

CXIII.—*The Influence of Different Centres of Absorption on the Spectra of Substances.*

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THE author (J., 1925, 127, 2771; 1926, 775) has shown that the specific and general absorption of various esters is controlled by the nature and type of the basic and acidic constituents, and, in other substances, by the nature and type of the different absorbing centres in the molecule. The observations have been continued with other esters and substances possessing various centres of absorption.

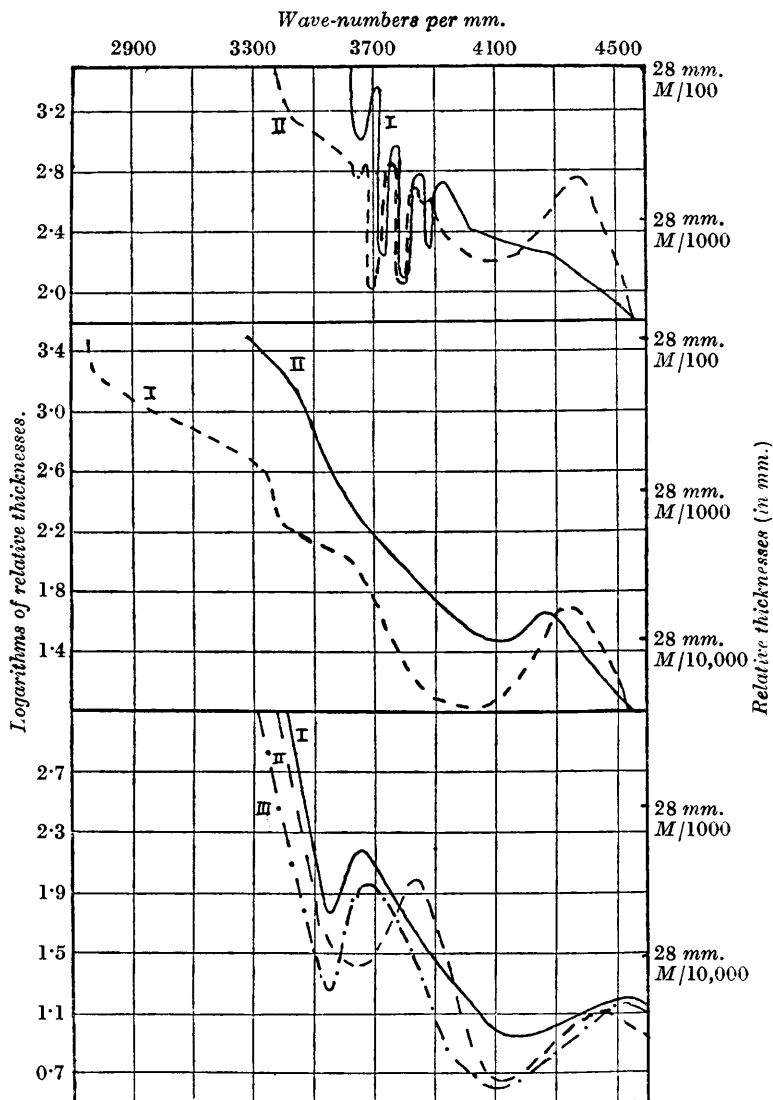
Benzyl Phenylacetate.—The curve (Fig. 1, upper curves) shows the remnants of several benzene bands which are not unlike those of toluene (J., 1915, 107, 965); and the rapid extension of the rays between $1/\lambda$ 4030 (λ 2480) to $1/\lambda$ 4250 (λ 2352) indicates the remainder of the well-known benzene bands in this region. The author has shown (*loc. cit.*) that these remnant benzene bands occur in phenylacetonitrile, benzyl chloride, benzylidene chloride, and phenylacetic acid, the slight differences being in their position and intensities. In each of these substances the benzene residue retains a certain measure of freedom. Crymble, Stewart, Wright, and Glendinning (J., 1911, 99, 451) state that phenyl acetate has one moderately weak band at about $1/\lambda$ 3880 (λ 2576). Acetic acid has no band.

Phenylacetaldehyde.—The curve (Fig. 1, upper curves) indicates that this substance also shows some residues of the original benzene bands. In addition, there is a weak acetaldehyde band between $1/\lambda$ 3420 (λ 2923) and $1/\lambda$ 3600 (λ 2777). Acetaldehyde itself shows a band at about $1/\lambda$ 3500 (λ 2856) as first shown by the author and McClelland (J., 1912, 101, 1810).

Benzoin. Benzoinoxime.—In benzoin, the curve (Fig. 1, middle curves) shows a rapid absorption of the rays towards the red end and a fairly large band at about $1/\lambda$ 4000 (λ 2498), whereas in the oxime this absorption is not so well marked and the band at $1/\lambda$ 4130 (λ 2420) is considerably reduced. These results are comparable with those for benzil as described by Hantzsch and Schwiete (*Ber.*, 1916, 49, 213), who confirmed the earlier observations of Baly and Stewart (J., 1906, 89, 502). The benzoinoxime curve is also comparable with those of the benziloximes described by Hantzsch (*Ber.*, 1910, 43, 1651).

Benzoic Anhydride. Benzoyl Peroxide. Phenyl Benzoate.—The curves (Fig. 1, lower curves) of these three substances, in their general form, are not unlike the curve of benzoic acid, and differ only in strength and position. The author has shown (J., 1915, 107,

FIG. 1.

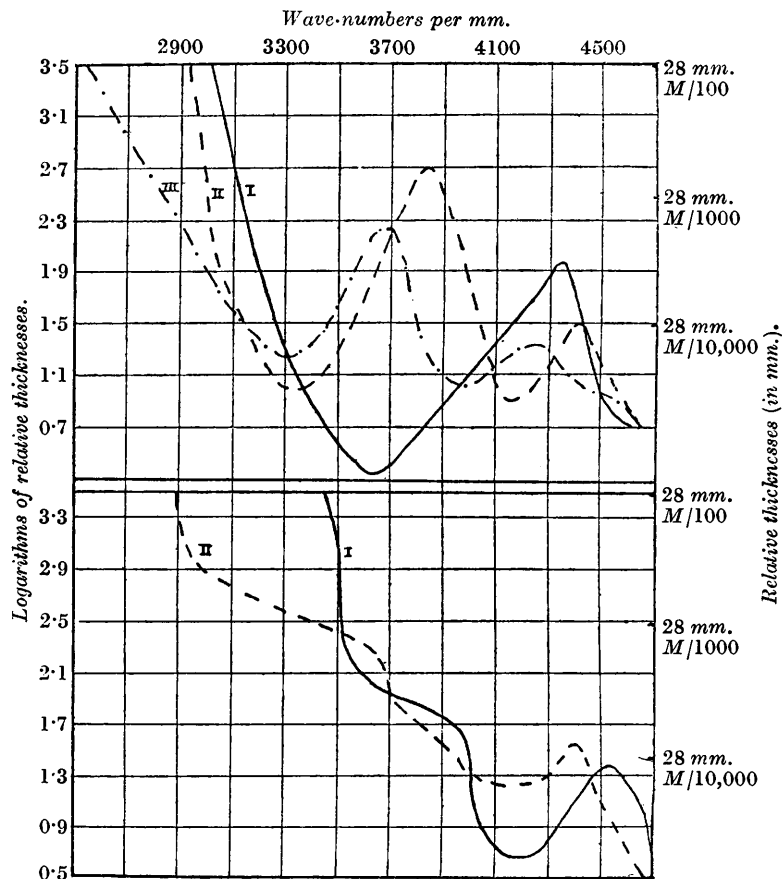


Upper curves : I Benzyl phenylacetate (—). II Phenylacetaldehyde (---).
 Middle curves : I Benzoin (---). II Benzoinoxime (—).
 Lower curves : { I Phenyl benzoate (—). II Benzoyl peroxide (---).
 III. Benzoic anhydride (---).

966) that various benzoates also differ from benzoic acid only in the strength and position of the bands.

Benzyl Salicylate. Benzyl Cinnamate.—Hartley (J., 1888, 53, 641) first described the two bands of salicylic acid. The author (*loc. cit.*) compared salicylic acid with a number of salicylates, and noticed differences dependent on the nature and type of the base.

FIG. 2.



Upper curves : { I Benzyl cinnamate (—). II Benzyl salicylate (---).
 III Thiosalicylic acid (- · - ·).
 Lower curves : I Phenylurethane (—). II Phenylbenzylurethane (---).

The curve of benzyl salicylate (Fig. 2, upper curves) shows the two bands of salicylic acid, but there is no appearance of any of the residues of the benzene bands like those which appear in benzyl phenylacetate. Similarly, benzyl cinnamate (Fig. 2, upper curves) shows the strong band of cinnamic acid at $1/\lambda$ 3620 (λ 2760) as first described by Stewart (J., 1907, 91, 199). In each case, the general

form of the curve is similar to that of the original acid, the slight differences being in position and intensity.

Thiosalicylic Acid.—The curve (Fig. 2, upper curves) is similar to that of salicylic acid, except that the bands are shifted a little more towards the red end, and the line of general absorption is also more towards the red end. Hantzsch and Scharf (*Ber.*, 1913, **46**, 3570) noticed similar differences in a comparison of benzoic and thiobenzoic acids.

Phenylurethane. Phenylbenzylurethane.—The curve of phenylurethane (Fig. 2, lower curves) shows a large band at $1/\lambda$ 4200 (λ 2380). The phenylbenzylurethane shows a weaker band in the same region, but the line of general absorption shifts rapidly towards the less refrangible regions. None of the well-known benzene bands is visible in either substance. Urethane itself gives no absorption bands (Brannigan, Macbeth, and Stewart, *J.*, 1913, **103**, 406) and it is very transparent.

These results, therefore, confirm the author's previous observations of other organic salts and esters in that the absorptive capacity of the basic and acidic parts is modified, and is no longer exactly the same as that of the free base or free acid. The various centres of absorption in any compound, in fact, do not act independently of each other; each centre modifies that of other centres to such an extent that one centre may overpower the influence of the others, as, for example, in the extreme cases of benzyl salicylate and benzyl cinnamate, in which the benzyl bands disappear.

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