CCCLXXXVII.—*The Rotatory Dispersion of Organic Compounds. Part XIX. The Validity of Drude's Equation.*

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THE author's applications of Drude's equation for optical rotatory dispersion have recently been criticised in three publications which are cited in the Annual Reports for 1928 (pp. 14—19). On account of the attention that has thus been directed to them, a reply to these criticisms is now submitted.

(1) Livens, in a paper which was communicated by the author (*Proc. Roy. Soc.*, 1929, **A**, **122**, 245), has introduced a formula in which each optically active band gives rise to *two* terms, thus:

$$\alpha = k_1/(\lambda^2 - \lambda_0^2) \pm k_2/(\lambda^2 - \lambda_0^2)^2.$$

Since *nine* arbitrary constants are used to fit the data for quartz from 25,000 to 1854 Å.U., whilst *five* constants in Drude's equation gave an equally good agreement from 25,000 to 2200 Å.U., the new equation has no obvious superiority over the old; moreover, the number of arbitrary constants is so large that no reliance can be placed on the characteristic frequencies derived from the equation, which is too flexible to give trustworthy numbers. The constants assigned by Livens to the ultra-violet *squared* terms are, however, only 1/2000 and 1/6000 of the values assigned to the Drude terms; this correction, even if it could be established in the case of quartz, is therefore negligible in measurements of the rotatory dispersion of organic compounds. For instance, the specific rotatory power of *sec.*-octyl alcohol (J., 1924, **125**, 1593) over the range 6708—3814 Å.U. is expressed so exactly by one term of Drude's equation (the maximum deviation in the visible spectrum being only 0·01°) that no further improvement could be looked for as a result of introducing a squared term with an additional arbitrary constant.

(2) C. E. Wood and Nicholas (J., 1928, 1671 *et seq.*) have recently elaborated R. W. Wood's theory of " spurious " anomaly (" Physical Optics," 1923, p. 492), according to which anomalous rotatory dispersion in transparent media may be caused by the combined action of optically active absorption bands in the infra-red and ultra-violet regions. As an example of this phenomenon, R. W. Wood cited the early observations of Biot (*Ann. Chim. Phys.*, 1850, **28**, 351) on solid amorphous tartaric acid; but his interpretation of this anomaly is ruled out by the later experiments of Bruhat (*Trans. Faraday Soc.*, 1914, **10**, 84), who has shown that the fused acid exhibits the same " real " anomaly as its aqueous solutions.* C. E. Wood and Nicholas, on the other hand, put forward as a test case the behaviour of a solution of ethyl tartrate in carbon tetrachloride (Lowry and Dickson, J., 1915, **107**, 1173), where " the curves do not become asymptotic to the zero axis in the negative region." They suggest that " it is hard to reconcile this phenomenon . . . with the founding of a general explanation of optical rotation on a Drude equation with the infra-red term omitted," and they make the definite assertion that " by the influence of the infra-red term, the curve is drawn over the axis into the positive region." An examination of this dispersion curve, however, reveals no peculiarities beyond the fact that the reversal of sign occurs in the red region of the spectrum at 6550 Å.U., so that the maximum and the inflexion are displaced into the infra-red at 9020 and 10940 Å.U.

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* The dispersion of the crystalline acid appears to be simple (Longchambon, *Compt. rend.*, 1924, **178**, 951; Lowry and Austin, *ibid.*, p. 1902; *Nature*, 1924, **114**, 430).

(calc.), respectively. The rotatory dispersion of the solution can, in fact, be expressed accurately, like that of the other members of the series, by means of two ultra-violet terms of opposite sign, but in this case of nearly the same magnitude, as may be seen from Table I; and the manner in which the curve crosses the axis is not dependent in any way on the presence or absence of a hypothetical infra-red term.

TABLE I.

Rotatory dispersion of ethyl tartrate in carbon tetrachloride.

$$a = 21{\cdot}65/(\lambda^2 - 0{\cdot}03) - 20{\cdot}13/(\lambda^2 - 0{\cdot}058).$$

λ	6708	5893	5780	5461	4358
$[a]$ obs.	+0·20	−1·34	−1·73	−3·11	−17·17
$[a]$ calc.	+0·20	−1·35	−1·72	−3·08	−17·19
Diff. (obs. − calc.)	± 0	+0·01	−0·01	−0·03	+ 0·02

The agreement shown in this table is so precise that the addition of an infra-red term could only increase the divergence between the observed and the calculated values. This result is in harmony with that given by the homogeneous ester (Lowry and Cutter, J., 1922, **121**, 532), where accurate measurements of the specific rotatory power of 6 dm. of the pure recrystallised compound agreed, throughout the visible spectrum, with a maximum error of only 0·01°, with values calculated with the help of *two ultra-violet terms* of opposite sign, leaving no systematic error for correction with the help of an infra-red term. Another test case is found in the alcohols, which give rise to strong selective absorption in the infra-red, but not in the accessible ultra-violet region. Nevertheless, the optically active carbinols conform closely to the law of simple rotatory dispersion, the rotations being expressed accurately by a single ultra-violet term, with $\lambda_0 = 1500$ Å.U. approx., but without the slightest indication of any disturbance arising from optical activity of the infra-red bands.

C. E. Wood and Nicholas agree with this conclusion to the point of admitting that " quantitative measurements show that the infra-red term is practically negligible in the visible region "; but they support their views by citing the fact that an infra-red term was included in an obsolete equation for the rotatory dispersion of quartz,* which was put forward with ample reservations in 1912 (*Phil. Trans.*, **A**, **212**, 261) as a means of correlating the limited

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* This equation, which contains one infra-red term, and two ultra-violet terms of opposite sign, anticipates by 16 years the principal feature of the theoretical discussion of Wood and Nicholas. The subsequent omission of infra-red terms in equations for the rotatory dispersion of organic compounds is therefore not due to an oversight or to an incomplete consideration of the problem, but has been dictated solely by the experimental results.

range of observations which had been completed up to that date. In the more exact equation, which was set out with full experimental evidence in 1927 (*Phil. Trans.*, **A**, **226**, 391), but which Wood and Nicholas have not cited, this infra-red term has been replaced by a small constant term representing less than 1% of the total rotation in the green. The theoretical significance of this constant is still open to discussion, and it is not certain what will become of it when the equation is extended to cover the whole range of transmission of light by quartz; but even if the data for quartz can no longer be used to vindicate Drude's conclusion that " the kinds of ions whose natural periods lie in the ultra-red are inactive " (" Physical Optics," 1907, p. 413), there is at present no experimental evidence whatever on which a contrary opinion can be founded in the case of transparent organic compounds. It is therefore clear that Wood and Nicholas, in seeking to deduce the configuration of optically active organic compounds from the sign of an infra-red term, are attempting a task which is impossible in the present state of our knowledge, since the *existence* of such a term must surely be proved before its *sign* can be determined. The criterion which they use is in fact the sign of the *high-frequency ultra-violet term,* in compounds which exhibit anomalous rotatory dispersion of the ordinary non-spurious type. Since this high-frequency term is a measure of the " fixed " asymmetry of the molecule, there can be no objection to using it as a guide to the configuration of the compound; moreover, if this criterion is used, it does not matter whether the rotatory dispersion is simple or complex, normal or anomalous; but they do not provide any justification, either theoretical or experimental, for the auxiliary proposition (*Ann. Reports*, 1928, **25**, 16) that "in all cases of anomalous dispersion the sign of the high-frequency term in the Drude equation is . . . opposite to that of the infra-red term." This correlation of the real ultra-violet term with a purely hypothetical infra-red term is indeed a mere speculation, and must remain so until the reality of the latter term has been demonstrated.

(3) Descamps's observations on the rotatory dispersion of borotartaric acid (Thesis, Brussels, 1928, p. 44; compare *Compt. rend.*, 1927, **184**, 453, 876) have formed the basis of experiments (preceding paper) in which the isolation of the borotartrate, KBT_2, is described, and need not be discussed again. It is, however, desirable to state that simple rotatory dispersion cannot be used of itself as evidence of chemical homogeneity, since mutarotating sugars such as glucose may give rise to simple rotatory dispersion if the dispersion constants of the dynamic isomerides are equal; nor can it be used as evidence that there is only one asymmetric centre in the molecule, since the rotatory dispersion of cane sugar, with nine asymmetric carbon atoms

in the molecule, is simple within the limits of experiment. Conversely, complex rotatory dispersion cannot be used of itself as evidence of chemical heterogeneity, since it would then be necessary, not merely to postulate (with Lucas, *Ann. Physique*, 1928, **9**, 381) the existence of isomeric forms of camphor, but even to regard crystalline quartz as a mixture. On the other hand, in the case of camphylcarbinol (J., 1919, **115**, 309), the rotatory dispersion of which was simple (within the limits of Rupe's experiment, *Helv. Chim. Acta*, 1918, **1**, 452) when the carbinol was purified to maximum rotatory power, but complex in the case of less active specimens, it was suggested " that the simple dispersion law may be of value as a test of purity, and that deviations from it may in some cases justify a further examination of the chemical composition of the material used for the measurements." In the same way, therefore, in view of the observations recorded by Descamps, the discovery (if it were to be made) of complex rotatory dispersion in the ultraviolet region in solutions of potassium borotartrate would be regarded as *a priori* evidence of dissociation of the complex ion rather than of complex dispersion in the ion itself.

(4) Greater interest attaches to the deductions made by Kuhn (*Z. physikal. Chem.*, 1929, **B**, **4**, 14), in which the theories of Born (*Physikal. Z.*, 1915, **16**, 251; *Ann. Physik*, 1918, **55**, 177), Oseen (*ibid.*, 1915, **48**, 1), and Landé (*ibid.*, 1918, **56**, 225; compare Gans, *Z. Physik*, 1923, **17**, 353; 1924, **27**, 164; *Ann. Physik*, 1926, **79**, 548; and Rosenfeld, *Z. Physik*, 1928, **52**, 161) have been developed in a simple form which attributes optical rotatory power to an asymmetric coupling of pairs of charged particles, such that when one moves along the axis of x the other has a component along the axis of y. This theory leads to equations of the Drude type, without the squared term introduced by Livens, and practically eliminates the infra-red terms on account of the small amplitude of the low-frequency nuclear oscillations. This last conclusion is supported by the experimental work of Ingersoll (*Physical Rev.*, 1917, **9**, 257), who found no evidence of optically active infra-red bands in an aqueous solution of cane sugar or of tartaric acid, or in an alcoholic solution of camphor, the rotatory powers of which diminished progressively with increasing wave-length right up to the limit of transmission in the infra-red, or in the cases of limonene and pinene, where the rotations were examined on both sides of the hydrocarbon-overtone at 1·8 μ but without giving any indications that the dispersion curves were distorted by passing through this important infra-red band. Since the curves also passed, without a perceptible ripple, through the weaker absorption bands at 1·2 and 1·4 μ, it is clear that the phenomenon which Cotton discovered in

the electronic bands is not reproduced in the three bands due to nuclear oscillations of these hydrocarbons and that, in the only cases in which observations have yet been made, the inactivity of the infra-red absorption bands has thus been established beyond dispute.

Kuhn's equations also lead to the important deductions (i) that the sum of the rotation constants in Drude's equation must be zero, and (ii) that the influence of a pair of coupled oscillators depends on the difference of frequency between them, which may be modified to a larger or smaller extent by the coupling. The first deduction is in accord with the fact that the signs of the partial rotations due to a *fixed* and to an *induced* asymmetry are usually opposite in sign (compare J., 1925, **127**, 1264). Exceptions,* such as α′-bromocamphor, may be attributed to the existence of more than two partial rotations in a given molecule. The second deduction accounts for the fact that the rotatory power of saturated compounds is usually small, and that large rotations are found almost exclusively in unsaturated compounds. It therefore appears that modern physical theory not only endorses the validity of Drude's equation, but is in general agreement with the deductions which have been made from an empirical study of the experimental data.

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