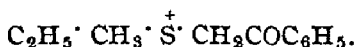


THE PRODUCTION OF OPTICALLY ACTIVE SUBSTANCES AND METALLIC FILMS OF SILVER, PLATINUM AND PALLADIUM BY MEANS OF CIRCULARLY POLARISED LIGHT.*

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In 1824 Fresnel showed that two oppositely circularly polarised light of the same amplitude might not travel through a refracting medium with the same velocity. On passing through such a medium, a plane polarised beam of light, which can be resolved into two such circular vibrations, will show a rotation of the plane of polarisation. Pasteur showed that in transparent crystals, such rotatory powers are associated with hemihedral faces which are so oriented that the *dextro* crystal is the mirror image of the *laevo* one. This kind of asymmetry is not confined to crystalline structures only. Molecules themselves may be asymmetric, and in solution or the gaseous state, can rotate the plane of polarisation of light. Van't Hoff arranged the atoms of the chemical molecule in three dimensions and directed the four valences of the carbon atom towards the corners of a tetrahedron with the carbon atom at its mass centre. If all the four atoms or radicals attached to the central carbon atom are different, optical isomerism will arise, one configuration being the mirror image of another and not superposable. Van't Hoff also foreshadowed the existence of dissymmetric compounds of the allene type which would show optical activity even in the absence of an asymmetric central atom. In the case of complex co-ordination compounds containing six radicals round a central metal atom, Werner postulated an octahedral model, and demonstrated the conditions which would produce optical isomerism. The list of elements from which optically active compounds have been prepared has now been extended to twenty-one elements as follows :—

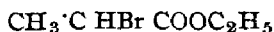
Be, B, C, N, Al, Si, P, S, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Te, Ru, Rh, Ir and Pt. In preparing these compounds no fundamentally new principles have been discovered other than those postulated by Van't Hoff and Werner excepting perhaps the significant one, that a lone pair of electrons in an octet can take the place of a radical in bringing about optical isomerism in ions of the type



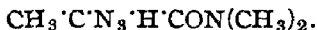
* Presidential address delivered at the Annual General Meeting of the Indian Chemical Society, at Lahore on Jan. 7, 1939.

In synthetic work in the laboratory, racemic mixtures are always obtained consisting of exactly equal proportions of the two optical isomers. Pasteur's original method of resolving these racemic mixtures by the use of optically active acids or bases has been considerably extended by Pope and others in recent times, and it is now possible to effect resolution for any such mixture.

In living organisms, however, only one type of optically active molecule is produced, and the artificial resolution of racemic compounds in laboratories is effected by optically active substances which ultimately owe their origin to natural sources. Ever since Wöhler's synthesis of urea, the upholders of the vitalistic theory have continually retreated from their untenable positions until they held on to the production of optically active compounds as the chief plank in their support. As early as 1894, Van't Hoff remarked that it is exceedingly probable that under asymmetric conditions of experiment, the same direct formation of optically active bodies will result as we observe in the processes of natural synthesis, *e.g.*, in transformations taking place under the action of *dextro* or *laevo* circularly polarised light. It is only, however, almost a century after the classical work of Wohler, that in 1930 Kuhn and collaborators succeeded in decomposing a solution of



in alcohol with the aid of circularly polarised light ($\lambda = 2800\text{\AA}$). It was found that if 50% of the ester were decomposed with the aid of *dextro*-light, the solution that remained over, was found to show *dextro*-rotation, indicating that under the influence of *dextro*-light in the ultraviolet, the *laevo*-ester decomposed much faster than the *dextro*-ester. The next important investigation was that of Freudenburg and Kuhn where the following ester was used :—



Hexane solutions of this compound were exposed to *laevo* rotations ($\lambda = 2800\text{\AA}$). After 37% decomposition by *laevo*-light, the unchanged dimethylamide was separated from hexane and other decomposition products by distillation under reduced pressure. It showed a rotation of, 1° in a decimeter tube in mrrcury yellow light.

It may be asked that these experiments are not very difficult—why then was there a long tale of frustrated attempts between Van't Hoff's prophecy of 1894 and Kuhn's achievement in 1930. I shall try to indicate the explanation

in simple language. The rotatory power of an optically active substance is generally measured for the sodium D line, but this power changes with wave-length much in the same way as does the refractive index of a medium. Indeed, Drude long ago derived an equation for rotatory dispersion of the form

$$\alpha = \frac{D}{\lambda^2 - \lambda_m^2}$$

where α is the observed rotation at wave-length λ , λ_m is the wave-length corresponding to a characteristic frequency of vibration in the neighbourhood of an absorption band caused by the vibration of an asymmetric electronic band, and D is a constant characteristic of the molecule. Thus for tartaric acid in aqueous solution,

$$\alpha = \frac{A}{\lambda^2 - 0.03} - \frac{B}{\lambda^2 - 0.054} \theta$$

For $\lambda_m^2 = 0.054$, $\lambda_m = 2330 \text{ \AA}$ which is close to an absorption band in the ultraviolet for tartaric acid. For $\lambda_m^2 = 0.03$, λ_m lies far in the Schumann region.

Besides rotating the plane of polarisation, optically active molecules may possess another property — circular dichroism, *i.e.*, the absorption of *dextro*-light may be different from that of *laevo*-light. On emergence from a medium, which is both optically active and circularly dichroic, the plane polarised light becomes not only less intense, but it also becomes elliptically polarised, with the major axis of the ellipse inclined to the original plane of polarisation at an angle, which for small ellipticities, we may also call, the rotation of the plane of polarisation. Optical instruments of considerable sensitiveness have been devised by Bruhat for measuring such ellipticities and rotation.

Modern theories of photochemical reactions postulate that the amount of photochemical transformation is proportional to the number of light quanta absorbed by the reacting molecules. If a racemic mixture is illuminated by *dextro*-light, and the dichroism is such that the *dextro*-molecules absorb more of the *dextro*-light than the *laevo*-molecules, then it is expected that the rate of transformation of *dextro*-molecules will be faster than that of *laevo*-molecules. The result will be, that if the reaction proceeds, the optically inactive racemic mixture will show increasing *laevo*-activity. The essential conditions for success are however the following :—

1. The radiations used for photochemical transformation should correspond with the absorption band, which is characteristic of the asymmetric electronic bonding as indicated by Drude's equation of rotatory dispersion.

2. The substance should exhibit circular dichroism in the neighbourhood of the band head.

Kuhn's success was due to the fact that the propionic acid derivatives, which he used, gave a rotatory dispersion which indicated a characteristic band in the neighbourhood of 2800 \AA and that the absorption of *dextro*-light of this wave-length by *dextro*-molecules was different from that of *laevo*-molecules.

In the plant kingdom, the process of photosynthesis takes place with the aid of catalytic agencies like chlorophyll, xanthophyll, etc. The exact mechanism by which they produce complex organic molecules from carbon dioxide and water with the aid of the visible radiations from the sun, is even now a subject for considerable speculation. It is found that the complex molecules produced as a result of photosynthesis, are either *dextro*-rotatory or *laevo*-rotatory, if they contain one or more asymmetric carbon atom. Experiments now in progress in our laboratories indicate that an acetone solution of one of the photocatalysts, chlorophyll-*a*, is both optically active and circularly dichroic.

TABLE I.

Measurement of rotatory dispersion and ellipticity of chlorophyll-a in acetone solution.

($M/20,000$)

λ .	Length of solution.	Rotation in degrees.	Ellipticity in degrees.
6700	1.5 cm.	-0.04	+0.04
6200	2.5	-0.1	+0.05
5780	4.0	-0.01	+0.00
5460	8.0	-0.05	+0.04
4916	5.0	-0.04	+0.07

It has also been possible to prepare colloidal solution of inorganic catalysts which are circularly dichroic. Thus, if we take dilute solutions of sodium tungstate and hydrochloric acid and immediately after mixing them together, expose them to powerful *laevo*-circularly polarised ultraviolet radiations (between $3100\text{--}3600 \text{ \AA}$), the molecules during the process of aggregation to form colloidal micelles appear to be subjected to the directive

influence of such radiation. Table II gives the values of circular dichroism which have been observed for such colloidal solutions.

TABLE II.

Induced anisotropy of photo-sensitive sols in 366 $\mu\mu$.

Substance studied.	Conc.	Period of pre-excitation (Intensity of exciting radiation incident = 950 ergs per sq. cm. per sec.).	Nature of exciting radiation.	Photometric method.	Thermopile-electrometric method.
				$g = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\parallel}}$	$g = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\parallel}}$
1. Tungstic acid	0.0125 M (in terms of tungstate.)	6 hours	<i>l</i> -Circularly polarised	+0.0271	+0.016
"	0.0125	6	<i>d</i> -Circularly polarised	-0.0221	-0.012
"	0.0125	...	Kept in the dark	+0.0001	Nil
2. Ceric borate	0.0036	12	<i>l</i> -Circularly polarised.	...	+0.0246
"	"	"	<i>d</i> -Circularly polarised.	...	-0.0257
"	"	...	Kept in the dark for 12 hrs.	...	Nil
3. Vanadic acid	0.0025M (in terms of vanadate)	10	<i>l</i> -Circularly polarised	+0.0289	Nil
"	0.003	12	"	...	+0.013
"	0.0025	10	<i>d</i> -Circularly polarised	-0.0054	Nil
"	0.003	12	"	...	-0.0084 -0.0084 -0.008
			Kept in the dark	+0.0087	Nil

TABLE II (contd.).

Thickness of the cell = 0.2 cm.

Substance studied.	Conc.	Period of pre-excitation.	Nature of the exciting radiation	Photometric method.	*Thermopile-electrometric method.
4. Chromic tungstate	0.02 M (in terms of tung. state).	10 hrs.	<i>l</i> -Circularly polarised	—	+0.0227
		10	<i>d</i> -Circularly polarised.	-0.0284	-0.0296
			Kept in the dark	-0.0067	Nil

A colloidal solution of tungstic acid does not reduce glucose in the dark. But in presence of light, the glucose is oxidised and tungstic acid is reduced to form a blue colloidal solution. The velocity of this photochemical reaction has been carefully studied. A colloidal solution of tungstic acid is taken in which circular dichroism has been developed by maturing it in *laevo*-light, mixed with a solution of glucose, and then the velocity of photochemical reaction studied under the influence of *dextro*- or *laevo*-light ($\lambda = 3660\text{\AA}$) of the same intensity. It is found that the velocities are not identical.

TABLE III.

The reaction was carried in the ultraviolet (3660\AA) K_0 , the zero-molecular velocity constant, denotes the number of g. mol. transformed per unit cell per second.

Sol, pre-activated in <i>l</i> -circularly polarised light for 6 hours, the intensity of the exciting light being 113 ergs.	Reaction carried in	I_{abs} in ergs in which the reaction was carried.	$K_0 \times 10^3$.
	<i>l</i> -Circularly polarised light.	113	0.93
	<i>d</i> -Circularly polarised light.	113	0.806

* The photometric method has been described (*J. Indian Chem. Soc.*, 1937, 14, 502-518). The thermopile-electrometric method will be described in a paper to be published shortly.

A photocatalytic dichroic system for visible radiations can be obtained by reducing in ordinary light a mixture of sodium vanadate and excess of *dextro*-tartaric acid. If we take a solution of sodium vanadate and add *dextro*-tartaric acid in excess (final concentrations:—0.05 M-NaVO₃ and 0.08M-tartaric acid) the solution is coloured red due to the formation of a complex of vanadic acid sol with *d*-tartaric acid. The solution is not circularly dichroic. If, however, it is exposed to ordinary light until the whole of the vandate (V⁵) has been reduced to the quadrivalent (V⁴) stage, a violet coloured solution is obtained which is both circularly dichroic and optically active. The rotatory dispersion and ellipticities of such solutions are given in Tables IV and V.

TABLE IV.

Mixtures containing d-H₂T complex.

E - ve is right-handed. *E* + ve is left-handed. Conc. same as in Table I.

Wave-length.	Length of solution.	Rotation.	Ellipticity (E).	Mol. extn. coeff.	Anisotropy factor (g).*
6700Å	3 cm.	+0.18°	-0.25°	13.68	-0.00739
6200	6	+0.66	-0.14	13.03	-0.00218
5780	6	+0.48	-0.09	12.38	-0.00147
5460	6	+0.30	-0.04	11.74	-0.00069
5200	6	+0.26	-0.06	11.10	-0.00109
4916	6	+0.16	+0.14	9.83	+0.00288
4358	6	+0.10	+0.14	8.58	+0.00288

TABLE V.

Mixture containing l-H₂T complex.

Concentration same as in Table I.

Wave-length.	Length of solution.	Rotation.	Ellipticity (E).	Mol. extn. coeff.	Anisotropy factor (g).*
6700Å	3 cm.	-0.20°	+0.50°	13.68	+0.0148
6200	6	-0.50	+0.30	13.03	+0.00467
5780	6	-0.35	+0.20	12.38	+0.00327
5460	6	-0.30	+0.23	11.74	+0.00397
5200	6	-0.27	+0.22	11.10	+0.00400
4916	6	-0.25	-0.05	9.83	-0.00103
4358	6	-0.24	—	8.58	—

* $g = \frac{\text{Extinction coefficient for } l\text{-light} - \text{Extinction coefficient for } d\text{-light}}{\text{Extinction coefficient for ordinary light}}$

It will be noticed that with *l*-tartaric acid, similar results but in the opposite sense are obtained both for circular dichroism and rotatory dispersion.

By the use of a solution of potassium persulphate as an oxidant, it is possible to oxidise tartaric acid with this reduced vanadium complex as a photo-catalyst. The reaction is zero-molecular in light and does not take place in the dark. Velocities are given in Table VI.

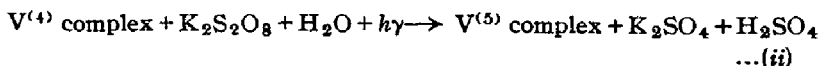
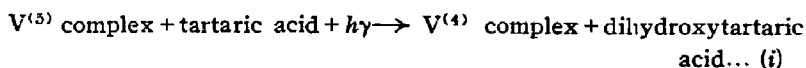
TABLE VI.

Concentration of vanadium in the reduced vanadium tartaric acid complex = 0.025*M*. Concentration of $K_2S_2O_8$ = 0.05 *M*. Temperature = 25°. $I_{abs} = 1384$ ergs (in all cases).

Light.	$\frac{dx}{dt} \times 10^5$ for				
	Reduced complex of <i>d</i> -H ₂ T.	<i>l</i> -H ₂ T.	<i>dl</i> -H ₂ T.*	Reduced complex of <i>r</i> -H ₂ T.	
<i>d</i> -Light	2.71	Mean 1.29	1.87	2.3	2.3
<i>l</i> -Light	1.87	Mean 2.29	2.71	2.3	2.3

Quantum efficiency of the reaction in circularly polarised light varies from 0.247 to 0.358. For *dextro*-light, the reduced vanadium complex of *d*-tartaric acid has a greater extinction coefficient and the quantum efficiency in *dextro*-light is greater than that in *laevo*-light. The reverse is the case when *laevo*-light is used for the oxidation of the reduced complex of vanadium with *l*-tartaric acid. A larger fraction of the incident light is absorbed by the surface layers of the colloidal micelles when the extinction coefficient is larger, and since the chemical reaction mostly takes place on such surface layers, the quantum efficiency is expected to increase.

If tartaric acid is present in excess, the following photo-catalytic cycle continues until the whole of the persulphate is reduced.



* *dl*-H₂T means mixtures of *dextro*-tartaric and *laevo*-tartaric acid in equivalent proportions.

The $V^{(5)}$ complex is not circularly dichroic and the velocity of reaction (i) is independent of the nature of polarisation of the photoactive radiations. For reaction (ii), as we have already seen in Table VI, the observed velocity in *dextro*-light, when racemic tartaric acid is used for complex formation and photo-reduction of persulphate, will be the mean of the velocities observed for reactions with *dextro*-tartaric acid and *laevo*-tartaric acid taken separately. With racemic acid, the initial rotation is zero, but with the progress of oxidation in *dextro*-light, *d*-tartaric acid will be oxidised faster than *l*-tartaric acid and the residual mixture will develop *laevo*-rotation. Table VII shows that this is found to be the case.

TABLE VII.

Length of solution = 2.5 cm. Time of exposure = 8 hours.

Wave-length = 5890 Å. Concentration same as in Table I.

Observed rotation.			
Light.	<i>dl</i> -H ₂ T-complex.	<i>r</i> -H ₂ T-complex.	Calculated value (for <i>dl</i> -H ₂ T or <i>r</i> -H ₂ T).
<i>d</i> -Circular	-0.06°	-0.06°	-0.061°
<i>l</i> -Circular	+0.06	+0.06	+0.061

In Table VII the calculated value for the expected rotation is given by

Rotation (calculated) =

$$\mp \frac{\text{Change in rotation on oxidation}}{\text{Change in titre}} \times \frac{a-b}{a+b} \times c.$$

for *dextro* and *laevo*-light respectively where the ratio $\frac{\text{change in rotation}}{\text{change in titre}}$ is a constant which is pre-determined for mixtures of $K_2S_2O_8$ and *d*-H₂T or *l*-H₂T complex, *a* and *b* are the velocities for reaction in *dextro*- and *laevo*-light respectively (Table VI) and *c* is the actual change in titre observed immediately after the rotation, as given in Table VII, has been measured. There is good agreement between the observed and the calculated values,

Production of Metal Films which are Optically Active and Circularly Dichroic.

It is well known that enzymes yield end-products which are always optically active if they contain one or more asymmetric carbon atom. Take for instance fumaric acid. By addition of water, it can produce malic acid, and by addition of ammonia, aspartic acid. Enzymes from muscle extract or *B. coli* often produce *l*-malic acid and *d*-aspartic acid. Enzymes are colloidal aggregates and it is probable that when produced inside living organisms, they are endowed with some kind of asymmetric structure. Early in the beginning of this century Bredig found that colloidal platinum behaves, for purposes of oxidation and reduction, like enzymes, and he gave such sols the name of inorganic enzymes. But of course they do not simulate the enzymes in the matter of producing optically active substances. We have been for some time trying to produce films of catalytically active metals like silver, platinum and palladium with definite asymmetric structure so that they may exhibit both optical rotation and circular dichroism. The results that have been obtained are such as to encourage the hope that asymmetric synthesis analogous to that brought about by enzymes, may be effected with such asymmetric films of inorganic metal catalysts.

The pioneering work of Weigert gave the clue to such investigations. A glass plate is covered with a thin layer of a suspension of silver chloride in gelatin. It is dried and exposed to normal light till the colour turns bluish red—photochloride is formed. This layer is then exposed to strong plane polarised red light from an arc-lamp. The red spot produced is found to be dichroic. Spots produced by vertical vibration have far greater transmission for vertical vibrations and the same is true of horizontal vibrations. Various theories have been proposed for this Weigert effect but without entering into their merits, we shall recognise the fact that the photomicrospheres are arranged with their axis parallel to the direction of vibrating light which is used for excitation. It is natural to expect that circularly polarised light will bring about such a circular arrangement of the photomicrospheres of AgCl, and some preliminary experiments on this point were reported by Zoehrer about a decade ago.

Gelatin is an optically active material, and if optical rotation and circular dichroism are to be developed in photomicrospheres in films of AgCl, gelatin as a supporting material has got to be altogether excluded; and very thin glass discs free from all strain can only be used. A film of AgCl

on such glass in absence of gelatin is extremely delicate, being often washed off in contact with water. Adhesive films of AgCl, after many fruitless efforts, have been prepared in our laboratories according to the following technique.

Microscopic cover-discs, free from ellipticity, were cleaned with chromic acid, alkaline solution, water and absolute alcohol and dried. Silver mirror was deposited on these films by the evaporation of a pure silver wire placed between two tungsten electrodes in a chamber evacuated to 10^{-6} mm. The presence of Hg vapour in the chamber was excluded by traps of copper gäuge. The silver mirrors were converted into silver chloride films by placing them above chlorine water in a closed chamber. After complete chlorination, the discs were immersed in purest distilled water and in successful experiments AgCl film was often found to adhere to the glass surface. This moist film was then exposed to the ordinary light of mercury arc until by the production of photomicelles a violet colour was obtained. If such a violet film is next exposed for 30 minutes to *dextro*-light from a carbon arc at 6 amperes, it develops both optical activity and circular dichroism.

Rotation at 6700 Å	-0.1°
Ellipticity	+0.04

The thickness of the silver film was determined by a method of microchemical analysis developed in Kodak laboratory and was of the order of 0.3×10^{-4} cm., i.e., half of the wave-length of red light. It means that calculated on the basis of 1 cm. thickness, the film would show the extraordinary rotation of $-10,000^\circ$.

The AgCl film can be developed either physically or chemically by the oxalate developer or rhodinal developer. The resulting film of silver gave

Rotation	-0.06°
Ellipticity	+0.04

The silver film can be toned with platinum and the resulting platinum film gave

Rotation	-0.1
Ellipticity	+0.15

Such platinum films have been tested as regards complete substitution of silver by platinum by the action of nitric acid, the rotation and ellipticity remaining unchanged even under such drastic changes.

Toning with palladium also gives similar results.

Investigations on the physical properties of these films and the catalytic action of these films with the object of producing optically active substances are now in progress.

My thanks are due to my collaborators Dr. T. Banerjee, Dr. B. C. Kar and Messrs T. L. Ramachar, K. R. Kar, and my colleague Mr. S. K. Mukherjee for much of the experimental work recorded in this paper.

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