water, very little light is diffused, the chief road brightness coming apparently from the image of the lamp. So far, means have not been found of rendering visibility anything like as good under wet as under dry conditions.

The use of a large quantity of light merely to claim compliance with a higher class of specification of the British Standards Institution without ensuring that it gives a proportionally higher road brightness is wasteful. Competition in illumination is useless, but competition in road brightness is of real value and importance. However, it is inadvisable to skimp the light and reduce its amount to the minimum

required for the road surface. A certain amount of light on buildings and fences makes a great difference to the appearance of the lighting effect and sometimes aids visibility.

Mr. Paterson's address contains much novel matter, and it looks as if our ideas on street lighting would be considerably modified in the next few years. To all who drive motor-cars or ride bicycles, a good road brightness is essential as safety depends on it. Only in this way can we safely eliminate the use of headlights and the risky situations which arise from their use on busy roads.

Polarimetric Methods in Chemistry*

By PROF. T. M. LOWRY, C.B.E., F.R.S.

ARREST OF MUTAROTATION

FURTHER fortuitous observations showed that the mutarotation of nitrocamphor is not an independent intramolecular process, but depends on extramolecular circumstances, since under favourable conditions it may be arrested more or less completely over a period of several days. This discovery (which was made more than twenty years before Kurt Meyer's experiments on the aseptic distillation of ethyl acetoacetate in alkali-free vessels of silica glass) was also the result of a fortunate accident. The mutarotation of a solution of nitrocamphor in chloroform had been followed to completion during a period of about eight days, but had been accompanied by some loss of solvent (and possible concentration of the solution) by evaporation. The remainder of the solution had been left in the small graduated flask in which it had been prepared, and there was no reason to suspect that it would behave in any respect differently from the sample in the polarimeter tube. It was therefore a great surprise when, at the end of seventeen days, on attempting to confirm the *final* reading, it was found that the residue in the flask gave a rotation almost identical with the *initial* reading recorded more than a fortnight before. The transfer of the solution to the polarimeter tube, however, sufficed to initiate the mutarotation, which then proceeded with the same velocity as before.

Nearly ten years later, a further series of experiments was being made on the catalysis of mutarotation by acids and bases. It was then observed that solutions of nitrocamphor in chloroform, to which trichloroacetic acid had been added, developed an intolerable and pungent odour. This observation showed that the peculiar inertness of chloroform was due to its oxidation to carbonyl

chloride or phosgene, and to the consequent elimination of traces of nitrogenous bases, in the form of inert carbamides. The same series of experiments had already shown that some of these bases have an amazing catalytic activity. Thus an acceleration of mutarotation was detected as a result of adding piperidine to benzene in the proportion of 1 part of the base in 10 million parts of the solvent. This acceleration was also one of the earliest examples of a phenomenon which has since become very familiar, namely, a catalysis by bases, which could not be attributed to the presence of hydroxyl ions, and was therefore outside the scope of the conventional theories of catalysis by acids and bases, as developed and used by Ostwald and his colleagues.

An immediate sequel to this discovery was the arrest in silica vessels of the mutarotation of solutions of nitrocamphor in benzene and in ether, to which traces of an anticatalyst had been added. Subsequent experiments showed that mutarotation could also be arrested in solutions of tetramethylglucose in chloroform, benzene, ethyl acetate and pyridine; and Owen developed to a fine art the process of arresting, almost at will and with very few failures, the mutarotation of solutions of tetra-acetylglucose in dry ethyl acetate.

The climax of this work was reached when Faulkner found that the mutarotation of tetramethylglucose could be arrested both in cresol and in pyridine, but proceeded too rapidly for convenient observation in mixtures of these two solvents. Since these mixtures gave velocities of mutarotation which were much greater even than in water, it was clear that the essential factor in promoting mutarotation was not an oxygenated solvent, or an ionising solvent (as had been suspected at earlier periods), or even the ionisation

* Continued from p. 921.

of the sugar by an acid or basic catalyst (as most other workers had assumed), but that an amphoteric solvent must be provided to serve as a complete catalyst for the process.

PROTOTROPY

The migration of a hydrogen atom, in compounds such as nitrocamphor and the sugars, was thus shown to depend on the addition and removal of a proton at two opposite poles of the organic molecule. Since no satisfactory name had been adopted for this important group of isomeric changes, I proposed in 1923 to describe them by the term *prototropy*. The migration of a proton was, however, regarded as only a special example of the more general phenomenon of *ionotropy*, in which a radical migrates from one part of a molecule to another either as an anion or as a cation.

The addition and removal of the ion from the two poles of the organic molecule may be either simultaneous or consecutive, but in either case it leaves behind a positive or negative charge. In order that this type of isomeric change may proceed, it is essential that these opposite charges should be neutralised. The electronic theory of valency allows us to recognise that this is done by the rearrangement of bonds which accompanies prototropic change, since a valency electron is thereby transferred *through the interior of the molecule*, to neutralise the charge of the proton, which is transferred *through the amphoteric solvent*.

The migration of a hydrogen atom, to which the most fertile types of mutarotation are due, was thus linked up to an extended definition of acids and bases, which I set out in 1923, at a time when it must have been in the minds of many other workers, and which was described more fully by Brönsted a few months later. Thus, if we define an acid and a base as a proton donor and acceptor respectively,

where B is the base and HA the acid, the migration of a proton in a prototropic compound under the combined action of a base B and an acid HA can be expressed by the equation

used by Brönsted and Guggenheim, where HS and SH represent the two isomeric forms of the substrate.

The process of isomeric change, as set out above, can be regarded as an electrolysis of the organic molecule between positive and negative poles, provided by the acid and basic components of the amphoteric solvent. This mechanism has there-

fore been described as an "electrolytic theory of catalysis by acids and bases". Similar conditions, however, prevail in all conjugated systems, and these can now be formulated in general terms, as systems in which opposite charges at the ends of the system can be neutralised by a migration of valency electrons through the system.

ROTATORY DISPERSION

At the time when the earlier measurements of mutarotation were made, it was customary to measure the optical rotations of organic compounds only for the yellow sodium line. Work on rotatory dispersion had indeed been suspended almost completely since the death of Biot in 1862, and the discovery of the Bunsen burner in 1866. It was, however, certain that little progress could be made in elucidating the origin of optical rotatory power, or in predicting its magnitude, until the values of the rotatory power were known over a wide spectral range, instead of for a single casually determined point on the curve of rotatory dispersion.

The ignorance then prevailing in reference to this important aspect of the subject is shown by the fact that, when Drude wished to test his equation for optical rotatory dispersion, he was only able to make use of data for quartz, since the rotatory dispersion of no one of the hundreds of optically active compounds prepared and studied by organic chemists was known with sufficient accuracy to be used for this purpose; and his equation for magnetic rotatory dispersion was tested on data for five wave-lengths only, for carbon disulphide and for creosote.

Experiments carried out in order to supply the data required to determine the form of the curves of rotatory dispersion in organic compounds soon led to definite conclusions. Thus in 1913 I was able to show, with T. W. Dickson, that the optical and magnetic rotations of many simple organic compounds for eight wave-lengths in the visible spectrum could be expressed by *one* term of Drude's equation:

$$\alpha = k/(\lambda^2 - \lambda_0^2).$$

In the following year we found that *two* terms of opposite sign:

$$\alpha = k_1/(\lambda^2 - \lambda_1^2) - k_2/(\lambda^2 - \lambda_2^2),$$

could be used in the same way to express the anomalous rotatory dispersion of ethyl tartrate. This result confirmed the conclusion reached at a much earlier period by Biot and by Arndtsen, that anomalous rotatory dispersion has its origin in the superposition of two partial rotations of opposite sign and of unequal dispersion. These partial rotations may be due to very diverse

causes, ranging from the presence of two optically active absorption bands in the same molecule, to the case in which two liquids of opposite rotatory power and unequal dispersions are arranged in series in separate polarimeter tubes. This diversity has resulted in a certain amount of controversy as to the *origin* of the partial rotations which give rise to anomalous rotatory dispersion, but the essential facts represented by Drude's equation are established beyond dispute.

SIMPLE AND COMPLEX ROTATORY DISPERSION

On the basis of observations such as these, we proposed to describe as *simple* those rotatory dispersions which can be expressed by one term of Drude's equation, and as *complex* those which cannot be so expressed.

This classification is more fundamental than the earlier classification of those rotatory dispersions which increase progressively with decreasing wave-length as *normal* and of those which exhibit an inflexion maximum or reversal of sign as *anomalous*. Thus, no progress can be made in studying the optical rotatory power of organic compounds until the observed *total rotations* have been resolved into their component *partial rotations*. On the other hand, the distinction between normal and anomalous rotatory dispersion in compounds such as ethyl tartrate depends only on the relative magnitude of the two rotation constants, k_1 and k_2 , of a Drude equation with two terms of opposite sign.

In general, simple rotatory dispersions are only observed when the characteristic frequencies of all the partial rotations lie close together in the Schumann region, giving a dispersion ratio $\alpha_{4368}/\alpha_{5461} = 1.6$ approximately. Thus, in the sugar series, the partial rotations associated with the nine asymmetric carbon atoms of cane-sugar give rise to a simple dispersion; but this is not always so, since even in a sugar the characteristic frequencies of the radicals may cover a wide range in the Schumann region, and the foot of the absorption bands often extends into the ordinary ultra-violet.

ROTATORY DISPERSION IN ABSORBING MEDIA

Additional partial rotations of lower frequency give rise in the region of transparency to complex or anomalous rotatory dispersions. In the region of absorption they give rise to the remarkable anomalies which have been known since 1896 as the *Cotton effect*. These anomalies are much more dramatic than those observed in the region of transparency in compounds such as ethyl tartrate. Thus the specific rotation of camphor vapour,

which is only about 55° in the yellow visible region, rises rapidly to $+2,000^\circ$ on entering the region of absorption, then passes through a zero value at about 3000 Å. and finally falls to a negative maximum of about $-1,800^\circ$ before emerging from the absorption band.

In the remarkable case of tetra-acetyl- μ -arabinose, $H[CHOAc]_4.CHO$, the partial rotations associated with the three asymmetric carbon atoms cancel out. The whole of the rotatory power is therefore due to the partial rotation associated with the carbonyl group. This gives rise to a symmetrical loop, with equal and opposite maxima $[\alpha] = \pm 1,200^\circ$ on either side of a zero rotation at 2909 Å. The form of this loop cannot be expressed by Natanson's form of Drude's equation, in which the width of the absorption bands was attributed to a 'damping factor'. It can be represented, with a maximum deviation of 200° , by the equation of Kuhn and Braun, who assumed a probability distribution of *frequencies* in the absorption band; but this deviation is reduced to 30° by using the equation of Lowry and Hudson in which the absorption is distributed symmetrically on a scale of *wave-lengths*.

INDUCED DISSYMMETRY

The existence in camphor and its derivatives of a partial rotation having the characteristic frequency of the ketonic absorption band was attributed by Lowry and Walker in 1924 to the *induced asymmetry* (or better *induced dissymmetry*) of the carbonyl group. According to this conception, the symmetrical carbonyl group becomes dissymmetric under the influence of the unsymmetrical field of an optically active molecule, when coupled sufficiently closely to an asymmetric carbon atom. It therefore contributes directly to the optical activity of the molecule, whereas less polarisable groups, such as $>CH_2$ or $>CMe_2$, contribute relatively little to the total rotation, even when they are exposed to a similar dissymmetric field.

This hypothesis has received support from the molecular theory of optical rotatory power, recently developed by de Malleman and by S. F. Boys. According to their theory, optical rotatory power in a region of transparency depends on a product of four refractivities divided by the square of the wave-length of the light. It has been shown that this theory can only be extended to the region of absorption by postulating an additional centre of dissymmetry within the chromophoric group in optically active aldehydes and ketones. This extension is in harmony with the conception of induced dissymmetry, which thereby receives important confirmation.