probable error in calculated $\log_{10} K$ of 0.6%. The heat of dissociation of the dimer of benzoic acid is computed to be 9000 ± 400 cal.

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

Reversible Photochemical Processes in Rigid Media. A Study of the Phosphorescent State

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Introduction

When light is absorbed by an organic substance dissolved in a rigid solvent, various processes may occur. Radicals, ions or electrons may be thrown off, and in another paper we shall describe several interesting phenomena of this type. On the other hand, even without losing any of its parts, the molecule which is absorbing light may reach an excited state in which it persists, sometimes for a second or more, and then returns to the normal state with emission of light. This afterglow, or phosphorescence, is the subject of this paper. The phenomenon of phosphorescence has been studied extensively with the mineral phosphors, and with dyes adsorbed on various materials, in which latter class we may include the so-called solutions in substances like gelatin and collodion. In order to simplify the problem we shall limit our attention to phosphors consisting of organic dyes dissolved in a homogeneous non-crystalline solvent. Here also there is an extensive literature and we shall attempt in the remainder of this introduction to present briefly the information hitherto existing regarding such phosphors.

That dyes phosphoresce when dissolved in liquids which have been supercooled until they reach a rigid glassy state was discovered by Schmidt[1] as early as 1896. Tiede[2] found that powerful phosphors were obtained by dissolving dyes in fused boric acid, the phosphorescence depending on the way the boric acid is treated and the amount of water allowed to evaporate.

There has been some controversy as to the true law for the rate of phosphorescent decay, but the work of Schischlowski and Wawilow[3] and of Lewschin and Vinokurov[4] indicates that when the phosphorescence is due to a single excited substance the rate of decay is exponential. In other words, it is a reaction of the first order. If the process were due to the ejection of some part of the molecule, which then returned slowly, owing to the high viscosity of the medium, the order of the reaction would depend upon the distance of ejection but would never be of the first order.

Phosphorescence is not merely an extension of the life of ordinary fluorescence.[5] Indeed, most dyes show two phosphorescent bands, representing two processes so different that Perrin[6] proposed the use of the two names, "true phosphorescence" and "fluorescence of long duration." However, we prefer to keep the name phosphorescence for the total afterglow and avoid implications by speaking of the alpha and the beta process, respectively.

The alpha process gives a band that is indistinguishable from the fluorescence band, while the beta band is of lower frequency. The velocity of the alpha process increases rapidly with temperature, while that of the beta process is far less dependent upon temperature. Consequently at low temperatures the beta band alone is usually observed. Another difference is found when the phosphor is excited by polarized light, in which case the alpha emission shows a large degree of polarization while the beta band shows little or no polarization. Jablonski[7] has interpreted some of these facts by assuming that a single excited state is responsible for both of these processes and that while the beta process is essentially spontaneous, the alpha process requires thermal activation up to the fluorescent state. We shall find it possible to give a quantitative corroboration of this theory.

Spectroscopic Study of the Alpha and Beta Bands of Fluorescein in Boric Acid Glass

Fluorescein, as used in research upon luminescence, has not always been the same substance.

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[1] Schmidt, *Ann. Physik*, **58**, 103 (1896).

[2] Tiede, *Ber.*, **53**, 2214 (1920); Tiede and Wulff, *ibid.*, **55**, 588 (1922).

[3] Schischlowski and Wawilow, *Physik. Z. Sowjetunion*, **5**, 379 (1934)

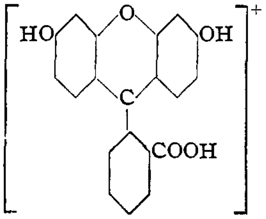
[4] Lewschin and Vinokurov, *ibid.*, **10**, 10 (1936).

[5] Wawilow and Lewschin, *Z. Physik*, **35**, 920 (1926).

[6] R. Delorme and F. Perrin, *J. phys. radium*, **10**, 177 (1929).

[7] Jablonski, *Z. Physik*, **94**, 38 (1935).

The brilliant green fluorescence in alkaline solution is due to the doubly negative ion. As such a solution is acidified, hydrogen ions are added successively until a strong blue fluorescence appears which is characteristic of the ion with which the present investigation is concerned.



A dilute solution of fluorescein in any acid solvent which has been cooled, without crystallization, to a glassy state is phosphorescent. The solvent may be concentrated sulfuric acid, sirupy phosphoric acid or fused citric, tartaric or boric acid. It may be partially hydrated aluminum sulfate. It may be an acid solution in glucose, glycerol or alcohol. At a given temperature the phenomenon is essentially the same in all of these solvents provided that the solvent is rigid at this temperature. In all cases the light emitted at low temperatures is a pure yellow, but in those cases in which the phosphorescence can be observed up to room temperature its color changes through green to a nearly pure blue.

While phosphorescence is a property characteristic of rigid media, it is presumably not macroscopic rigidity that counts. A substance that is rigid by ordinary criteria might permit atomic motions, or even the rapid diffusion of molecules. A colorless lubricating oil known as crystal oil becomes highly viscous and then rigid in the same temperature range in which glycerol shows like behavior, but it is a very poor solvent for displaying any of the phenomena of luminescence. On the other hand, a solution of fluorescein in 85% phosphoric acid shows phosphorescence at −80°, although at this temperature a glass rod imbedded in the supercooled acid may be rotated without much difficulty. All of the solvents that we have used for phosphors contain many hydroxyl groups and we conceive that through the hydrogen bonds thus afforded the solvent molecules are clamped tightly, not only to one another, but often to the dye molecules as well.

The boric acid phosphors were prepared by heating crystalline boric acid previously mixed with the desired amount of fluorescein until about 90% of the combined water was driven off. The resulting clear liquid was poured onto a metal plate and pressed with a second plate to form slabs of the desired thickness. A glass prepared from the boric acid alone was found to have a faint blue phosphorescence of its own. However, the intensity of this light was found to be less than 1% of that emitted by the fluorescein. Different samples of fluorescein behaved alike and no attempt at further purification was made, especially as it is probably impossible to prepare the phosphor without slight decomposition of the fluorescein.

The instrument used for photographing the phosphorescence spectra was a Steinheil (Model GH) three-prism glass spectrograph with a lens system having a focal length of 195 mm. The dispersion at 5800 Å. was 100 Å. per mm. The light source used for exciting the phosphorescence spectra, whose microphotometer tracings (obtained on a Zeiss recording microphotometer) are shown in Fig. 1, was a 500-watt (General Electric Co. T-20) tungsten-filament projection lamp. In later experiments where stronger excitation was required, a high pressure mercury arc[8] (General Electric Co., type A-H6) with a glass water-jacket and glass lens system was used.

In order that only phosphorescent light should enter the spectrograph, a simple type of phosphoroscope was used. A rapidly rotating disk (1800 r. p. m.), with a hole near the periphery, was placed so that when the hole was in a given position, light from the exciting source struck the front surface of the sample (which was placed in a bath in an unsilvered dewar). When the disk had rotated 180° from this first position the hole was now so situated that phosphorescent light from the front surface of the sample was able to pass through it and into the spectrograph. For obtaining the spectra whose tracings are shown in Fig. 1, Eastman Kodak Co. I–F spectroscopic plates were used and for light emission beyond 6500 Å. ammonia-sensitized I–N plates were used.

The phosphorescence spectrum of our solutions of fluorescein in boric acid shows at room temperature a strong band (alpha band) with its maximum in the blue, upon which is superimposed a fainter yellow band (beta band). As the temperature is successively lowered, the blue band gradually disappears and at all temperatures below −35° the yellow band alone remains. Figure 1 shows the photometric tracings of spectrograms taken (1) at 20° and (2) at −40° on I–F plates. The curves represent the actual plate darkening and have not been corrected for change in sensitivity of the plate with wave length.

The I–F plates become insensitive for wave lengths above 6400 Å. and therefore additional photographs were taken with the I–N ammonia-sensitized plates. These photographs showed that both bands tail off gradually. In the yellow

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(8) Noel and Farnham, *J. Soc. Motion Picture Engineers*, **31**, 221 (1938).

band there was still appreciable energy emission down to 8500 Å.[8a]

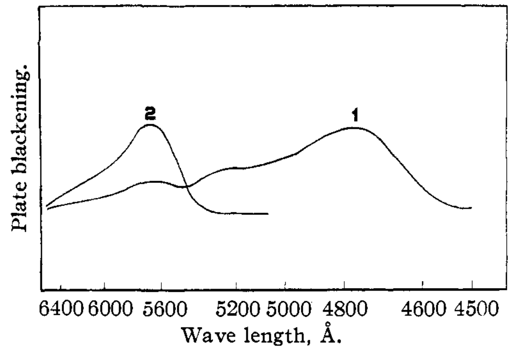

Fig. 1.—Phosphorescence spectra of fluorescein in boric acid at (1) 20° and (2) −40°.

We shall show later that when the phosphor is being illuminated there is a new substance present which has absorption maxima at 5050 and 6500 Å. It seemed possible that part of the phosphorescence in the infrared might be due to that substance. This, however, was disproved by irradiating through a blue filter (Corning no. 511) which did not transmit beyond 4800 Å. Photographs obtained were identical with those without the filter.

Law of Decay and the Half-life of the Phosphorescent State

Using these same phosphors of fluorescein in boric acid, Lewschin and Vinokurov[4] found at room temperature that if I is the intensity of phosphorescence, log I falls off linearly with time. Whether they observed the phosphorescence through a blue filter or a yellow filter, they obtained the same half-life. This is one of the pieces of evidence that a single excited state is returning to the normal state by two independent processes, each with its own type of emission.

The phosphoroscope used for determining half-lives was of the Becquerel type, but modified to avoid the errors in half-life measurements inherent in Becquerel's original apparatus.[6] It consisted of two disks mounted on a common shaft, which was rotated at a constant speed of 26.5° per second. The first disk had cut in it a 90° sector of an annulus, so that light from the exciting source (the high-pressure mercury arc) impinged upon the phosphor for one-quarter revolution of the disk. The second disk had cut in it a 2.6° sector of an annulus having the same radii as the annulus on the first disk, so that light from the phosphor could pass through it and impinge on the photocell. The angle between the openings in the two disks could be changed, so that the time elapsed between the illumination of the sample and the exposure of the photocell to the phosphorescing material could be varied.

For measuring the intensity of the phosphorescent light a Weston photronic cell (Model 594, Type 2) was used in conjunction with a lamp and scale galvanometer having a sensitivity of 0.005 microampere per mm. The photocell and galvanometer were matched so that only about 0.2–0.3 second was required for the galvanometer to swing from zero to full scale deflection. Under our conditions it was found by means of calibrated wire screens that the galvanometer throw was proportional to light intensity. To study the alpha and beta processes separately a blue (Jena BG-1) or orange (Jena OG-2) filter was placed in front of the photocell.

To study the half-life at various temperatures the phosphor was immersed in an unsilvered dewar, containing a bath at the desired temperature, placed between the two disks of the phosphoroscope. For the two lowest temperatures liquid hydrogen and liquid air were used as baths. Between liquid air temperatures and −80° a bath of isopentane containing a small amount of ethanol was used and from −80° to room temperature an acetone bath.

We have studied the rate of decay of the phosphorescence with many samples of the phosphor and over the wide range of temperature from 37 °C. down to the temperature of boiling hydrogen. For illustration we show the results for three sets of experiments in Fig. 2, where the ordinate is the common logarithm of the intensity of phosphorescence (in arbitrary units) and the abscissa is the time in seconds after the illumination has ceased. The sets of points 1, 2, and 3 were obtained, respectively, at 20, 88 and 296 °K. Every set of such experiments made below 8 °C. gave straight lines. Single measurements might fall

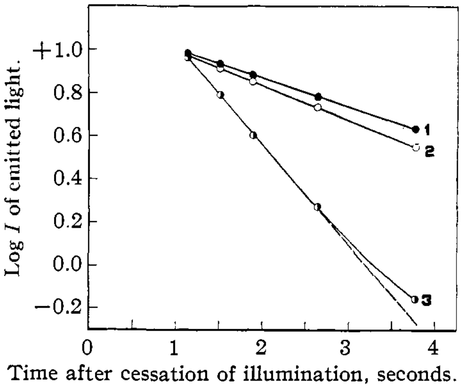

Fig. 2.—Rate of decay of phosphorescence of fluorescein in boric acid at (1) 20°K. (orange filter), (2) 88°K. (orange filter) and (3) 296°K. (blue filter). (The photocell was arbitrarily adjusted to give the same I at $t = 1$.)

(8a) Our spectrograms agree in the main with previous visual observations of Tomaschek [*Ann. Physik*, [4] **67**, 612 (1922)] on fluorescein in boric acid and of Travnicek [*ibid.*, [5] **17**, 654 (1933)] on fluorescein in aluminum sulfate glass. The former reports indications of a band at 5100 Å. and the latter of one at 6200 Å. The former, and perhaps also the latter, are suggested by our curves, but until further experiments are made we shall treat both alpha and beta bands as single.

above or below the line, due to small experimental errors, but there was no evidence of curvature in either direction. At room temperature and above, when the blue filter was used, there was evidence of curvature such as is illustrated in Set 3 of Fig. 2. We believe that this curvature is real, but that it is not a property of the fluorescein. The curvature is found only when the phosphorescence has a very short life and has fallen to less than one-tenth of its initial intensity, so that any small phosphorescence due to impurities would become noticeable. In fact the boric acid alone gives a glass with a slight blue phosphorescence, which is nearly if not quite enough to account for the curvature. The slight decomposition of the fluorescein may also give products with a phosphorescence of their own.

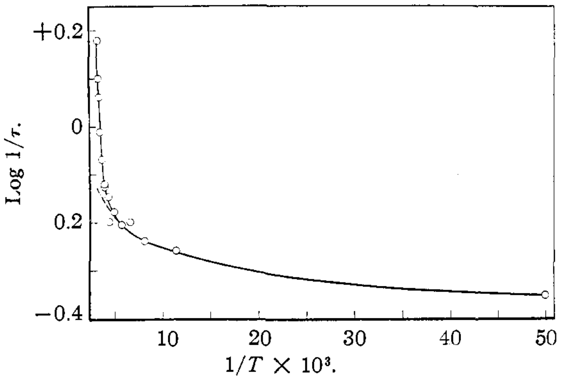

Fig. 3.—Effect of temperature on the phosphorescent half-life of fluorescein in boric acid. In this set of measurements the samples were all from a single batch and the orange filter was used throughout. The fourth, fifth and sixth points from the right were bad because of temperature uncertainties. Other similar sets helped determine the dotted line.

The half-life, as determined from the slope of such lines as given in Fig. 2, depends not only upon the temperature but also upon the way in which the sample has been prepared.[2] This is especially noticeable at liquid air temperature. Various batches of the fluorescein in boric acid phosphor at this temperature had half-lives varying from 1.77 to 2.50 seconds. The chief factor responsible for this variation was probably the amount of water lost by the boric acid, but the rate of cooling may have been important. Different portions of the same batch, which was poured out in a thin sheet upon a cold metallic plate, gave half-lives which were the same within a few per cent., which is about the range of experimental error.

The Effect of Temperature upon the Half-life.—If the half-life is designated as τ, then $1/\tau$ is proportional to the specific rate of disappearance of the phosphorescent state. Making the customary plot of log $1/\tau$ against the reciprocal of the absolute temperature, we obtained the curve of Fig. 3. In the experiments plotted the blue phosphorescence, or alpha process, is only appreciable at the higher temperatures, where $1/T$ is less than about 4×10^{-3}. The remainder of the curve, together with the dotted part which represents a rough extrapolation thereof, shows the rate of decay due to all other processes except the alpha process.

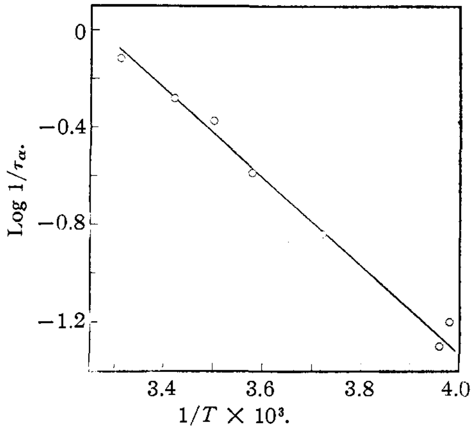

Fig. 4.—Variation of the rate of the alpha process with temperature.

We cannot conclude without further investigation that the beta process is the only one remaining. In fact, the rapid diminution in total luminescence at 30–40°C. indicates that a very considerable number of molecules find their way back to the normal state by processes involving no light emission. On the other hand, there is indication that these processes fall off very rapidly with diminishing temperature and we therefore believe that the right-hand portion of our curve represents very closely the rate of the beta process alone. The experiments strongly indicate that the yellow phosphorescence would persist down to the absolute zero with a half-life not very different from that we have found at the temperature of boiling hydrogen. We may mention a qualitative experiment in which a number of different phosphorescent dyes in boric acid and in glucose were illuminated at the temperature of boiling hydrogen. As far as could be observed visually, the phenomena were the same as at the temperature of liquid air. These processes at low temperature we shall discuss further in a later section.

Turning now to the alpha process, we can determine its specific rate, $1/\tau_\alpha$, by subtracting from the observed values of $1/\tau$ the values corresponding to the dotted line of Fig. 3. This procedure causes considerable exaggeration of errors, but the values of log $1/\tau_\alpha$ so obtained plotted against reciprocal absolute temperature (on a very different scale from that of Fig. 3) give an approximately straight line as shown in Fig. 4. Unlike the beta process, this alpha process behaves like a normal chemical reaction, and from the slope of the line we may calculate the heat of activation of 8.4 kcal. An independent, and less reliable, series gave a heat of activation of 7.1 kcal. We may take roughly 8 ± 1 kcal. as the heat of activation of the alpha process. We shall inquire further into the nature of this process in a later section, but may point out at this time that the rate of this unimolecular reaction, the alpha process, is extraordinarily small, considering the low heat of activation.

The Effect of Concentration.—A large effect of concentration of dye on the life of the phosphorescent state has been found by Lewschin and Vinokurov[4] for fluorescein in boric acid, and by Schischlowski and Wawilow[3] for Rhodulin Orange N in glucose. These authors do not state, however, just how these phosphors were prepared. We have already seen that phosphorescence in boric acid depends upon the extent to which the boric acid is dehydrated, and possibly upon the rate and conditions of cooling. We have studied the effect of concentration of fluorescein on the half-life of phosphorescence in glycerol containing 5% by volume of sirupy phosphoric acid, in order to have at room temperature a fluid solution of known composition.

Even such solutions when plunged into liquid air gave half-lives which depended on the rate of cooling and the time between cooling and measurements. However, when the same volumes of solution, in tubes of the same size, were plunged into liquid air, and measurements made after fifteen minutes, reproducible results were obtained. Studied in this way, the half-lives obtained were 1.96, 1.96 and 1.72 seconds, respectively, for the concentrations 5×10^{-5}, 5×10^{-3} and 5×10^{-2} moles per liter. The difference in the last case seemed to be real, but at this high concentration there was enough solute to change materially the character of the solvent. On the whole we may conclude that in our case the half-life of the phosphorescence is hardly affected by the concentration.

Another apparent effect of concentration was seen in the solutions of fluorescein in boric acid. The more concentrated samples at room temperature appeared to give out a larger fraction of yellow light. As far as we could see, however, this is due entirely to self absorption, since the samples absorb strongly in the blue and hardly at all in the yellow. If a thick plate of the phosphor is illuminated, the phosphorescence appears blue-green on the face which has been illuminated but yellow when viewed from the opposite side.

Further Study of the Properties of the Phosphorescent State

Before attempting to interpret the two paths by which the phosphorescent state disappears, let us show further evidence of the existence of this state. A substance which lasts for a second or so is in its own right a chemical individual, with its own set of properties. When light shines upon a phosphor there should be a photostationary state and the fraction of molecules in the phosphorescent state should increase with the absorption coefficient of the initial substance, with the half-life of the phosphorescent state and with the intensity of illumination. If a considerable part of the excited molecules go into the phosphorescent state, a simple calculation shows that our source of intense illumination should suffice to keep the greater part of the substance in that state. The following experiments were carried out with the purpose of testing this prediction and of studying the properties of the phosphorescent state itself.

The Attainment of Maximum Phosphorescence.—Lewschin and Vinokurov[4] found that when a fluorescein–boric acid phosphor was exposed to light of increasing intensity, the phosphorescence was at first proportional to the illumination, but at higher intensity tended toward a constant value. However, all their light sources were so feeble that it seemed impossible that their observations could be explained by the accumulation of any large percentage of the molecules in the phosphorescent state. In fact, their observations can be reproduced if the sample of phosphor is suspended in air and subjected to light of no great intensity. It is simply a temperature effect. The effect disappears when the sample is suspended in a liquid bath so that the heat produced by the illumination can be carried away.[9]

However, we have been able to obtain true saturation by means of the intense light from the high-pressure mercury arc. Using the same apparatus as in the half-life experiments, we varied only the intensity of the exciting light, by interposing calibrated wire screens between the lamp and the phosphor. The results are shown in Fig. 5, in which the abscissa shows the intensity of the exciting light and the ordinate represents intensity of phosphorescence, both in arbitrary units, (1) in an acetone bath at 18° and (2) in liquid air.

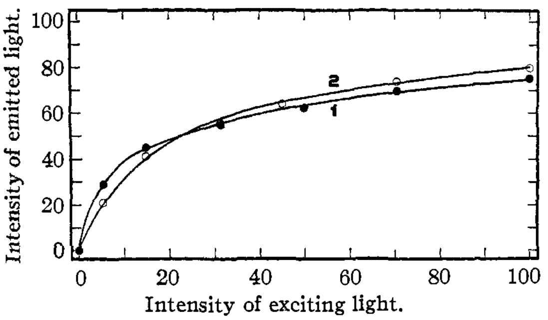

Fig. 5.—Saturation of phosphorescence of fluorescein in boric acid: (1) +18°; (2) −185°.

The ratio of phosphorescence intensity at 50% and at full illumination is in both cases about 84%. We should approach nearer to saturation at low temperatures than at high, because of the greater half-life. In fact, in the experiments plotted in the figure the liquid air was murky and therefore the intensity of the exciting light was less. When the experiment with liquid air was repeated under conditions of greater transparency, the corresponding ratio of phosphorescence intensities rose to 91%. It is possible that even in the acetone bath the results were not quite correct owing to a slight warming of the sample, but at liquid air temperature the intensity of phosphorescence depends hardly at all upon the temperature. It is to be noticed that the very rapid approach to saturation in the left portion of the curve would lead us to expect a more nearly horizontal line in the right portion than we actually found. We shall later correlate this observation with certain others.

Light Absorption by the Normal and by the Phosphorescent Molecules.—Wawilow and Lewschin[5] attempted to find a change in the absorption of dye phosphors under intense illumination, but were unsuccessful. We have, however, obtained a very decided effect in our fluorescein in boric acid phosphors.

The apparatus used for obtaining absorption spectra was constructed as follows. Light entering through a slit was reflected by means of a 90° prism to a two-inch concave grating ruled with 14,437 lines per inch. The first order spectrum, which alone was used, acted upon a cesium oxide photoelectric cell (G-M Visitron, Type 75-AV) contained in a housing with a slit in front of the cell. This cell and housing could be moved across the spectrum by means of a screw. The dispersion of the instrument was 16.33 Å. per mm. and the width of the slit on the photocell housing corresponded to 33 Å. The entire assembly was housed in a thermostated box. The current from the photoelectric cell was amplified by means of an FP-54 vacuum tube amplifier[10] and measured by means of a lamp and scale galvanometer having a sensitivity of 0.0026 microampere per mm.

The light source used in conjunction with this spectrophotometer was a 500-watt tungsten-filament lamp operated from a Raytheon voltage regulator. The light from this source was focussed by means of an achromatic lens, passed through the sample and impinged on the slit of the spectrophotometer after passing through a shutter. Since there was a small amount of scattering by the grating, and since the photoelectric cell was so much more sensitive to red light than blue light, it was found desirable to place a blue filter (Jena BG-12) in front of the light source when observations were being made at and below 4115 Å. Whenever the galvanometer deflections were too large to be read on the scale, wire screens transmitting known percentages of light were interposed in the light beam in order to bring the readings on scale.

The samples of fluorescein in boric acid used for studying the absorption spectra consisted of plates about 1 mm. thick. In those cases where we determined molar extinction coefficients ($\epsilon = (1/cd) \log_{10} I_0/I$, where ϵ = molar extinction coefficient, c = concentration in moles per liter, d = thickness of sample in cm.) the weight of fluorescein per gram of phosphor, the density of the phosphor, and the thickness of the phosphor were determined. Since the samples were not completely transparent it was necessary to measure their transmission at a wave length where there was no absorption and then make a suitable correction throughout the spectrum. In order to keep the samples at the desired temperature, they were immersed in a suitable bath contained in a glass dewar with an unsilvered strip.

Light from the high-pressure mercury arc previously mentioned was focussed on the phosphor by means of a lens in order to enable us to study the absorption spectrum of the phosphorescent state. This light beam made an angle of 30° with the light beam from the tungsten lamp. It was shown that none of it entered the slit of the spectrophotometer.

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[9] Recently Lewschin and Tugarinov [*Compt. rend. acad. sci. U. R. S. S.*, **28**, 115 (1940)] have made similar experiments with a stronger light source and have concluded that fluorescence and phosphorescence come from two distinct types of molecule, which is opposite to the conclusion we are going to draw from our experiments. Here also we suspect that their experiments were vitiated by lack of temperature control.

[10] Dubridge and Brown, *Rev. Sci. Instr.*, **4**, 532 (1933).

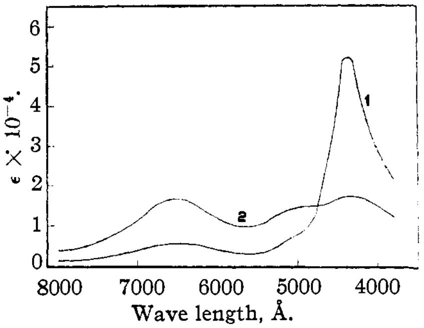

Fig. 6.—Absorption spectrum of fluorescein in boric acid: (1) without illumination other than measuring light; (2) illuminated by high-pressure mercury arc.

Using a plate of the phosphor of known thickness and concentration, at −95°, by our normal method we obtained for the absorption of fluorescein in boric acid Curve 1 of Fig. 6. When, however, the intense mercury arc was turned on the sample, we obtained Curve 2 of the same figure. The band at 4360 Å. has been greatly diminished, while bands at 5050 and 6500 Å. have been greatly enhanced. If the last two bands were due to the substance in the phosphorescent state, it seemed that their appearance in Curve 1 must be due to the relatively feeble measuring light itself. This supposition was verified by placing a yellow filter between the tungsten lamp and the sample. Under these conditions the absorption at 6500 Å. dropped to zero. If under the ordinary conditions of measurement some of the normal molecules were removed to the phosphorescent state, the maximum at 4360 Å. of Curve 1 is less than it would be for the pure normal molecules. To obtain the true height of this maximum we studied it in a series of experiments in which the wire screens were interposed between the tungsten lamp and the phosphor. The specific absorption rose with diminishing illumination and was extrapolated to zero illumination. Thus we obtained Curve 1 of Fig. 7 for the absorption coefficients of the normal state. From the height at 4360 Å. of this curve and of Curve 2 of Fig. 6, we see that under the conditions of intense illumination we have converted 75% of the substance from the normal state to the phosphorescent state. Making use of this fact that Curve 2, Fig. 6, is for a mixture containing 75% phosphorescent state and 25% normal state, we may obtain Curve 2, Fig. 7, for the absorption coefficients of the substance when it is all in the phosphorescent state. Curves 1 and 2 of Fig. 7 give then the absolute molar extinction coefficients of the two pure substances.

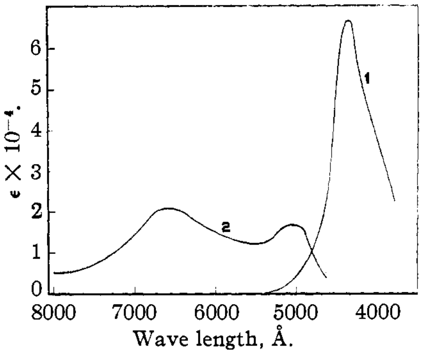

Fig. 7.—Molar extinction coefficients of fluorescein in boric acid: (1) normal (*N*) state; (2) phosphorescent (*P*) state.

To obtain further information as to the fraction of phosphorescent molecules as a function of intensity of illumination, we have set our measuring apparatus at 6500 Å. and measured the absorption with various wire screens between the mercury arc and the sample. If I_0 is the intensity of the incident measuring beam and I that of the transmitted beam, we may plot log I_0/I against the intensity of the light from the mercury arc. We thus find Curve 1 of Fig. 8 showing the building up of the substance which absorbs at this wave length, namely, the phosphorescent state. This experiment is comparable with that illustrated in Fig. 5, except that the zero of our present curve is not for zero total illumination. We have seen from Figs. 6 and 7 that with the tungsten light alone about one quarter of the molecules are in the phosphorescent state. When we examine the right-hand portion of the curve we note, as in the experiments illustrated in Fig. 5, the apparent reluctance, at high exciting intensities, to go completely into the phosphorescent state. At first it seemed to us that this must indicate that some of the molecules

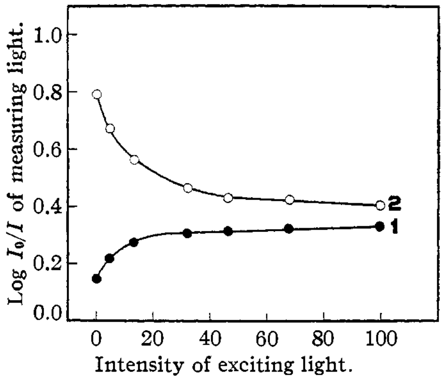

Fig. 8.—Effect of intensity of exciting light on the absorption of fluorescein in boric acid: (1) 6500 Å.; (2) 4360 Å.

can pass more easily than others into the phosphorescent state. We shall see, however, that the phenomenon is much more simply explained when the spatial orientation of the dye molecules is considered.

Setting the measuring apparatus at 4360 Å. where only the normal molecules absorb, we obtain Curve 2 of Fig. 8, which shows the gradual disappearance of the normal molecules, with increasing illumination.

The Energy Diagram. Theory of the Alpha Process

In interpreting the two types of phosphorescence we shall adhere closely to an important theory of Jablonski.[7] He considered three energy levels represented by the base lines N, F and P in Fig. 9. Molecules in the normal state N, on absorption of light, are for a short time (10^{-9} second) in the state F, from which they may return to N, giving the characteristic band of fluorescence. Some of the F molecules, however, instead of going directly to the ground state, pass into a state P, which Jablonski calls the metastable state, but which, to avoid any implications, we have called the phosphorescent state. At low temperatures these P molecules can return to the normal state only by the beta process. The energy of the beta band should be equal approximately to the difference in the energy levels P and N. When the temperature is raised, an increasing number of the P molecules may be thermally activated, so that they return to the state F. Thence they return to the normal state with the emission of the alpha band, which is identical with the band of fluorescence.

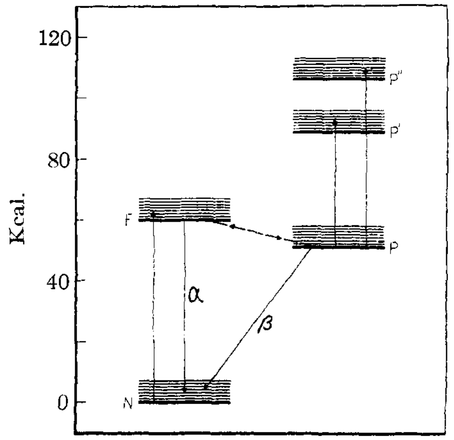

Fig. 9.—Energy diagram of fluorescein in boric acid.

This simple scheme of Jablonski has been criticized on several grounds by Pringsheim and Vogels.[11] In their experiments on trypaflavine in silica gel (here we are dealing not with true solution, but with adsorption) the phosphorescence phenomena cannot be explained without assuming more than one phosphorescent state. Their experiments do not show whether these two states are excited by the same frequency. In our experiments on crystal violet dissolved in glucose we have found two phosphorescent states, but one is produced by blue light, the other by orange. It seems to us that the scheme of Jablonski is sufficiently flexible to take care of such complexities as they arise.

A second objection raised by Pringsheim and Vogels to Jablonski's scheme was that an inspection of the qualitative data existing in the literature made it seem doubtful whether the heat of activation of the P to F molecules would at all coincide with the difference in energy between the alpha and beta bands. Our present experiments give the first opportunity of testing this question quantitatively.

Before proceeding to this analysis it is necessary to point out that there is always some difficulty in determining exact energy levels when, instead of the fine lines of atomic spectroscopy, we have the broad bands of absorption and emission which are characteristic of the dyes. In addition to our main levels there are various vibrational levels which are indicated, purely schematically, by the thinner horizontal lines of Fig. 9. When the normal molecules absorb light they pass to various states of the F group and then drop to the basic F level in a time which is supposed to be short compared to the life of the fluorescent state. These molecules now produce fluorescence by dropping not to the basic N state but to some state of higher vibrational energy. Thus the energy of the fluorescence maximum is lower than that of the absorption maximum (Stokes' law). Similarly, the molecules from the P state fall back to the vibrational N levels and the most probable level reached is not necessarily the same as the one reached by the F molecules. In other words, the difference in energy of the maxima of the alpha and beta bands need not be exactly equal to the difference in energy between the basic levels F and P.

In the case of fluorescein in boric acid, whose

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(11) Pringsheim and Vogels, *J. chim. phys.*, **33**, 345 (1936).

energy diagram we have given as nearly quantitatively as possible in Fig. 9, we find from the two maxima of phosphorescence a difference of 9 kcal. between the levels F and P. From the temperature coefficient of the rate of the alpha process, the heat of activation required by Jablonski's theory to take molecules from the P to the F level we have found previously to be 8 ± 1 kcal.

Finally we must discuss the levels P′ and P″. On account of the simplicity of the beta phosphorescence band of fluorescein in boric acid (Fig. 1), it seems probable that the P state is single, although this is a question which deserves further study. In order, therefore, to account for the two absorption bands of the substance in the phosphorescent state, as shown in Fig. 7, it is necessary to assume two states of still higher excitation due to the absorption of light by the P state. The two arrows give the energies corresponding to the two absorption maxima.

It is interesting to inquire what happens to these highly excited P′ and P″ molecules. If any large number of them should return directly to the N state or the F state, or in fact if they do anything except return to the P state, this should be detectable in the following way. In our experiments represented in Fig. 6 we first thought that the failure to obtain nearly 100% of the P state, even under the strongest illumination, might be due to a photochemical destruction of the P state. In other words, while the blue light was carrying molecules from the N state to the P state, the accompanying red light might be taking molecules from the P back to the N states. Since the amounts of red and blue light from our source were approximately equal, and since the integrated absorption of the P molecules is about the same as that of the N molecules, it seemed that excitation by blue light alone might make a great change in Curve 2 of Fig. 6. The light from the mercury arc was, therefore, passed through a blue filter, but the resulting curve was almost unchanged. It therefore appears to be certain that all, or nearly all, of the molecules in the phosphorescent state return, after absorbing light, to this same state. This is an amazing fact when we consider that the P state itself is 50 kcal. above the ground state.

A Chemical Process at the Absolute Zero

According to classical ideas no chemical process could occur at a finite rate at the absolute zero of temperature. The first exception to this rule was found when radioactivity was discovered. Again in spectroscopy it was found necessary to ascribe certain lines to slow, nearly forbidden, processes. Such are certain lines from the nebulae, which come from atoms that must be very nearly at the absolute zero. Furthermore, it has been shown by Cremer and Polanyi[12] that the spontaneous conversion, in the solid state, of ortho hydrogen into para hydrogen is temperature independent between 12 and 4°K. These three processes have been readily interpreted in terms of quantum mechanics. Accepting the beta process of phosphorescence as a fourth exception to the classical rule, a decision as to its proper interpretation is a difficult one.

From the shape of Curve 2, Fig. 1, it is evident that we are dealing with a rather well-defined phosphorescent state. That the transition from this state to the N state with the emission of beta phosphorescence is a peculiar one is shown by the great difference in polarization of alpha and beta phosphorescence to which we shall later refer.

There seem to be but two reasonable assumptions as to the nature of the phosphorescent state. The first assumption is that a molecule in the F state changes from a state of electronic excitation to a very highly excited vibrational level of the N state.[13] As a part of this energy is given up to the neighboring solvent molecules they also become "hot," but when these have lost their temporarily acquired energy they may once more set firmly about the dye molecule, holding it now in a new shape. The new molecule could now be regarded as a geometrical isomer of the normal molecule although it would be a likely supposition that the distortion produces some signal change in the molecule, such as the breaking of a bond, thus giving rise either to an inner salt or to a biradical.

The second reasonable assumption is that in the P state the atomic configuration is approximately the same as in the N state, but that one is an electromer of the other, such as a triplet state (biradical), which has a low probability of returning to the normal state because of quantum inhibitions. It might seem that this assumption is incompatible with the appearance of phosphorescence only in rigid media. There is, however, a property of rigid solvents that may be as important in our present consideration as the property of

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(12) Cremer and Polanyi, *Z. physik. Chem.*, **B21**, 459 (1933).

(13) As in the case of *cis*-stilbene recently discussed by us (This Journal, **62**, 2973 (1940)).

holding particles in fixed positions. When a moving shot strikes a pile of similar shot, its energy is largely given up to the pile and it comes nearly to rest. If, however, the shot in the pile are welded together, then the moving shot will rebound without much loss of energy. There is a similar difference between a fluid and a rigid solvent. In a fluid solvent a molecule of high vibrational energy loses that energy in less than 10^{-10} seconds by imparting it to the molecules of the solvent, which dissipate it further as thermal energy. We can make no quantitative estimate of the increase in this dissipation time in a rigid solvent, but it is probably enormous. We thus have the picture of the excited dye molecule leaving the F level and moving slowly down through the vibrational levels of the N state.[13a] At some stage of this slow dissipation the molecule might find opportunity of entering the electromeric state.

Let us consider again the first assumption, that the phosphorescent state is an isomer produced by so great a distortion as to account for the 50 kcal. difference in energy between this and the normal state. We must ask whether the return to the normal state is a process which would be possible at the absolute zero. Considering the great distances and the high potentials through which the atoms must move, it is evident that no ordinary quantum mechanical leak could account for the process. On the other hand, there is a possibility which as far as we can now see is not inconsistent with quantum mechanics or thermodynamics. We could think of the P molecules as held by the rigid medium in their unstable configuration, as though by the jaws of a powerful trap. Now these jaws themselves are in motion, and open or close with the undulations (Debye waves) of the medium; so that they may open to a degree that permits the trapped molecule to assume its normal configuration. These undulations by no means cease at the absolute zero. In fact, the zero point energy of the medium is so great that the undulations are not very much greater at 100°K. than at the absolute zero. If this explanation is to be entertained it will still be necessary to discover a mechanism by which the released molecule could give out its energy as light.

Polarization of the Phosphorescent Light

The Alpha Band.—When a fluorescent substance is illuminated by polarized light and viewed in approximately the same direction, the fluorescent light is often found to be partly polarized. The direction of maximum polarization is usually parallel to that of the primary light, but is sometimes found in a perpendicular direction (negative polarization), a phenomenon that has recently been satisfactorily explained.[14]

In the early part of this paper we gave a representation of the acid fluorescein molecule. In that diagram the horizontal direction may be regarded as the main optical axis, in the sense that when light is absorbed in the neighborhood of 4360 Å., the excited molecules have an electronic oscillation in this direction. If this substance is illuminated by polarized light chiefly those molecules will absorb the light whose optical axes are nearly parallel to the electric vector of the polarized light. In fluorescence these molecules will emit light polarized along their own axes and therefore with a large component in the same direction as that of the polarization of the primary light. On geometrical grounds it is known that the degree of polarization of the fluorescent light cannot exceed 50%.[15]

With respect to phosphorescence, it has been found that the polarization of the alpha bands is ordinarily entirely similar to that of the corresponding fluorescence. However, it has frequently been stated that no polarization of phosphorescence is to be found in the boric acid phosphors. We have therefore examined our phosphors carefully in this regard.

The fluorescein–boric acid phosphor was poured into a shallow annular trough on an aluminum disk. This disk was mounted on a motor rotating at about 400 r. p. m. In order to excite the phosphor, light from the high-pressure mercury arc was passed through a heat filter (Corning no. 397) and then through a Polaroid disk to the sample. At the opposite end of a diameter of the disk from the point of excitation was placed a photocell with a collimating tube such that the photocell viewed only a small area of the phosphor at any given time. Before the photocell were placed another Polaroid disk and a color filter to determine the degree of polarization of the phosphorescence in various spectral regions. The color filters used were as follows: blue, Jena BG-1; blue-green, Corning no. 430; green, Jena VG-1; yellow, Jena GG-11; and red, Jena RG-1. The phosphor was viewed by the photocell on the same surface which was excited.

[13a] This effect is shown also in fluorescence. In a rigid medium fewer molecules in the F state find their way to the N state by dissipative processes and therefore the fluoresence efficiency increases. Thus, crystal violet fluoresces in a mixture of ether, iso-pentane and alcohol only at liquid air temperature; in pure alcohol, at a somewhat higher temperature; in glycerol, at about −60°; and in glucose, at room temperature.

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

(15) Pringsheim, "Fluorescenz und Phosphorescenz," Julius Springer, Berlin, 1928, 3rd ed., p. 195.

The measurements were carried out as follows. With the aluminum disk revolving at a constant speed, galvanometer readings were taken with each Polaroid vertical or horizontal. From these readings two measurements of the degree of polarization were obtained. If I_0 is the galvanometer reading when the Polaroids are parallel and I_{90} the galvanometer reading when the Polaroids are crossed, then the degree of polarization is equal to $(I_0 - I_{90})/(I_0 + I_{90})$.

At room temperature the degree of polarization, when the phosphorescent light passed through various filters, is given in Table I.

Table I

Filter	Blue	Blue-green	Green	Yellow	Red
% Polarization	15	10	8	6.5	5.5

At this temperature the blue and yellow (alpha and beta) bands were both present. Referring to Fig. 1, the results seem roughly consistent with the assumption that the alpha band is equally polarized in the various parts of the spectrum, while the beta band shows little or no polarization.

Similar experiments were made with a glucose glass containing fluorescein and salicylic acid. Here a polarization of 27% was obtained with a blue filter, in spite of the fact that the photocell had to be very close to the phosphor, on account of low phosphorescent intensity. If good collimation of the phosphorescent beam had been possible, the percentage of polarization would probably have been much higher still. That we obtained a smaller degree of polarization in boric acid, and that no polarization has been obtained by other observers, we attribute to the depolarizing effect of the boric acid glass itself. It was never possible to obtain a boric acid phosphor which was completely transparent and this lack of transparency, as we shall see in another experiment, had a large effect on the apparent degree of polarization.

It is not unlikely that, if all depolarizing effects were eliminated, the degree of polarization of the alpha band might reach the theoretical maximum of 50%. At first it seems surprising that there should be any large polarization of the alpha phosphorescence, considering the many changes through which the molecule passes. When the molecule absorbs light (Fig. 9) it loses several kcal. in dropping to the basic F state and then gives up 8 kcal. more in dropping to the P state. Later it regains this energy, drops to one of the N states, and finally loses several kcal. more in reaching once again the basic N state. In order to account for high polarization we must assume that the molecules maintain essentially the same orientation throughout these complicated processes. In fact, we shall later give more stringent proof that a molecule may go through this experience many times without appreciable turning in the rigid environment.

The Beta Band.—Until a few years ago it was stated that polarization is never to be found in what we have called beta phosphorescence. However, in 1935 Jablonski[16] found a small polarization of the beta phosphorescence from cellophane phosphors and immediately thereafter Pringsheim and Vogels[17] found in a true solution of acridine orange in glycerol a negative polarization of the beta band amounting to 5%.

We have looked for the polarization of the beta band from a thin plate of fluorescein in boric acid at −80°. Here we used a two-disk phosphoroscope with the photocell on the opposite side from the illumination. No polarization was observed. We next removed the photocell and examined the phosphorescent light by means of a Pfund plate.[18] No trace of polarization was observed. When, however, we examined the sample from the illuminated side a definite positive polarization was observed, the amount varying from sample to sample. We estimate that the degree of polarization was never greater than a few per cent. The failure to observe this effect from the unilluminated side showed again the strong depolarizing effect of the boric acid glass.

The Effect of Molecular Orientation upon Light Absorption. Temporary Dichroism

We have already called attention (Figs. 5 and 8) to the noticeably slow approach to saturation at high intensities of illumination. This suggested that some molecules are harder to bring into the phosphorescent state than others. However, we believe that the molecules differ only in their orientation with respect to a beam of light. Ordinarily we speak of an absorption coefficient without stressing the fact that those molecules are readily excited whose optical axes (corresponding to a band that is being measured) lie near the plane that is normal to the beam of light, while those molecules whose axes are nearly parallel to the beam have very small probability of excitation. This is unimportant when all the molecules are randomly oriented in all directions. However, in

(16) Jablonski, *Acta Physica Polonica*, **4**, 311 (1935).

(17) Pringsheim and Vogels, *ibid.*, **4**, 341 (1935).

(18) Pfund, *J. Optical Soc. Am.*, **26**, 458 (1936).

the system we are now studying we were able to change the relative numbers of molecules of a given species lying in certain directions.

In the experiments illustrated in Fig. 6 a beam of light at 30° to the beam of measuring light caused the production of P molecules and an apparent reduction of 75% in the number of N molecules. If the beam of light from the mercury arc had been almost exactly parallel with the measuring beam, the band at 4360 Å. might nearly have disappeared. Yet this would not have indicated that nearly all of the N molecules had been converted into P molecules. Even with moderate illumination those molecules with axes lying nearly in the plane normal to the exciting beam would almost all be converted into P molecules, while those molecules with axes lying nearly parallel to the exciting beam would only be excited at much higher illumination. In this way we account for the slow approach to saturation shown in Figs. 5 and 8. In order to test the correctness of these ideas we have made the following experiments with polarized exciting light.

The phosphor samples used in these experiments were unusually transparent and very thin, about 0.1 mm. They were made by drawing slowly a thin ribbon from the viscous melt. The apparatus was essentially the same as that used for studying the absorption spectra of the N and P molecules. However, by the use of a 90° prism, it was found possible to make the light beam from the high-pressure mercury arc almost parallel to the measuring light beam from the tungsten lamp, and yet not have any of the former light enter the slit of the spectrophotometer. Polaroid disks were used to polarize both the exciting and measuring light beams. At 6500 Å. a yellow filter (Jena GG-11) was interposed to avoid any formation of P molecules by the measuring light itself.

It was found that the spectrophotometer was not isotropic. At 4360 Å. there was a 3% difference in the intensity of the light impinging on the photoelectric cell, depending on whether the light entering the slit was vertically or horizontally polarized. At 6500 Å. this difference amounted to 25%. Therefore, in all of our measurements suitable blanks were run in order to correct for this effect. Correction was also made as before for lack of transmission due to causes other than absorption by the dye.

If a thin plate of our phosphor were placed normal to the almost parallel beams of the exciting and measuring light, and the exciting light were polarized, let us say in the horizontal direction, then the molecules that are converted to the P state should be chiefly those with axes lying in this direction, and the number of N molecules in this same direction should be diminished.

Our first experiments were made at −80°, with the spectrophotometer set at 4360 Å. The expected effect was immediately observed and a series of measurements were made with the exciting light polarized horizontally (H) and vertically (V), and the measuring light polarized horizontally (h) and vertically (v). The results are given in Table II.

Table II

	No excitation	Excitation with Hg arc H_h	V_v	H_v	V_h
log I_0/I	...	0.069	0.067	0.096	0.102
Mean log I_0/I	0.182	0.068		0.099	

Here I_0 and I differ by the amount of light absorbed by the dye molecules. Although the measurements are of no high accuracy, the average deviation of individual measurements amounting to about 10%, it is evident that the extinction of the blue light is greatest when there is no exciting light, less when the two polarizations are perpendicular, and least when the two polarizations are parallel.

This is the first observation in a homogeneous, isotropic solvent of dichroism with respect to polarized light.[19,20] After illumination this dichroism presumably lasts only as long as the phosphorescent state; at least we have ascertained experimentally that in the interval between measurements with the exciting light on and off the dichroism entirely disappeared.

When we consider the degree of orientation of the N and P molecules separately, we must bear in mind the following fact. Consider a beam of unpolarized light with a frequency corresponding to one of the absorption bands of a colored substance, and consider that the molecule has a unique optical axis for that band. If these axes lie in various directions all the molecules will not absorb equally, but the absorption probability for each molecule is proportional to $\cos^2 \varphi$, where φ is the angle between the axis and the plane normal to the light beam. If n is the number of dye molecules whose axes all make the angle φ with that plane, we may call $\eta = n \cos^2 \varphi$ the *effective number* of those molecules for the given beam of light. When we use a beam of polarized light which deter-

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(19) This is true unless we accept the small effect which Kuhn, Dührkop and Martin [*Z. physik. Chem.*, **B45**, 121 (1939)] believed they obtained with *p*-nitrosodimethylaniline in a powerful electric field. Their apparent effect, amounting to only 2 parts in 10^6, seems to us to be at right angles to that which was to be predicted.

(20) Weigert [*Z. Physik*, **5**, 410 (1921)] produced a permanent dichroism in a thin collodion film containing an adsorbed dye, by partially decolorizing the dye with a beam of polarized light.

mines a unique direction in the plane normal to the beam, the projection of the optical axis of the molecule upon that plane makes an angle θ with the direction of polarization. Under these circumstances the *effective number* is $\eta = n \cos^2 \varphi \cos^2 \theta$.

The three values of log (I_0/I), 0.182, 0.068, 0.099, of Table II are proportional to the three *effective numbers* η, η'_0 and η'_{90} for the three cases of no exciting light, and exciting light with polarization at angles of 0 and 90° to the polarization of the measuring light. From the figures obtained we find the two fractions

$$\frac{\eta'_0}{\eta'_0 + \eta'_{90}} = 0.41 \text{ and } \frac{\eta'_0}{\eta'_0 + \eta'_{90}} = 0.59$$

These fractions, which may be called the orientation coefficients with respect to the two directions, are for the unchanged N molecules. If we wish to find corresponding orientation coefficients for the P molecules which are produced by the light, we must write

$$\frac{\eta - \eta'_0}{2\eta - \eta'_0 - \eta'_{90}} = 0.58$$

$$\frac{\eta - \eta'_{90}}{2\eta - \eta'_0 - \eta'_{90}} = 0.42$$

These results are not very accurate and we have been able to get much better information regarding the orientation of the P molecules by studying their own absorption band. One important question arises: Will the new P molecule have the same optical axis for its own main absorption band as the N molecule has for absorption at 4360 Å.? Even our preliminary measurements gave to this question a definite affirmative answer.

Once more at −80° and with our spectrophotometer set at 6500 Å., we were working under much simpler conditions than before, for (1) by using a yellow filter in the measuring beam we avoided the formation of any P molecules by that beam, and (2) we were working in that part of the spectrum where there is no absorption, except when P molecules are present, so that $I = I_0$ when there is no exciting light. Also, our spectrophotometer was more sensitive in the red than in the blue. As a result, our sixteen individual measurements showed an average deviation from the mean of only 3% and we obtained the reliable results shown in Table III.

Table III

	H_h	V_v	H_v	V_h
log I_0/I	0.198	0.209	0.127	0.130
Mean log I_0/I	0.204		0.129	

From these figures we obtain once more the orientation coefficients

$$\frac{\eta'_0}{\eta'_0 + \eta'_{90}} = 0.61 \text{ and } \frac{\eta'_{90}}{\eta'_0 + \eta'_{90}} = 0.39$$

These are to be compared with the less accurate values 0.58 and 0.42 that we obtained before, for the orientation of molecules that had been taken out of the N state.

Of course the absolute magnitude of these orientation coefficients is not significant until the absolute intensity of the exciting light is known. Mathematical analysis of the problem, involving a simple integration, shows that the two orientation coefficients for the P molecules should be 0.75 and 0.25 when illumination is faint, and should both approach 0.50 as the intensity of exciting light is indefinitely increased. On the other hand, the two coefficients for the N molecules should both start at 0.50, remain near this value for faint illumination, but approach 1 and 0 as the intensity of the exciting light is indefinitely increased.

Finally, we must mention a significant qualitative experiment which shows that even under circumstances far more favorable for change of position of the dye molecules than those under which we have been working, no appreciable change in direction of the molecular axes occurs. A very transparent cube of the boric acid–fluorescein phosphor was prepared and after heating to nearly 100° it was allowed to cool slowly while traversed in a north–south direction by a strong beam from the mercury arc. The radiation was continued for thirty minutes, at the end of which time the material had come nearly to room temperature. It was thought that at some temperature in this range the excited molecules, which would be chiefly those in the plane perpendicular to the beam, might undergo a change in the direction of their axes so that there would be some depletion of such molecules. This would lead to a permanent dichroism when the cube was viewed in the east–west direction through a Polaroid disk. No such effect was observed.

We wisk to thank Professor Peter Pringsheim who has been kind enough to read our manuscript and to call our attention to several items in the literature which we had overlooked.

Summary

The peculiar state which is responsible for phosphorescence when a dye is illuminated in a

homogeneous, rigid solvent has been studied theoretically and experimentally. Most of the experiments were made with fluorescein in boric acid glass. Here, as in many similar phosphors, there are two emission bands (alpha and beta) associated with two different processes by which the phosphorescent state may return to the normal state. These two processes are both unimolecular. The rate of the beta process has been studied down to 20°K. and presumably would be little changed by proceeding to the absolute zero. As to the nature of the phosphorescent state and of the beta process two possible interpretations are offered. The alpha process obeys the Arrhenius equation and the heat of activation is found to be 8 ± 1 kcal., which agrees with the spectroscopic value of 9 kcal. found for the difference in energy of the fluorescent and phosphorescent states. A full energy diagram of the several states is given.

With intense illumination the phosphorescence approaches a maximum and a new absorption spectrum appears which belongs to the phosphorescent state. By slight extrapolation it has been found possible to obtain the pure spectrum of that state.

Our experiments indicate that excitation by light does not cause appreciable turning of the dye molecule in its rigid environment. This accounts for our observations on the polarization of the phosphorescent light, and leads to a new kind of dichroism. From quantitative measurements of this dichroism we have been able to calculate the degree of orientation of the molecules in the phosphorescent and in the normal states.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ultraviolet Absorption Spectra of Organic Molecules. II. The Effect of Substituent Groups upon the Absorption of Biphenyl

BY BARBARA WILLIAMSON AND WORTH H. RODEBUSH

In the preceding paper of this series,[1] ultraviolet absorption was shown to be a reliable measure of the existence of conjugation and the resulting resonance in organic molecules where these effects are pronounced. The degree of correlation between the absorption and the possibility of resonance structures was surprisingly high; in fact, it is probable that the absorption is a more direct measure of resonance than any other property. Chemical reactivity, for example, is affected by many variables and often depends upon several different mechanisms so that a good correlation with the predicted resonance structures is unlikely.

The article referred to above showed the effect of restricted rotation with the resultant displacement from coplanarity upon the resonance as measured by the ultraviolet absorption. The general conclusions of this paper may be stated in the following way: molecules involving saturated carbon chains or rings show absorption in the Schumann region below 2000 Å. If, however, the structure is one in which resonance structures are possible, the absorption is shifted to longer wave lengths which fall within the range of the quartz spectrograph. For many molecules one or more maxima are observed in the range mentioned above and it becomes possible, by comparing the spectra obtained for these molecules modified by further substitution, to study two effects—the change in extinction coefficient and the shift in wave length of the absorption maximum. These effects were interpreted in the paper referred to as being due to a change in the extent or number of resonance structures. It will be recognized, of course, that, according to this way of looking at things, an absorption maximum is not to be identified as belonging to any particular functional group but is to be considered as a property of the molecule as a whole or of such parts of the molecule as are capable of conjugation with each other. Naturally, in the case of a molecule such as phenyl acetic acid we should have two distinct resonance units, a phenyl group and a carboxyl group, and the absorption observed would be that resulting from the superposition of the effects due to these two units.

As a continuation of the work described in the paper referred to we have studied the dependence of extinction coefficient and wave length of the ab-

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[1] M. T. O'Shaughnessy and W. H. Rodebush, THIS JOURNAL, 62, 2906 (1940).