XCII.—*The Absorption Spectrum of Camphor.*

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WITH a view to determining the nature of their atomic absorption, various homocyclic compounds were examined and compared with the spectra of benzene and its derivatives, both with regard to the intensity of the general absorption and the presence or absence of an absorption band. The typical substances for comparison were principally the hydroaromatic hydrocarbons, benzene hexachloride, camphor oil, camphoric acid, and camphor (Hartley and Huntington, *Proc. Roy. Soc.*, 1880, **31**, 1; W. N. Hartley, *Trans.*, 1881, **39**, 153.)

It was pointed out that any one of the formulæ proposed for camphor and camphoric acid at that time would be consistent with these substances being compounds with a more diactinic character than either benzene and its homologues or the terpenes. Neither camphor oil nor camphoric acid showed any absorption band, and both substances transmitted the ultraviolet rays more freely than hydroaromatic derivatives. Of the several specimens of camphor examined, only three were described.

No. 1.—Crystals of camphor which had separated from camphor oil boiling between 200° and 220°.

No. 2.—A specimen of the finest commercial camphor, which was resublimed prior to its examination.

No. 3.—Fine crystals of camphor, spontaneously sublimed from a quantity of the solid No. 2, placed in a capacious bell-jar, and exposed for many days to the action of sunlight. As is well known, camphor vapour condenses on the sides of the glass most exposed to the sun's rays. In this instance, the best crystals obtained were 5 mm. in length by 2.5 mm. in width, of perfect transparency, and a brilliant appearance. These were selected for examination. The specimens No. 1

and No. 2 exhibited an absorption band which, on account of its feeble character as compared with bands seen in the spectra of benzene derivatives, and the ease with which dilution caused the disappearance of the band, was thought to be due to some impurity.

No. 3, on the other hand, transmitted a continuous spectrum, "and was, in fact, so transparent that a solution in alcohol containing 1/500th of the substance transmitted all rays less refrangible than Cd 25. This far exceeds in diactinic quality the numerous specimens of terpenes I have examined."

Having made preparations in the summer of 1907 for re-examining this substance, I became aware that Baly, Marsden, and Stewart had been led to the conclusion that camphor shows an absorption band but camphoroxime does not (Trans., 1906, 89, 979), and that the band is attributed to the "reactivity" of the carbonyl and the neighbouring CH_2 groups. These authors state that their solution was ten times as strong as that examined by me. If this were so, but of that I am doubtful, it might account for the difference between their conclusions and mine with respect to camphor. As the matter is of considerable interest, I have for my own satisfaction continued the experiments which had been projected.

As camphor readily forms solid solutions of substances presented to it in a state of vapour, it was difficult to obtain it quite free from minute traces of such compounds as would affect its absorption spectrum; but the refining of camphor on a manufacturing scale has now been carried to a state of great perfection, and I am indebted to Mr. W. E. B. Blenkinsop, of the firm of May and Baker, Ltd., of Battersea, for an ample supply of the doubly-refined material. This was again submitted to sublimation, but in the absence of sufficient sunlight the warmth of a 10-candle-power electric glow lamp placed in a bell-jar of about 5 litres capacity was substituted. The crystals as deposited were observed with a low power microscope; they were all in stellate groups, with the exception of a single crystal of small size. In this respect, they differed from the large crystals obtained in 1881 by the action of sunlight.

To ascertain whether the crystals were homogeneous, the original sample, the resublimed substance, and, lastly, the residue remaining after about five-sixths had been sublimed were each examined separately.

The concentration was ten times that usually examined, being one centigram-molecule in 100 c.c. of absolute alcohol.

Measurements of the Absorption Band Observed in Specimens of Camphor Solutions at Different Concentrations.

Camphor No. 1.—Doubly refined.

At. wt.	Solution.	Thickness of layer of solution in mm.				
		49	25	15	10	5
152	N/10	$1/\lambda$	$1/\lambda$	$1/\lambda$	$1/\lambda$	$1/\lambda$
	1.52 grams in	Rays trans- mitted to		Band	Band	Band
	100 c.c. of alcohol					Very feeble
		3064	3190	3190	3210	3455
				to	to	to
				3886	3720	3692

At 4 mm. there is a complete transmission of all rays to $1/\lambda$ 3954, and at 0.5 mm. all rays are transmitted to $1/\lambda$ 4673.

Camphor No. 2.—Sample No. 1, resublimed.

This differs but very slightly from No. 1, in the continuous rays being transmitted feebly between $1/\lambda$ 3455 and $1/\lambda$ 3692 in a thickness of 5 mm., whereas in No. 1 there is a band at this point.

Camphor No. 3.—Residue from No. 2, after sublimation.

The photographs differed slightly from the foregoing, the absorption band being somewhat stronger even than in No. 1.

To determine more accurately the termination of the band and the extent of the transmitted spectrum beyond this point, the instrument was carefully focussed for the more refrangible rays.

Concentration, 1 Centigram-molecule in 100 c.c.

Layer of liquid examined.	Proportional thicknesses of solution containing 1 milligram-molecule in	Termination of band.	Rays transmitted to
	10,000 c.c.	$1/\lambda$	$1/\lambda$
49 mm.	49,000 mm.	4176	4411
39 "	39,000 "	4037	4460
30 "	30,000 "	3817	4552
20 "	20,000 "	3817	4552
10 "	10,000 "	3635	4662
5 "	5,000 "		4671

Curve I. According to Baly, Marsden, and Stewart.
 Curve II. Hartley.—Sample doubly refined.

Concentration, 1 Centigram-molecule in 100 c.c.

The less refrangible rays were accurately focussed so as to give the position of the less refrangible edge of the band :

Layer of liquid examined	Proportional thicknesses of solution containing 1 milligram-molecule in	Commencement of band.
	10,000 c.c.	$\frac{1}{\lambda}$
49 mm.	49,000 mm.	3064
25 "	25,000 "	3190
15 "	15,000 "	3190
10 "	10,000 "	3210
5 "	5,000 "	Indication of a band at 3500.

$\frac{1}{\lambda}$

Indication of a band at 3500.

Concentration 1 Milligram-molecule in 100 c.c.

Focussed for the more refrangible rays :

Layer of liquid examined.	Proportional thicknesses of solution containing 1 milligram-molecule in	Termination of spectrum.
	10,000 c.c.	$1/\lambda$
10 mm.	10,000 mm.	4673
5 „	5,000 „	4673
3 „	3,000 „	4673

The absorption band and the curve drawn is not precisely identical with that observed by Baly, Marsden, and Stewart, and their curve has been introduced for comparison.

The specimens of camphor more recently examined transmit the rays lying beyond the band more freely.

Conclusion.

The band observed in the spectrum belongs to camphor, and it is accounted for by the juxtaposition of the CO and CH₂ groups in the molecule.

The absorption band being a shallow one, and observed only in more concentrated solutions than those of benzene, would account for its not being photographed in solutions containing 1/500th of camphor. The various specimens of camphor originally examined, with the exception of that described as No. 3, undoubtedly did contain an impurity which was not improbably cymene.

I desire to express my thanks to Mr. A. G. G. Leonard, A.R.C.Sc.I., for the care he has exercised in taking the latter photographs and drawing the curves, and to Mr. W. E. B. Blenkinsop for the camphor presented to me.

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