid increase, so that the general absorption was already almost level with the maximum of selective absorption (at $\log \varepsilon = 1{\cdot}54$) when the last readings were taken at about 2327 Å.U., in the clear aqueous solution. Apart from camphor, this compound was the only one in which the standard wave-length, $\lambda = 2500$ Å.U., selected for the comparison of general absorptions, fell within the limits of the band of selective absorption.

(iii) Although chlorine is not greatly inferior to bromine in its ability to intensify the selective absorption of camphor, it is relatively impotent in producing general absorption. Thus, apart from camphor and camphor-β-sulphonic acid, the only compounds in which the absorptive power did not reach the standard value of 1·5 within the limits of our experiments were the α- and α′-chlorocamphors (Curves II, *a* and *b*). Again, αα′-dichlorocamphor (Curve V), where the growth of general absorption is much more rapid than in the monochlorocamphors, has an exceptionally deep minimum at $\log \varepsilon = 0{\cdot}22$; and the persistence of the band, $\log \varepsilon\,(\text{max.}) - \log \varepsilon\,(\text{min.}) = 1{\cdot}60$, is greater than in any compound of the series except camphor itself, where it exceeds 1·72 (Lowry and French, *loc. cit.*, p. 1925), and απ-dichlorocamphor (Curve XI), where the general absorption only begins to be perceptible at a wave-length of about 2600 Å.U., after the band has attained a persistence of 1·68.

(iv) Bromine, on the other hand, which produces a strong general absorption even in α-bromocamphor, becomes extremely efficient in this respect when reinforced by an atom of chlorine or bromine in the other α-position. Thus, the general absorption at the standard wave-length of 2500 Å.U. *increases* from $\log \varepsilon = 1{\cdot}83$ in α-bromocamphor to 2·45 in αα′-chlorobromocamphor and to 2·86 in αα′-dibromocamphor. At the same time, as a result of the increase of general absorption, the persistence of the band *decreases* from 0·75 in α-bromocamphor to 0·3 in αα′-chlorobromocamphor and to 0·1 in αα′-dibromocamphor (Fig. 2). The general absorption in αα′-di-

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* The fact that even this very " clean " band attains a width of 1000 Å.U. in solutions of only moderate concentration will explain why accurate measurements of rotatory dispersion can only be made for wave-lengths much greater than that of the crest of the band.

bromocamphor is indeed so great that at 2900 Å.U. it is already twice as strong as that corresponding with the maximum of the camphor band at the same wave-length. It is, therefore, only because the camphor band has been displaced by about 350 Å.U. in the direction of longer wave-lengths that the dibromo-derivative is able to exhibit a selective absorption at all : apart from this, nothing but a "step-out " would be observed in the curve.

(v) The reinforcement of the general absorption of α-bromocamphor by a second halogen in the β-position is comparatively small. Thus the general absorption remains practically stationary on passing from α-bromocamphor, where $\log \varepsilon = 1{\cdot}83$ at 2500 Å.U., to αβ-bromochlorocamphor, where $\log \varepsilon = 1{\cdot}90$, although this number rises to 2·5 in αβ-dibromocamphor. In the case of the π-compounds,* the general absorption actually *falls* from $\log \varepsilon = 1{\cdot}83$ at 2500 Å.U. in α-bromocamphor to 1·45 in απ-bromochlorocamphor, and remains stationary at 1·83 in απ-dibromocamphor. A sulphonic group in the β or π-position is also practically without influence in augmenting the general absorption of α-bromocamphor, since the value of log ε is only increased from 1·83 at 2500 Å.U. in α-bromocamphor to 1·90 in the two bromocamphorsulphonates.

4. *Superposition of Selective and General Absorption.*

In accordance with the usual behaviour of negative radicals, halogens in the contiguous α-position have been found to augment the selective absorption of the ketonic group. Conversely, one must suppose that the ketonic group augments the power of the contiguous α-halogen atom to develop a general absorption, just as it increases the readiness with which reduction or reverse substitution takes place. In these cases, therefore, any superposition of general and selective absorption by mere addition would be out of the question, since it would ignore the known mutual influence of the negative atoms. This mutual influence diminishes, however, as the distance between the negative atoms is increased; and in β-bromocamphor the band of selective absorption is very similar to that of camphor itself, showing that one of the two mutual influences (namely, that of the halogen upon the ketonic group, but not necessarily that of the ketonic group upon the halogen) has become almost negligible. We have therefore attempted to reproduce the absorption curve of β-bromocamphor by superposing the general absorption of a compound containing the group $-CH_2Br$ (see Part VII) on the selective absorption of camphor itself. The general absorption of *one* molecular proportion of methyl bromide was found

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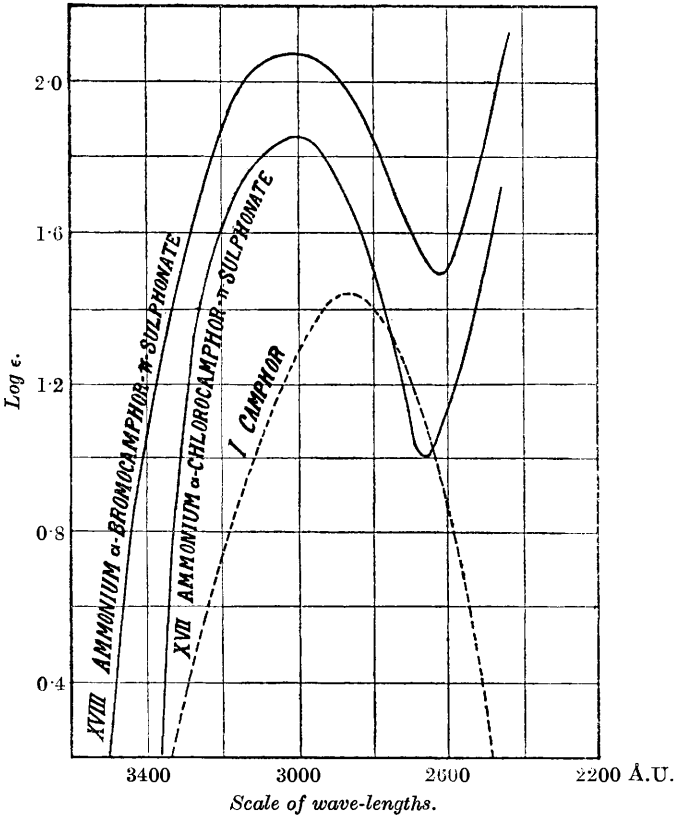
* Anomalies in the optical properties of the π-derivatives have already been noted and discussed (J. 1925, **127**, 1504).

to be too small, whilst that of *half* a molecular proportion of methylene bromide or of ethylene bromide was too great, on account of the excessive mutual influence of the two halogens. Finally, by using a mixture of one molecular proportion of camphor with half a molecular proportion of trimethylene bromide (in which the two negative atoms are separated by three intermediate atoms of carbon, just as in β-bromocamphor), we have obtained an absorption curve (Fig. 7) which pursues very much the same course as that of β-bromocamphor, although it is not identical with it. In this way the validity of the principle of superposition of general and selective absorptions appears to be sufficiently established, whilst the theory which assigns the selective absorption to the >CO group and the

FIG. 6.

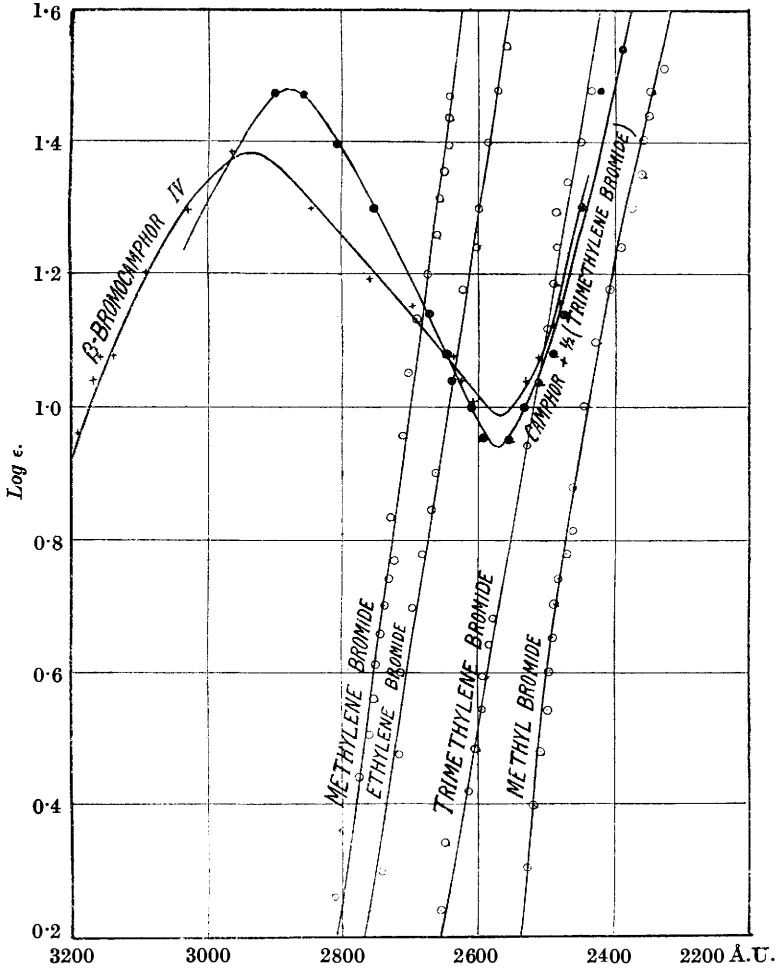


Molecular extinction coefficients of I *camphor in* cyclo*hexane,* XVII *ammonium α-chlorocamphor-π-sulphonate,* XVIII *ammonium α-bromocamphor-π-sulphonate in water.*

general absorption to the $>$C Br group (see following paper) receives a direct experimental confirmation.

In addition to the absorption curve for β-bromocamphor, and the

FIG. 7.



Molecular extinction coefficients of IV *β-bromocamphor in* cyclo*hexane. Also of methyl, methylene, ethylene, and trimethylene bromide and of a solution of camphor with half a molecular proportion of trimethylene bromide in* cyclo*hexane.*

curve for a mixture of camphor and trimethylene bromide, Fig. 7 shows the curves of general absorption for solutions of methyl, methylene, ethylene and trimethylene bromides in *cyclo*hexane, the curves plotted in Part VII being for solutions in alcohol. On account of the narrower range of wave-lengths and intensities which it covers, this diagram was plotted on twice the scale of Figs. 1 to 6; it was therefore possible to insert, without overcrowding, all the experimental points on which the curves were based.

5. *Auxochromic Influence of Alkyl Radicals and of Halogens.*

Bielicki and Henri (*Ber.*, 1913, **46**, 3627) and Rice (*Proc. Roy. Soc.*, 1915, *A*, **91**, 76) have shown that the absorption band of acetone is displaced towards the visible region when the hydrogen atoms are replaced by alkyl groups. Thus according to Rice "the shifts obtained in the successive substitution of the three α-hydrogen atoms are 23, 50, and 30 Å.U." for the first methyl, and the total shift of 103 units is doubled ($\lambda = 2747 \rightarrow 2850 \rightarrow 2950$ Å.U.) when the three hydrogens of the second methyl group are also replaced. On the other hand, Henri finds that a shift *in the same direction* occurs when the whole methyl group is replaced by hydrogen, since aldehydes give a band of longer wave-length and smaller intensity than ketones, in addition to showing a much stronger general absorption.

In order to determine the influence of halogens (and of negative radicals generally) on the absorption spectra of the ketones, it is convenient to take camphor instead of acetone as the parent compound, since the liquid halogen derivatives of acetone are less easy to prepare and purify than the alkyl derivatives (which are easily synthesised) and are in every respect inferior to the analogous compounds of the camphor series, where crystalline products are available in large numbers, and with the substituent in four different positions, namely, α or α′, β and π. It is a mere accident of nomenclature that in the α- and α′-derivatives of camphor the substituent is attached to a carbon atom in the " α " position relative to the ketonic group, and that in the case of the β-derivatives we can now assign the substituent to a methyl group of which the carbon atom is in a " β " position relative to the ketonic group (Lowry and Burgess, J., 1925, **127**, 279). In the π-compounds, the substituent is attached to a carbon atom in a " γ " position relative to the ketonic group, although it can also be reached by a longer route which would make it a " δ " carbon atom. It is therefore possible, by working in the camphor series, to compare the effect on the selective absorption of the ketonic group of introducing a negative substituent in an α-, β- or γ-position. The fact that the camphor nucleus is relatively complex is not a matter of great importance, since we have no reason for supposing that the influence of a negative group depends on the *shape* of the chain of atoms through which it is transmitted. It is, however, important to remember that there is already evidence to show that the optical properties of the π-derivatives are sometimes abnormal (Richards and Lowry, J., 1925, **127**, 1504).

With these facts in mind, the experimental data given above can be summarised by saying that, whilst the general absorption is influenced profoundly by the introduction of a negative group *in any position in the molecule,* the selective absorption is influenced strongly by a halogen atom only when this occupies a contiguous α-position, the effect of a halogen or of a sulphonic group in the more distant β- and γ (π)-positions being negligible. Thus the increment for a single atom of bromine in the α- or α'-position is about 200 Å.U. (mean of 220, 240, 180, 150), and for a single atom of chlorine about 160 Å.U. (mean of 170, 180, 150, 130), when the other α-position is occupied by hydrogen; and it is about 120 Å.U. for bromine and 50 Å.U., for chlorine, when the other α-position is already occupied by a halogen. For a halogen in the β-position, the increments are $-$ 20, $+$ 50, $+$ 10, $-$ 20 Å.U. and for a halogen in the π-position, $+$ 30, $+$ 50, $+$ 20, $-$ 30 Å.U. A comparison with Rice's observations shows that the increments for two α-atoms of chlorine, or for a single α-atom of bromine, in camphor is already larger than for six α-methyls in acetone.

6. *Origin of the Ketonic Band.*

At the time when the earlier observations of absorption spectra were made (J., 1909, **95**, 807, 1340; 1910, **97**, 899, 905) it was thought that selective absorption was due to an oscillation in the molecule of the same period as that of the absorbed light. The experiments then described showed, however, that the ketonic band could not be due to the " isorropesis " or intramolecular oscillation of a mobile hydrogen atom, since bands were developed by many compounds which were incapable of undergoing isomeric change in the manner suggested. The conclusion was therefore drawn that " the camphor band is evidently in some way a function of the ketonic group," but that " it is not at all easy to say in what way the group acts in promoting the formation of the band."

This problem has, however, been simplified considerably by recent developments in physical optics, which lead us to ascribe the absorption, not to an intramolecular vibration, but to the presence of a system which when activated by light can take up energy quanta of suitable magnitude. On inquiry amongst physicists, we find that the ultra-violet ketonic band cannot be attributed to activation of the nuclei of the carbon and oxygen atoms relatively to one another, since this would give bands in the infra-red region; nor can it be due to the ionisation of the unshared electrons of the oxygen atom (*all* the carbon electrons are shared), since the ionisation potential for oxygen corresponds with a wave-length far out in the Schumann region. The ketonic band can therefore only be attributed to an activation of the valency electrons of the double bond which forms the link between carbon and oxygen.

These valency electrons differ from the others in being simultaneously under the control of two nuclei, A and B. They can therefore be raised to a higher energy level relatively to A, or to B, or to A and B simultaneously. If A is carbon and B is oxygen (or in general if A is a less " negative " element than B), it will be easier to activate the valency electrons relatively to A than relatively to B. The effect will be to produce a " polar activation " of the double bond, since the valency electrons which absorb the light will be displaced from carbon towards oxygen, a process which (if continued far enough) would culminate in the ionisation of one link of the bond, and the conversion of the " non-polar " into a " semi-polar " double bond, as indicated by the scheme $>C=O \rightleftharpoons >\overset{+}{C}-\overset{-}{O}$.

The theory of polar activation, now used to explain the absorption of light by the unsaturated carbonyl radical, corresponds closely with the explanation given by Norrish (in Part III of this series of papers, J., 1923, **123**, 3006) of the arrest of the interaction of ethylene with bromine or chlorine, when enclosed in a vessel lined with paraffin wax, *i.e.*, that the interaction depends on a " polar activation " of the olefine and halogen, which can only be brought about at a polar surface. It should also be noted that, whilst semipolar double bonds are permanent in the systems $>SO$, $\geq NO$, and $\geq PO$, they are not stable in $>C=C<$ or $>C=O$ (Sugden, J., 1925, **127**, 1525); they are, therefore, available as unstable or activated forms of the molecule in order to account for phenomena such as those discussed above.

The views now set out in reference to the utilisation of the energy absorbed by double bonds in unsaturated compounds could obviously be extended to single bonds; but since these are usually much more stable than double bonds, the quanta of energy required to activate them must be much larger, and the wave-lengths much smaller, than in the case of the ketonic band, corresponding, for instance, with a frequency in the Schumann region of the spectrum. Since this region is still inaccessible to our present methods of investigation of absorption spectra, saturated compounds generally give rise only to " general absorption."

7. *Summary.*

(*a*) Quantitative data are given for the general and selective absorption of twenty halogen and sulphonic derivatives of camphor.

(*b*) Halogen atoms in the α-position intensify both the general and the selective absorption of camphor; but halogen atoms and sulphonic groups in the β- or π-position are relatively impotent in increasing the selective absorption of the ketone, although they may contribute substantially to its general absorption.

(*c*) The origin of the ketonic band is discussed.

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