

recovered polymer (2450) (visc.) indicated only very slight degradation but the recovery of only 75% of the starting material suggests that the other 25% was degraded sufficiently to have remained in solution during purification by reprecipitation.

To test whether the oxygen might have entered the polymer by reaction with oxygen or peroxide in the dioxane during purification, a sample of oxygen-free polystyrene (3 g.) which had been prepared by the action of chloroacetyl peroxide on styrene at 95°, was dissolved in 100 cc. of ordinary dioxane which gave a positive test for peroxide with potassium iodide. After standing for three days exposed to air and sunlight, the polymer (2.9 g.) was recovered unchanged.

Anal. Before exposure: C, 91.54; H, 7.53; Cl, 1.05; mol. wt., 10,700 (visc.). After exposure: C, 91.14; H, 7.87; Cl, 1.01; mol. wt., 10,350 (visc.).

Summary

Polystyrene prepared with 3,4,5-tribromobenzoyl peroxide as catalyst has been found to contain bromine corresponding to about one tribromophenyl radical per polymer molecule. It has been shown that these tribromophenyl groups were acquired during the course of polymerization.

URBANA, ILLINOIS

RECEIVED AUGUST 10, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Orientation of Molecules Produced Photochemically in Rigid Solvents

BY GILBERT N. LEWIS AND JACOB BIGELEISEN

It was recently discovered by Lewis and Lipkin¹ that when certain substances are irradiated in a rigid solvent by polarized light the molecules of the colored substances produced are so oriented that the absorption coefficients vary with the direction of polarization of the measuring light. This observation is not only of interest as offering the first instance of permanent dichroism² in a homogeneous solution, but it affords a valuable means of studying the relation between the structure of a molecule and its optical axes.

In the quasi-classical interpretation of absorption spectra that was developed by Lewis and Calvin³ emphasis was placed not only upon the energies of electronically excited states but also upon the spatial direction of the oscillations of groups of electrons, which oscillations were assumed to characterize these excited states.⁴

(1) Lewis and Lipkin, *THIS JOURNAL*, **64**, 2801 (1942).

(2) Temporary dichroism, during the lifetime of the phosphorescent state, was found by Lewis, Lipkin and Magel, *ibid.*, **63**, 3005 (1941); **64**, 1774 (1942). Earlier, Weigert similarly obtained dichroism in adsorbed dyes (*Z. Physik*, **5**, 410 (1921)).

(3) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(4) In the theory of Lewis and Calvin the swinging of the entire cloud of mobile electrons is considered to be quantized as a whole. In a conjugated molecule which is long and nearly linear the electric oscillations are assumed to be along the molecule, that is, in the direction of high polarizability. The first electronic band (the band of lowest frequency) may be called the x band of the first order. This may be followed at a higher frequency (which would be twice the first frequency if the oscillations were harmonic) corresponding to an oscillation of higher amplitude in the same direction. This is the x band of the second order.

In a nearly planar molecule, which is not radially symmetrical, there is a unique direction of maximum polarizability. The first absorption band, again called the x band, will correspond to oscillations in that direction which will be called the main optical axis. The second absorption band may be a second order x band, but ordinarily will be a y band with oscillations perpendicular to those of the x

All of the substances discussed in this paper are of the type illustrated in Fig. 1 in which, at least approximately, the structural formula is symmetrical with respect to a vertical line at the center. On grounds of symmetry, therefore, we must expect the direction of any electronic oscillation to be either parallel or perpendicular to such a line of symmetry.

Our experimental procedure has been to illuminate a colorless substance dissolved in a rigid medium, by a beam of plane polarized ultraviolet light, and then to examine the absorption of the colored sample produced, using measuring light polarized at various angles to the direction of polarization of the illuminating beam. Except in one case the illuminating and measuring beam were passed through the sample in the same direction. The details of the method will be described in the experimental section.

Normal Orientation: Tetramethyl- and *sym*-Diphenylbenzidine

In studying the phosphorescence of fluorescein in acid media it was shown² that the molecules in the phosphorescent state had a main optical axis for absorption in the same direction as that of the molecules in the ground state. Whenever in general this relationship holds between a parent molecule and the molecule produced from it by some photochemical process we shall speak of a bands and along the line of minimum polarizability in the plane. In the present paper we deal solely with x bands and, except in one instance, with x bands of the first order. We are going to show how the directions of electronic oscillation, or the optical axes, may be studied experimentally.

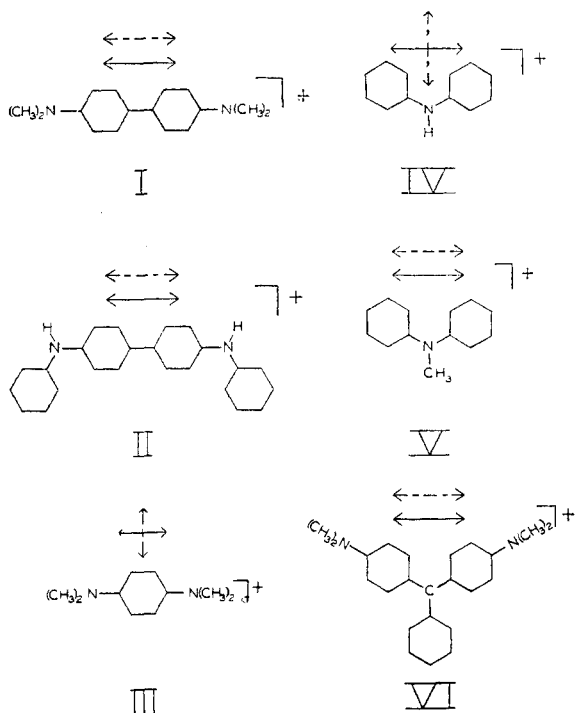


Fig. 1.—The same formulas with the plus sign omitted give the parent substance, except in the case of malachite green where the parent substance is the leuco cyanide. The main optical axis is represented by a dotted arrow for the parent substance, a solid arrow for the substance produced.

normal orientation effect. This *normal* effect, which is to be predicted universally when a long and nearly linear molecule goes over into another *similar* molecule, may also be confidently expected whenever the structure of the original and the resulting molecules indicates that the same direction in both is the one most favorable to electronic oscillations (direction of maximum polarizability). At least this should be true if we consider for each substance only the absorption band of lowest frequency.

Such a pair of substances should be tetramethylbenzidine and the positive ion obtained from it when an electron is ejected by the process of photochemical oxidation. The absorption spectrum of this ion (formula I, Fig. 1) has been obtained by Lewis and Lipkin.¹ There is an intense band in the infra-red ($\lambda_{\text{max.}} = 7900 \text{ \AA.}$). We have produced this ion in a flat Pyrex cell by illuminating in liquid air with vertically polarized light. Measurements were made at each setting of the spectrophotometer with the measuring beam polarized first vertically then horizontally. The measured extinctions are plotted in Fig. 2, in which circles represent the readings with vertical

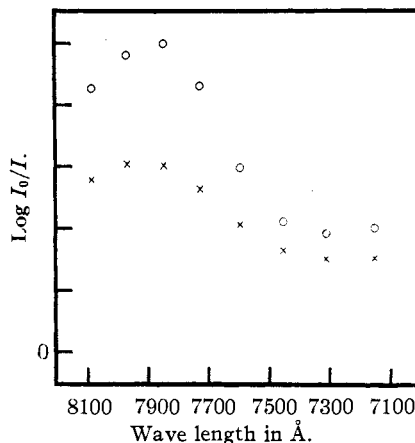


Fig. 2.—Extinction of tetramethylbenzidine ion (I) produced by vertically polarized light: upper curve with measuring light vertically polarized; lower curve with measuring light horizontally polarized.

polarization of the measuring beam, the crosses those with horizontal polarization. It is evident that a large orientation effect has been produced and in the expected direction. Those molecules of the parent substance whose optical axes lay predominantly in the vertical direction were the ones photo-oxidized by the ultraviolet light (about 3300 \AA.). Assuming not much turning of the molecules in the rigid solvent, the ions produced by the illumination should also lie with their axes predominantly in the vertical position, and the experiment shows that they do.

If a represents the extinction when polarization of exciting and measuring light are parallel and b the extinction when the two polarizations are perpendicular, the orientation ratio⁵ a/b is in this case 1.66. Within the limits of experimental error, which are larger in this experiment than in any of the others which we are to describe, the orientation ratio is the same throughout the band.

There is another intense absorption band of tetramethylbenzidine ion with maximum at about 4500 \AA. In many substances, such as malachite green, the second band is a y band corresponding to the excitation of an electronic oscillation at right angles to the oscillation belonging to the fundamental x band. In the present case, from the structure and dimensions of the ion, it seems that the y band should lie altogether in the ultraviolet. In that case the band at 4500 \AA. is to be regarded as a second order x band with oscillation in the same direction as that corresponding to the band at 7900 \AA.

(5) The orientation coefficients used by Lewis, Lipkin and Magel² are $a/(a + b)$ and $b/(a + b)$.

Since the second band of tetramethylbenzidine ion comes in a region which would have been awkward for our experiments, we turned to the like ion of symmetrical diphenylbenzidine (formula II, Fig. 1). This gives an absorption curve of quite similar type but with bands shifted to greater wave lengths. The first intense band lies far in the infrared and the band which we assume to be the second order α band has a maximum at 5010 Å. Using for the study of this band the same procedure as before, we obtained the results shown in Fig. 3. Here again we obtain a normal orientation effect, corroborating our assumption that this is also an α band. We thus conclude that both main bands of tetramethylbenzidine as well as of diphenylbenzidine show normal orientation. This is the most direct experimental confirmation^{5a} of the existence of the second order bands of Lewis and Calvin.

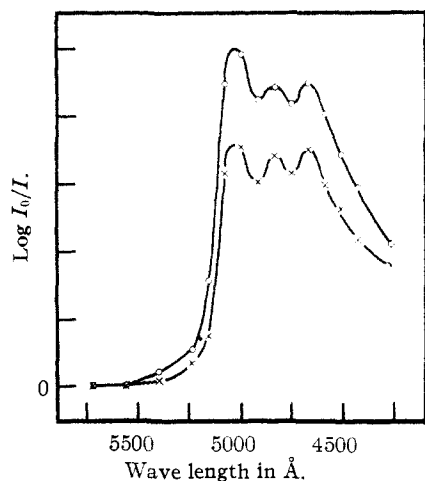


Fig. 3.—Extinction of diphenylbenzidine ion (II) produced by vertically polarized light: upper curve with measuring light vertically polarized; lower curve with measuring light horizontally polarized.

The electronic band of Fig. 3 shows a pronounced vibrational structure. The orientation ratios at the three values of $\lambda_{\max.} = 5010, 4830$ and 4670 Å. ($\bar{\nu} = 19,960, 20,700, 21,410$ cm.⁻¹) are, respectively, 1.39, 1.31 and 1.29. We think that the difference between these values is outside the limits of experimental error.⁶

(5a) Since the above was written, we have been able to study the second band of tetramethylbenzidine ion. Normal orientation was found with an orientation ratio of 1.5. We have thus proved even more directly the existence of the second order α band.

(6) It would be difficult to apply a generalized Franck-Condon principle to molecules of such complexity, but it seems likely that the relative transition probabilities to the three vibrational states would vary with the orientation of the molecule with respect to the direction of polarization of the light.

The absorption coefficient was measured at 5010 Å. not only with angles of 0 and 90° between excitation and measuring polarization, but also with intermediate angles. The extinction coefficient, as expected, proved to be at a maximum at 0° and at a minimum at 90°. Similar but more accurate experiments of this type will be discussed in the case of Wurster's blue.

Abnormal Orientation: Wurster's Blue and *p*-Phenylenediamine

The ion of Wurster's blue, formula III, Fig. 1, is readily obtained by illumination of the leuco base.¹ The main optical axis of the ion is doubtless horizontal, that is, along the line joining the two nitrogens. On the other hand, in the uncharged leuco base when the molecule would be radially symmetrical, except for the two dimethylamino groups, each of which tends to increase the density of the electron cloud in the ring, it would be difficult to predict whether the greatest polarizability would be in the horizontal or vertical direction. Experiment shows that it is the latter.⁷ When the illumination was carried out in the ordinary way, using vertically polarized light, the extinction proved to be greatest in the horizontal direction, as shown in Fig. 4. Considering only the first two vibrational bands $\lambda_{\max.} = 6240$ and 5720 Å. ($\bar{\nu} = 16030$ and 17480 cm.⁻¹) the values of the orientation ratios are 0.740 and 0.780, respectively.

Experiments over all Angles.—In a separate experiment we determined the values of the extinction at 6285 Å. at various values of the angle between the direction of illuminating and measuring polarizations. The results are given in Fig. 5 where it will be seen that within the limits of experimental error the individual measurements marked by circles fall on the theoretical

(7) We have been assuming that it is the first ultraviolet band and therefore the main optical axis of the parent substance that is chiefly responsible for our photochemical change. In the present case of Wurster's blue we were able to obtain a curve entirely similar to that of Fig. 4 by using an illuminating beam polarized by a Polaroid plate, which transmits in the ultraviolet only to about 3400 or 3500 Å. This near ultraviolet region is covered in part by the first broad absorption band of the base of Wurster's blue, which has a maximum at 3200 Å. It is evident, therefore, that in this experiment we are dealing with the main optical axis of the parent molecule. There is another and higher absorption band of this substance with a maximum at 2620 Å. and it will be interesting to determine the orientation produced by excitation at this higher frequency.

In the case of diphenylamine, of which the first absorption band is at about 2800 Å. [Menczel, *Z. physik. Chem.*, **125**, 151 (1927)], there is little photochemical action at higher wave length than $\lambda_{\max.}$ for it is difficult to obtain any color when the copper sulfate filter is used in the exciting beam and yet this filter does not absorb appreciably at wave lengths greater than 2800 Å. [Mecke and Ley, *ibid.*, **111**, 385 (1941)].

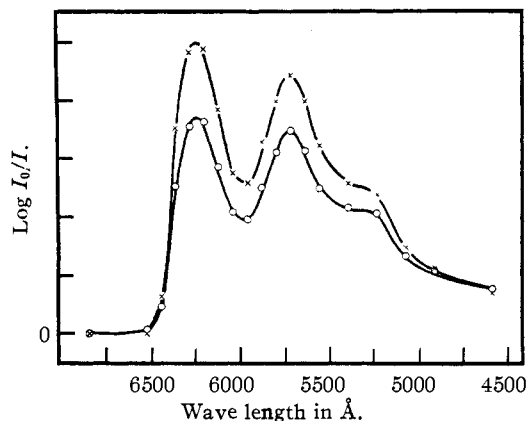


Fig. 4.—Extinction of Wurster's blue (III) produced by vertically polarized light: upper curve with measuring light horizontally polarized; lower curve with measuring light vertically polarized.

curve $\alpha = a \cos^2 \theta + b \sin^2 \theta$. In this experiment the orientation ratio, a/b , is 0.805.

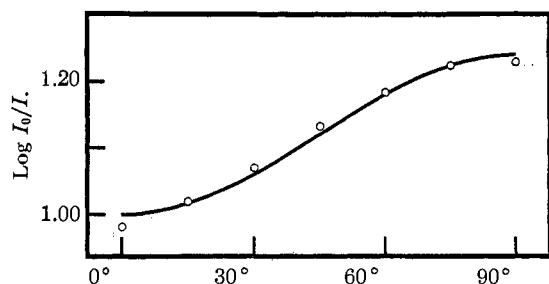


Fig. 5.—Extinction of Wurster's blue (III) at 6285 Å. as a function of the angle between the directions of polarization of the exciting and the measuring light: circles, experimental points; solid curve, theoretical.

Orientation with Unpolarized Light.—While in all the other experiments described in this paper the polarized exciting beam and the polarized measuring beam passed through the cell in the same direction, we tried a different type of experiment with Wurster's blue. The leuco base solution in a tube of square cross section was illuminated by a beam normal to one of the flat faces, using unpolarized light. The absorption was now studied with the measuring beam perpendicular to the former path of the exciting beam. As was expected, we found dichroism in this case also, as shown in Fig. 6. If we were dealing with the case of normal orientation we should expect maximum absorption with vertical polarization of the measuring beam. But in this case of abnormal orientation we expect and find the opposite. The direction, and the maximum possible amount of orientation in the various cases we have studied, will be discussed in a later section of this paper.

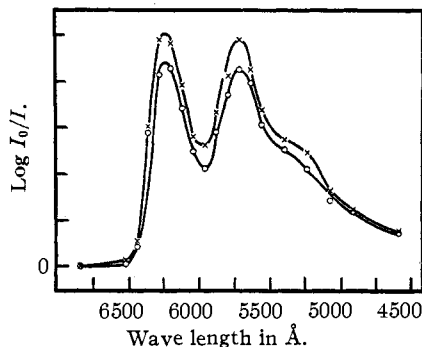


Fig. 6.—Extinction of Wurster's blue (III) after excitation of the base by unpolarized light along the z axis; measuring beam along the y axis: upper curve with measuring beam polarized along z ; lower curve along x .

All these experiments show, as indicated in Fig. 1, that if the axis for absorption for the ion is assumed to be horizontal, that for the leuco base is vertical. We may expect to find, therefore, that the direction of greatest polarizability in the leuco base is in the plane of the ring and perpendicular to the line joining the two nitrogens.

***p*-Phenylenediamine.**—The entirely similar compound in which the four methyls are replaced by hydrogen behaves just like Wurster's blue. The two main peaks of the absorption band are at 4990 and 4670 Å. The orientation was abnormal with an orientation ratio of 0.83.

Diphenylamine and its Analogs

There are numerous cases where the optical axis of a substance is not easily predictable. In the nearly planar molecules of diphenylamine (formula IV, Fig. 1, with the positive sign omitted) is the maximum polarizability in the horizontal direction, that is, along the line joining the two phenyl groups, or is it in the vertical direction, that is, from the nitrogen toward both phenyl groups? When diphenylamine was illuminated we found abnormal orientation, the orientation ratio in one experiment being as low as 0.73.

In the odd ion resulting from the photo-oxidation of diphenylamine, which has an absorption maximum¹ at 6800 Å., it is our belief that the optical axis is horizontal as we have indicated in Fig. 1, in which case the optical axis of diphenylamine itself is vertical.

On the other hand, experiments with carbazole showed no perceptible orientation, while with *N*-methyl-diphenylamine there was evidence of a small degree of orientation of the normal type. It appears that small changes in the chemical

structure have considerable influence in determining the main optical axis.

Orientation by Photo-ionization

Instead of producing the colored ion by removing an electron from a substance we may start with a leuco cyanide and by illumination cause it to dissociate into the positive dye ion and the negative cyanide ion. In this way we have studied malachite green (formula VI, Fig. 1), the very similar acid green (Colour Index No. 666) and *p*-methoxymalachite green. In these cases to obtain sufficient solubility of the leuco cyanides the content of alcohol in the solvent was increased. Here we start with a tetrahedral molecule and obtain a nearly planar ion. It was hard to predict whether any orientation would be found. However, in all three cases normal orientation was found in the main band, the orientation ratios ranging from 1.05 to 1.15.

The Maximum Orientation Experimentally Obtainable

The maximum orientation would be obtained if only an infinitesimal portion of the parent substance were used up in producing the photochemical product and if there were no rotation of the product molecule during or after the photochemical process. As we shall see, we can measure the rate of rotation after the illumination, but at present we have no way of estimating the amount of rotation immediately after the photochemical process, while the product molecule and its immediate environment are still "hot." It will be interesting to see in our various cases what the orientation would be under the most favorable circumstances.

Case I. Normal Orientation by Polarized Light; Viewing in the Direction of the Exciting Beam.—Take Cartesian coördinates with z along the irradiating beam and x in the direction of polarization. Consider any parent molecule whose main optical axis makes the angle ϕ with the xy plane while its projection on that plane makes the angle θ with the x axis. The chance that this molecule will suffer photochemical change is proportional to $\cos^2 \phi \cos^2 \theta$. The chance that the resulting molecule will absorb the measuring light is $\cos^2 \phi \cos^2 \theta$ when the polarization is along x and $\cos^2 \phi \sin^2 \theta$ when along y . The maximum orientation ratio is obtained by integrating $\cos^4 \phi \cos^4 \theta$ over all values of ϕ

and θ and dividing by the corresponding integral of $\cos^4 \phi \cos^2 \theta \sin^2 \theta$. The ratio is 3. This is the result given previously² for a similar case. In our experiments, where a large part of the parent substance was used up, the highest orientation ratio obtained was 1.66 in the case of tetramethylbenzidine.

In the following cases, if we start with no orientation, the integration must be over the element of solid angle $\cos \phi d\phi d\theta$.

Case II. Normal Orientation by Unpolarized Light; Viewing at Right Angles to the Exciting Beam.—Here the exciting beam is again along z , we view along y and consider the relative absorption coefficients in the x and z directions. Here we integrate $\cos^4 \phi \cos^2 \theta$ and $\cos^2 \phi \sin^2 \theta$. The ratio is 2.

Case III. Abnormal Orientation by Polarized Light; Viewing in the Direction of the Exciting Beam.—Here the geometry becomes more complicated. In addition to the angles ϕ and θ which show the direction of the optical axis of the parent molecule, we have perpendicular to this direction a plane in which any direction may equally well represent the optical axis of the product molecule. The angle between any such direction and the intersection of that plane with the xy plane is called ψ . The two expressions whose integration over ϕ , θ and ψ give the relative absorption coefficients for light polarized, respectively, in the y and x directions are $(\cos^4 \theta \cos^2 \phi \cos^2 \psi + \cos^2 \theta \sin^2 \theta \cos^2 \phi \sin^2 \psi)$ and $(\cos^2 \theta \sin^2 \theta \cos^2 \phi \cos^2 \psi + \cos^4 \theta \cos^2 \phi \sin^2 \psi)$. The ratio is 2. The ratio actually found with Wurster's blue was 1.33.

Case IV. Abnormal Orientation by Unpolarized Light; Viewing at Right Angles to the Exciting Beam.—With conditions as in Case II the ratio of the absorption coefficients to light polarized along z and along x , respectively, is the ratio of the integrals over ϕ , θ and ψ of $\cos^4 \phi \sin^2 \psi$ and of $(\cos^2 \phi \cos^2 \psi \sin^2 \theta + \cos^2 \phi \sin^2 \theta \cos^2 \theta \sin^2 \psi)$. The ratio is $4/3 = 1.33$ with which we may compare the value 1.15 obtained in our experiment of this sort with Wurster's blue.

In all of the substances that we have studied, the symmetry of the molecule has been such that the optical axis of the parent molecule must be parallel or perpendicular to that of its product. In cases of less symmetry this need not be the case. Nevertheless, in such cases also, experiments such as ours, where we always start with a

random distribution, must always show either a maximum or a minimum absorption when the exciting and measuring beams are polarized in the same direction, but the theoretical maximum of orientation would be less than in the cases that we have discussed.

The Rate of Deorientation and the Rate of Fading

The sample of Wurster's blue which gave us the results shown in Fig. 6 was kept in liquid air for seventy-two hours. Since the liquid air was replenished several times with constant enrichment of the oxygen content, the temperature may have risen to as high as 86°K. Yet the degree of orientation was found to be not much diminished. On the other hand, when the sample was now placed above rapidly boiling liquid air and thus allowed to warm slowly, the orientation disappeared while the amount of blue color as measured by the extinction of unpolarized light remained nearly constant. At a few degrees higher the color also faded rapidly.

This experiment shows that the molecules of the Wurster's blue ion rotate appreciably as the viscosity of the medium diminishes and assume a random distribution before the medium has become sufficiently fluid to permit the return of the electrons which had been ejected in the photochemical process. We hope shortly to be able to make a more quantitative study of the rates of rotation and fading. There are two other methods of determining the rate of rotation of a molecule as a function of the viscosity of the medium. One is Debye's method of determining the relaxation time in dipole measurements⁸; the other is the determination of the depolarization of fluorescence. In crystals, at low temperature, the rate of rotation of a single molecule like COS may be studied by the method of Kemp and Giauque.⁹

Experimental

In our first experiments the exciting light was polarized by a Nicol prism, which, because of its small size, made it difficult to illuminate the sample sufficiently and over a large enough region. Also the Canada balsam in the prism absorbs the high frequency light necessary for the photooxidation of substances like diphenylamine. Later the Nicol prism was replaced by a stack of four silica plates set at the Brewsterian angle for a wave length of about

3000 Å. The large and intense reflected beam showed a polarization of over 95%, which was adequate for our purpose. The measuring beam was polarized by a sheet of Polaroid except in the experiments with tetramethylbenzidine, where a Nicol prism had to be used, since Polaroid becomes useless in the infra-red. Extinctions were measured with the apparatus previously described.²

The substances to be examined were dissolved in the proper solvent, usually EPA (5 ether, 5 isopentane, 2 ethanol, by volume), and placed in cells of quartz, or glass when only near ultraviolet was required. The glass cells had to be carefully annealed to make them completely isotropic. The Dewar tube in which the absorption measurements were made with the sample over rapidly boiling liquid air was not completely isotropic but was clamped rigidly in a fixed position and measurements were made at each frequency with the cell in and out.

The substances used were purified only sufficiently to insure the non-appearance of any colored substances except those under investigation. The base of Wurster's blue and diphenylamine were purified by distillation in a high vacuum.

Summary

The permanent dichroism found by Lewis and Lipkin when they illuminated substances in a rigid solvent has been studied further to ascertain the optical axes of the irradiated molecules and their photochemical products. In all conjugated molecules, that have considerable extension in one direction only, that is the direction of electronic oscillations in the excited state for both parent and product molecules. Such molecules are the substituted benzidines and their positive ions. In these cases we have normal orientation; the substance produced shows a maximum of absorption with light which has a polarization parallel to that of the exciting light. In the benzidine ions second order x bands have been found with electronic oscillations in the same direction as for the first order bands.

In other cases, exemplified by Wurster's blue, the maximum absorption is found when the directions of polarization of exciting and measuring light are perpendicular—abnormal orientation. Wurster's blue was also illuminated by unpolarized light and orientation effects found by viewing at right angles to the exciting beam. When the oriented solution of Wurster's blue is warmed the orientation is lost through rotation of the molecules before there is any appreciable fading of the color.

Diphenylamine and methyldiphenylamine, although so similar in structure, show different orientation effects, being abnormal in the former, normal in the latter. The cyanides of several dyes

(8) Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929.

(9) Kemp and Giauque, *THIS JOURNAL*, **59**, 79 (1937).

of the type of malachite green gave normal orientation.

The maximum orientation obtainable in the

several cases is calculated and compared with the observed values.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, CORNELL UNIVERSITY]

Disappearance of Thiosulfate in Solutions of Maleic Acid; Catalysis of *cis-trans* Isomerization

BY HENRY TAUBE

Tanatar¹ observed that, when a solution of sodium thiosulfate is added to a solution of maleic acid, fumaric acid forms and the thiosulfate disappears. The complete reaction products are not known, although Tanatar² did identify the compound $\text{EtCO}_2\cdot\text{CHSH}\cdot\text{CHSO}_3\text{H}\cdot\text{CO}_2\text{Et}$ in an alcoholic extract of the reaction mixture. Sulfur is not observed as a product even when moderate amounts of mineral acid are added. The catalysis of the maleic-fumaric change by thiosulfate has been³ attributed to the separation of finely divided sulfur even though Tanatar¹ proved that no transformation takes place if the thiosulfate is decomposed by a mineral acid before adding the maleic acid, and that certain other reactions producing sulfur (which presumably is in a finely divided state at some stage of the reaction) do not induce the transformation. Finely dispersed sulfur does catalyze³ the transformation but only at higher temperatures where hydrolysis or other reactions of sulfur become possible, and in fact appear to be involved.

In the present work the rate of disappearance of thiosulfate in solutions of maleic acid and the rate of formation of fumaric in such solutions are studied as a function of concentration variables. The interpretation of the data leads to some conclusions about the mechanisms of the reactions.

Method.—In an experiment, the initial and final concentrations of thiosulfate, the amount of fumaric acid produced and the reaction time were measured.

Reaction mixtures were made up by adding known volumes of thiosulfate to known volumes of solution containing the other constituents. The reaction was quenched a short measured interval of time after mixing to measure the "initial" concentration of thiosulfate. To quench the mixture, the concentration of acid was decreased to low values by the addition of sodium hydroxide, or of potassium biphosphate solution if no other buffering agent was present.

Since some sulfite is usually produced in the reaction, the method of Kurtenacker⁴ for the analysis of mixtures of sulfite and thiosulfate was used. The method depends on the fact that in a solution which is only slightly acid, formaldehyde reacts rapidly with sulfite, yielding a product which does not reduce iodine in the ordinary titration of thiosulfate with that reagent.

In analyzing for fumaric acid, one sample was quenched at "zero" time by adding iodine solution; another was quenched in a similar fashion at the end of the reaction interval. Both samples were then made up to the same volume and a solution of potassium fumarate sufficient to supersaturate both solutions with fumaric acid was then added. Excess sulfuric acid was added to both and the solutions were allowed to settle in a constant temperature bath for about forty-eight hours. The fumaric acid was filtered off, washed with saturated fumaric acid solution and titrated with standard sodium hydroxide. The difference in titer was a measure of the fumaric acid produced in the reaction. Blank tests proved that the reactions: $\text{I}_2 + \text{S}_2\text{O}_3^{2-}$, $\text{I}_2 + \text{sulfite}$, $\text{sulfite} + \text{maleic acid}$ and the presence of I^- or $\text{S}_4\text{O}_6^{2-}$ did not induce a measurable transformation of maleic to fumaric acid in the experiments.

Materials.—Maleic acid was prepared by dissolving c. p. maleic anhydride in water, and a solution of potassium maleate was prepared by neutralizing a maleic acid solution with potassium hydroxide. The other chemicals were c. p. quality used without further purification.

Conditions and Definitions.—All experiments were carried out at a temperature of 25.3° and an ionic strength of ca. 0.61. The ionic strength was maintained by adding potassium chloride. In many experiments the desired (H^+) could not be attained with maleic acid. For such experiments (beginning at about experiment 17 in Table II and experiment 18 in Table III) hydrochloric acid was added to fix (H^+) at the tabulated values. The units used throughout are: time, t , in minutes, concentration in moles per liter.

Certain abbreviations are adopted for convenience. T represents total thiosulfate; H_2M , HM^- , M^{2-} represent maleic acid and its ions; H_2F represents fumaric acid.

Where (H^+) was fixed by a buffer solution, the composition required was calculated by using the following values of K_{diss} for maleic, phosphoric and oxalic acid, respectively: 1.78×10^{-2} , 1.43×10^{-2} , 7.9×10^{-2} . The value of K_{diss} for maleic acid at 25° and $\mu = 0.61$ was estimated

(1) Tanatar, *J. Russ. Phys.-Chem. Soc.*, **43**, 1742-1746 (1911).

(2) Tanatar, *ibid.*, **44**, 1320-1324 (1912).

(3) Freundlich and Schikorr, *Kolloid-Beihfte*, **22**, 1 (1926).

(4) Kurtenacker, *Z. anal. Chem.*, **64**, 56 (1924).