ANOMALOUS ROTATORY DISPERSION.

A Paper by **Professor Leo Tschugaëff**, of the Royal University, St. Petersburg, on "Anomalous Rotatory Dispersion" was communicated by Dr. T. Martin Lowry.

It has been well known since Biot's classical work on rotatory polarization that most of the colourless active bodies exhibit "normal" rotatory dispersion, the numerical values of the optical rotation continuously increasing with decreasing wave-length.*

The dispersion ratios $\frac{[\alpha]_F}{[\alpha]_C}$ of compounds of this class vary for the most part within the limits 1·8-2·0. Quartz, cane sugar, different active hydrocarbons, and alcohols may be cited as examples of such bodies.

Biot was also the first to point out that there are several exceptions to this rule, which belong to the domain of "anomalous" rotatory dispersion. This term is generally applied to those cases in which the optical rotation passes through a maximum or through a zero value or decreases with decreasing wave-length. The rotation and dispersion of these substances are, however, largely influenced by the *temperature* and by the nature of the *solvent*, so that a substance which shows anomalous rotatory dispersion under some conditions may become normal under other conditions.

In the present state of our knowledge we can assume that all the cases of anomalous rotatory dispersion hitherto described may be divided into three classes.

1. To the first class belong all those cases in which anomalous dispersion is due to the *superposition* of the optical rotations of two (or more) *different kinds of normally dispersing molecules* differing in rotatory dispersion as well as in the sign of their rotation.

It was shown by Biot that dispersion of this kind may be observed in mixtures of dextro-rotatory camphor with lævo-rotatory oil of turpentine, and Arndsen † put forward the supposition that the anomalous dispersion of tartaric acid is due to the same cause. Mixtures of *l* menthon with isomenthone ‡ may be cited as a further example.

2. Another type of anomalous rotatory dispersion is intimately related with the existence of *absorption bands* in the spectra of the active compounds in question. The discovery of this type is due to the French physicist, A. Cotton.§

Cotton pointed out in 1896 that the dispersion curves of certain coloured

* Cf. H. Landolt, *Das Optische Drehungsvermögen*, II. Aufl., Braunsch., 1898; P. Walden, *Berl. Ber.*, **38**, 345 (1905).

† *Ann. de chem. phys.*, [3], **54**, 858 (1858).

‡ L. Tschugaëff, *Zeitschr. f. physik. Chemie*, **76**, 469 (1911).

§ A. Cotton, *Recherches sur l'absorption et la dispersion de la lumière par les milieux doués du pouvoir rotatoire*. Thèse, Paris 1896.

solutions, containing, for example, double tartrates of copper or of chromium, go through a maximum in the next neighbourhood of the absorption band, the sign of the rotation being subsequently changed and the curve going through a second maximum of the opposite sign.

Cotton has shown further that the anomalous dispersion in absorbing bodies is intimately allied with the so-called circular dichroism, that is to say the two circular rays resulting from the original plane vibration are not equally absorbed by the active body.

It is well to mention here that Drude,* to whom we are indebted for a general electronic theory of dispersion, has shown that this theory is quite in accordance with Cotton's experimental results.

Cotton carried out his remarkable investigation with solutions of complicated composition; he was not able to isolate his active complex salts nor to obtain them in the state of purity. The same is true of the subsequent measurements of McDowell † and of Grossmann, ‡ who repeated and extended Cotton's experiments.

Five years ago I discovered § a series of coloured and active compounds showing anomalous rotatory dispersion of the same type as Cotton's double salts. These compounds were derivatives of the menthyl-, bornyl- and fenchyl-xanthates and of the corresponding thiourethanes.

It was pointed out that there is a general parallelism between the absorption spectra of these bodies and the shape of their dispersion curves. || A still closer parallelism holds between the dispersion and absorption produced by one and the same active body in different solvents, the absorption and the dispersion curves being always displaced in the same direction by passing from one solvent (toluene) to another (acetone).

On the other hand evidence was brought forward that the anomalous dispersion was not due to the influence of the solvent, since the compounds in question showed this property also in a state of superfusion. ¶ But still more noteworthy is the recent work of Bruhat ** and Cotton, †† who succeeded in observing circular dichroism in one of my substances—I : 2-diphenyl-3-l-bornylimido xanthide—of the following constitution—

and pointed out that the connection between this phenomenon and the sign of the optical rotation in both the antipodes is exactly the same as is required by theoretical considerations.

During the investigations performed in my laboratory it was shown that abnormalities may occur in the shape of the dispersion curve of an active and colourless compound if it exhibits an ultra-violet absorption band in the neighbourhood of the visible spectrum. ‡‡

* *Optik*, 1906.

† *Physical Review*, 1905, 163.

‡ *Chem. Centralblatt*, 1908, II, 1996; *Zeitschr. f. physik. Chemie*, **72**, 93 (1910).

§ L. Tschugaëff, *Berl. Ber.*, **42**, 2244 (1909).

|| L. Tschugaëff und A. Ogorodnikoff, *Zeitschr. f. physik. Chemie*, **74**, 503 (1910); **79**, 481 (1912).

¶ L. Tschugaëff und A. Ogorodnikoff, *Ann. Chim. Phys.*, [8], **22**, 137 (1911).

** G. Bruhat, *Comptes Rendus*, **153**, 248 (1911).

†† A. Cotton, *Comptes Rendus*, **153**, 245 (1911).

‡‡ L. Tschugaëff, *Zeitschr. f. physik. Chemie*, **76**, 469 (1911); *Bull. Soc. Chim.*, [4], **11**, 718 (1912). L. Tschugaëff et A. Kirpicheff, *Bull. Soc. Chim.*, [4], **13**, 796 (1913).

Thus the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ of many ketones goes far beyond the normal limits mentioned above, e.g. :

Substance.	$\frac{[\alpha]_F}{[\alpha]_C}$	Solvent.
Camphor	2.69	Methylic alcohol
Epicamphor	2.76	Methylic alcohol
aa-Dibromcamphor	3.13	Benzene
aa-Diodocamphor.....	3.41	Benzene
Dihydrocarvone.....	3.30	None
Pulegone	2.76	None
1-Methyl-cyclohexan-3-one	3.50	None
Nopinone.....	3.75	None
Pinonic acid	2.63	Methylic alcohol

The dispersion curves of such ketones for the most part cannot be expressed by the simple formula given by Drude—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

Moreover, the rotations are influenced very largely by the nature of the solvent, just as is the case in substances showing anomalous rotatory dispersion.

On the other hand it is well known that the ketones exhibit a general absorption band at about 3,500–3,800 A.U., whereas the saturated hydrocarbons and alcohols are practically diactinic for these radiations. We are therefore justified in concluding that the exaltation of the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ in the ketones is intimately associated with the nature of the absorption spectra of these compounds.

As a matter of fact it was shown by Darmois* that camphor exhibits the typical form of anomalous dispersion in the neighbourhood of the ultra-violet absorption band.

Quite the same seems to be true in the case of *aldehydes*, which, like the ketones, show selective absorption in the ultra-violet, as was pointed out recently by Henry and others. Miss S. Matthiesen undertook at my suggestion the optical study of the following members of the citronellal group :

Citronellal.

$$\frac{[\alpha]_F}{[\alpha]_C} = 2.42.$$

Dihydrocitronellal.

$$\frac{[\alpha]_F}{[\alpha]_C} = 2.40.$$

E. Darmois, *Recherches sur la polarisation naturelle et la polarisation rotatoire magnétique*. These, Paris, 1910.

Citronellyl alcohol.

$$\frac{[\alpha]_D}{[\alpha]_C} = 2.04.$$

Dihydrocitronellyl alcohol.

$$\frac{[\alpha]_D}{[\alpha]_C} = 1.93.$$

It will be seen that the aldehydes examined possess almost as high a dispersion as many ketones, whereas the corresponding alcohols give quite normal dispersion ratios.

3. We may now turn to the third and last type of anomalous rotatory dispersion.

It was recently shown by the author * that anomalous dispersion may be produced by the *superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body*, the necessary condition being that these partial rotations should be of *opposite sign* and should possess *different dispersion ratios*.

As an example of bodies which belong to this type, menthyl β -camphor-sulphonate may be cited, the two centres of activity being the menthyl and the camphor radicles :

R. W. Wood † has recently pointed out that there must exist a special case of anomalous dispersion which he denotes as "spurious," which is intimately related to the type just alluded to. Wood concluded from theoretical considerations that anomalous dispersion must ensue if we have two electrons in an active molecule, one in the infra-red and the other in the ultra-violet. If these electrons rotate in the same direction, the rotation may be expected to go through a zero value near the middle of the visible

* L. Tschugaeff, *Berl. Ber.*, **44**, 2023 (1911). L. Tschugaeff und G. Glinin, *Berl. Ber.*, **45**, 2759 (1912).

† *Physical Optics*, New York, 1911.

spectrum, whilst if they are of opposite sign, one being dextro-rotatory and the other laevo-rotatory, the rotation will have a minimum value. In Professor Wood's opinion the case of tartaric acid is of this type.

It is well to bear in mind also that each anomalous dispersion curve must necessarily be influenced by the superposition of the consequent partial rotations if more than one asymmetric carbon atom (or generally more than one centre of activity) is present in the molecule of the active substance.

For this reason it is not surprising that there is no complete parallelism * between the presence of an absorption band and the appearance of anomalous dispersion in the visible spectrum.

Thus menthyldixanthogenide, $C_{10}H_{19}-OCS-S-S-CSO-C_{10}H_{19}$, and bornyldixanthogenide, $C_{10}H_{17}-OCS-S-S-CSO-C_{10}H_{17}$, exhibit anomalous rotatory dispersion within the limits of the visible spectrum, whilst the fenchyldixanthogenide (isomeric with the bornyl derivative just mentioned and possessing a similar spectrum) does not possess this property.

In order to clear up the nature of the dispersion curves resulting from optical superposition it is necessary to examine first if the superposition rule is generally valid, and secondly in what degree these partial rotations themselves are influenced by mere constitutional factors.

The principle of optical superposition, first suggested by Van't Hoff,† was subsequently subjected to an experimental test by Guye and Gautier‡ and by Walden† and recognized as valid. Recently, however, Rosanoff‡ and Patterson§ and his pupils put forward theoretical objections and experimental evidence against the validity of this principle, their arguments being based on a comparison of the optical rotation produced by the methyl esters of the isomeric diacetyltartaric acids.

According to the theory of optical superposition the rotation of the ester corresponding with mesotartaric acid should be equal to half of the sum of the rotations produced by the ester of *d* and *l* tartaric acids. The maximum departure from the theoretical value in the experiments of Patterson amounted to 18 per cent. But the rotation values of these esters are largely influenced by the nature of the solvent used, and Van't Hoff suggested therefore that analogous experiments should be made in more comparable conditions.

As a matter of fact, experiments performed by Mr. Glebko|| at my suggestion with *l* menthyl and fenchyl urethanes of the isomeric diethyltartrates gave much better agreement with theoretical values, the difference varying from 1 to 5 per cent. Consequently the superposition rule seems to be valid at least to a first approximation.

Experiments quite recently performed in my laboratory have shown that the dispersion curve of an active substance is influenced not only by the absorption bands, but by the distance of the centres of activity from the chromophores of the active molecule. Thus a chromophore group situated in the neighbourhood of a centre of activity may produce anomalous dispersion within the limits of the visible spectrum, whilst if sufficiently remote from such a centre its influence on the shape of the dispersion curve may be small or negligible.

* L. Tschugaeff und A. Ogorodnikoff, *Zeitschr. f. physik. Chemie*, **85**, 481 (1913).

† Cf. Van't Hoff, *Lagerung der Atome in Raume*, III Aufl., Braunschweig, 1908.

‡ Rosanoff, *Zeitschr. f. physik. Chemie*, **56**, 565 (1906).

§ T. S. Patterson, *Fourn. Chem. Soc.*, **89**, 1539 (1906); **91**, 705 (1907).

|| *Berl. Ber.*, **46**, 2752 (1913).

To take an instance, of the two metameric esters corresponding to *l* menthol—

it is only the first (I) which shows anomalous dispersion in the visible region, the dispersion of the ester II being quite normal.*

Now in the ester I the chromophorous group CS-S is separated from the active radicle $\text{C}_{10}\text{H}_{19}$ only by a single oxygen atom, whilst in the second ester these two radicles are separated by a chain of three atoms

The above conclusion is quite analogous with a rule put forward by the author some sixteen years ago† for optical rotations corresponding with one definite ray of the spectrum, namely the D line of sodium. According to this rule the influence of an inactive substituent introduced into an active molecule at a point sufficiently remote from the centre of activity is very small, but its influence attains its highest value if the place occupied by the substituent is in the neighbourhood of the inactive complex.‡

It is particularly noteworthy that the radicles, the introduction of which into the molecule of an active substance causes the rotation values for the most part to be raised (*e.g.*, the radicles with a double linkage, the aromatic groups, etc.), and the chromophores which are responsible for anomalous dispersion possess the same chief feature, for they are both *unsaturated* groups.

In the author's opinion the modern electronic theory of rotatory polarization and dispersion created by Drude§ is capable of throwing some light on this question and of giving a rough idea of the influence which the constitutional factors just considered may exert on the sweep of the dispersion curve.

Drude has put forward the idea that optical rotation is due to a peculiar form of electronic motion. He assumes that the dispersion electrons which are capable of being set in vibration by the impacts of the light waves are forced in active bodies to move to and fro in a spiral path instead of along straight lines, the direction of the motion corresponding with the sign of the rotation. This motion is obviously due to the asymmetric distribution of matter within the molecules of the active compounds.

Drude makes no special hypothesis as to the position occupied by the active electrons, but it seems reasonable to suppose that the most active of them are attached to the asymmetric carbon atom itself, or are situated in the immediate neighbourhood of the centre of activity. As regards the other electrons which come into play in rotatory dispersion, we can assume that their activity is diminished with increasing distance from the asymmetric complex.

* This work (not yet published) was performed at my suggestion by Mr. W. Lebedinski.

† *Berl. Ber.*, **31**, 360, 1775, 2451 (1898); *Journal of the Russian physik. Chem. Society*, (II), **29**, 122, 227 (1897); **30**, 18, 51, 188, 217 (1898); (I), **34**, 606 (1902).

‡ These conclusions are by no means altered by the results of the very beautiful work of Messrs. Pickard and Kenyon, which show secondary irregularities in the rotation curves in homologous series at points at which the carbon chain can return upon itself (R. H. Pickard and J. Kenyon, *Journ. Chem. Soc.*, **99**, 45; **101**, 620, 1427; **103**, 1923). See also the very remarkable Presidential Address by P. F. Frankland (*Journ. Chem. Soc.*, **101**, 656).

§ *Optik*, 1906.

In the spectrum of colourless saturated organic compounds there seems to exist a very deep band (or several bands) in the inaccessible ultra-violet, and it is very probable that to this band is due the general shape of the "normal" dispersion curve, its "anomalous" portion being restricted to the neighbourhood of the band.

This view is in accordance with the results recently obtained by T. M. Lowry* in his very remarkable investigations on both magnetic and optical rotatory dispersion. Lowry pointed out that the dispersion of many colourless active compounds in the visible spectrum may be represented by means of an equation given by Drude with but two constants:

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2},$$

λ_0 being the wave-length of the remote ultra-violet band.

If, however, the substance in question possesses another absorption band within the limits of the visible spectrum, the dispersion curve becomes anomalous in the accessible spectral region, and even if the selective absorption occurs in the near ultra-violet, as in the case of the ketones above mentioned, the shape of the curve corresponding to the visible part betrays the neighbourhood of an absorption band, the dispersion ratios assuming abnormally high values.

Let us first turn our attention to colourless compounds and consider in what manner the different inactive radicles of an asymmetric molecule—

containing but one asymmetric carbon atom, can influence the rotation value and the shape of the dispersion curve.

As we have seen, the chief part of the optical rotation will be produced by the electron (or electrons) attached to the asymmetric carbon atom itself and will remain in direct relation to the deviation of the spiral path along which the electron moves from a straight line. Now it may be admitted that this deviation should be proportional to the degree of asymmetry of the molecule as measured by the product of the differences of four constants, K_1 , K_2 , K_3 , and K_4 , corresponding with the four groups R^I , R^{II} , R^{III} , and R^{IV} of the molecule $CR^I R^{II} R^{III} R^{IV}$, as was originally suggested by Ph. A. Guye† and by Crum-Brown.‡

$$P = (K_1 - K_2)(K_1 - K_3)(K_1 - K_4)(K_2 - K_3)(K_2 - K_4)(K_3 - K_4).$$

Perhaps we should not be far from the truth if we assume further with Guye that the variables $K_1 \dots K_4$ are functions of the masses of the radicles attached to the asymmetric atom, although we do not know the exact nature of this function; but in any case, if these four groups differ materially in their degree of saturation, we shall still have to consider the influence of another constitutional factor on rotation; thus, it would be expected that strongly un-

* T. M. Lowry, *Phil. Trans.*, **212**, 261 (1912); *Journ. Chem. Soc.*, **103**, 1062 (1913); T. M. Lowry and T. W. Dickson, *Journ. Chem. Soc.*, **103**, 1067 (1913); *Proc. Chem. Soc.*, **29** (1913).

† Ph. A. Guye, *Étude sur la dissymétrie moléculaire*, Geneve, 1891.

‡ Professor Crum-Brown, *Proc. Roy. Soc. of Edinburgh*, 1890, 181.

saturated radicles containing free-movable electrons would exert a considerable influence on the electric field produced by the molecule, the differences $K_1 - K_2 \dots$ being much larger if K_2 corresponds with a saturated group and K_1 to an unsaturated one than if both the groups are nearly equally saturated.

From this point of view it may easily be understood why the influence of unsaturated groups on the rotation values is considerable only when in immediate proximity to the asymmetric carbon atom.*

On the other hand, the rotation and dispersion produced by an active molecule

may be influenced by the vibration of the electrons attached to the radicles R' , R'' , R''' , $R''v$, as well as to the asymmetric carbon atom itself, for the asymmetry of the field within the molecule must cause all these electrons to move along spiral paths. Consequently, each radicle must contribute by means of its electrons to the value of the optical rotation produced by the molecule as a whole, and (the free periods of these electrons being in general different) also to the resulting dispersion. It may be noted also that it is by no means necessary that the electrons in the four radicles and in the central atom should rotate in the same direction. Consequently it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion. The anomaly will be due in this case to the superposition of the effect produced by the electrons attached to the different radicles of the same molecule. The question as to whether such cases can be realized in practice can be settled only by experiment, but it is possible that some cases of anomalous rotatory dispersion quite recently noticed by R. H. Pickard and J. Kenyon† should be classed in this category.

Time will not permit of further discussion of the influence of chemical constitution on the rotatory dispersion in active compounds, but I should like before concluding to touch briefly upon an allied question which claims a very considerable interest.

It was pointed out by Chr. Winther‡ and by P. Walden§ that the dispersion curves of several anomalously dispersing bodies are largely influenced by the temperature at which their rotations are taken and by the nature of the solvent used.

It seems to be the current opinion that this particular behaviour is due to a displacement of equilibrium between the two (or more) different kinds of molecules which are assumed to constitute the active substance.

A quite different hypothesis, however, was put forth recently by R. W. Wood, the distinguished American physicist. He assumes, as previously mentioned, that the anomalous dispersion of tartaric acid may be due to the existence of two active electrons in its molecule.

This hypothesis is in complete accord with the view just put forward, that

* It seems to be permissible in this case, at least to a first approximation, to compare the effects produced on the rotation by different substituents entering into the molecule for one determined wave-length, e.g., for the D sodium line, as has so often been done.

† *Proc. Chem. Soc.*, **29**, 296 (1913).

‡ Chr. Winther, *Zeitschr. f. physik. Chemie*, **41**, 161 (1902); **45**, 331 (1903).

§ P. Walden, *Berl. Ber.*, **38**, 345 (1905); *Zeitschr. f. physik. Chemie*, **55**, 1 (1906).

several electrons may be active in a molecule containing but one asymmetric carbon atom, in which case the rotatory power as well as the dispersion of the substance in question will be equal to the sum of the effects produced by its several active electrons.

On the other hand, it is very probable (1) that the configuration of the molecule, and consequently the degree of asymmetry of the corresponding asymmetric field, is a function of the temperature, and (2) that the intensity of this field is not equally influenced in its different parts by the same rise of temperature.

It seems to be quite possible, therefore, that the influence of different active electrons may become dominant at different temperatures, and that a substance which possesses normal rotatory dispersion at a certain temperature t_1 may become anomalous at another temperature t_2 . It is, however, very difficult in the present state of our knowledge to distinguish between such a case and the case of a mixture of two active bodies which present anomalous dispersion at certain temperatures only.

Similar considerations may apply in relation to the influence of solvents on anomalous rotatory dispersion. It is, therefore, easy to understand that, from the above point of view, active bodies which are especially sensitive to the influence of the temperature and of the solvents must have a marked tendency to present the phenomenon of anomalous rotatory dispersion.* Since nearly the whole of the experimental data concerning the influence of temperature and of the solvent on anomalous rotatory dispersion have been derived from derivatives of tartaric and malic acid,† it seemed advisable to undertake analogous experiments with active bodies representing the different types of anomalous dispersion above mentioned. This work has been carried out in my laboratory in conjunction with Messrs. Pigoulewsky, Pastanogoff, and Ogorodnikoff.‡

The results obtained have two important bearings : firstly, they show that sensibility to the influence of temperature and to the nature of the solvent is not confined to colourless bodies exhibiting anomalous dispersion of the type of tartaric acid, but occurs also in substances exhibiting Cotton's phenomenon and in those which possess anomalous dispersion due to intramolecular optical superposition.

It may be noted also that this sensibility can be very different in closely related substances. To take an instance, the dispersion of the thioanhydride of the menthylxanthogenic acid $C_{10}H_{19}O-CS-S-CS-O-C_{10}H_{19}$ is very considerably influenced by temperature, while the sensibility of the corresponding fenchyl derivative is quite insignificant, in spite of the fact that both dispersion curves are nearly identical in shape.

Secondly, it follows from our experiments that in many cases the anomalous dispersion curves are shifted by the influence of temperature or by the nature of the solvent in the same direction as in the case of tartaric acid and its esters. For instance, the behaviour of the thioanhydride of menthylxanthogenic acid $C_{10}H_{19}OCS-S-CSO-C_{10}H_{19}$ towards temperature and the influence of different solvents on the dispersion of menthyldixanthogenide,

* Quite recently R. H. Pickard and J. Kenyon stated that certain esters containing but one asymmetric carbon atom exhibit anomalous rotatory dispersion at high temperatures as well as in several solvents (*Proc. Chem. Soc.*, **29**, 296 (1913)). In the author's opinion this effect may be due to the intramolecular superposition of the effects produced by several active electrons.

† *Zeitschr. f. physik. Chemie*, **85**, 481, 553 (1913).

‡ The details of the experiments of R. H. Pickard and T. Kenyon above mentioned are not yet available.

$C_{10}H_{19}OCS-S-S-CSO-C_{10}H_{19}$, may be cited. In both cases the curves are at the same time raised and shifted to the violet end of the spectrum, precisely as Winther and others have observed is the case in the tartaric series. This analogy is a very remarkable one, and whatever its final interpretation may be, there is no doubt that there must exist some intimate relation as to the origin of the anomaly in both cases.