[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Photoreduction of Triphenylmethane Dyes in the Bound State[1a,b]

BY GERALD OSTER AND JUDITH S. BELLIN

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Triphenylmethane dyes do not undergo photoreduction unless they are bound to water-soluble high polymers. In contrast to their behavior in the light, the reduction of these dyes in the dark by strong reducing agents is actually inhibited when the dyes are bound. In several respects the photochemical behavior of the bound dyes is different from that of free fluorescein-type dyes. Whereas, with the latter, when free, the quantum yield of photoreduction decreases with increasing dye concentration, for bound dyes the quantum yield increases with increasing dye concentration. Nitrobenzene retards the rate of fading of free dyes, while in the case of bound dyes, the reaction is inhibited until all the nitrobenzene is consumed, after which the reaction proceeds at a rate equal to that for the inhibitor-free system. Analysis of the kinetic data shows that bound long-lived excited dye molecules react with the reductant to give colorless products. Interaction between bound dye molecules in the ground state and those in the first electronically excited singlet state is the principal mechanism for the formation of long-lived excited dye molecules. Confirmation of this reaction step is the fact that self-quenching of the fluorescence of bound dye molecules occurs at abnormally low concentrations. An analogy is drawn between these systems and those occurring in photosynthetic systems.

Introduction

It is our conviction that photochemical properties of dyes bound to high polymeric substrates differ considerably from those of the free dyes in solution.[2] There is evidence[3] that chlorophyll as it exists in plants is in the bound state and that the dye *in vivo* bears only slight photochemical resemblance to free chlorophyll in solution.

Acriflavine and fluorescein-type dyes in solution undergo photoreduction in the presence of mild reducing agents.[4,5] When these dyes are bound to water-soluble high polymeric substrates, however, the quantum yield of photoreduction is considerably increased.[4,6,7] We have found that some triphenylmethane dyes do not undergo photoreduction at all, unless they are in the bound state. It is the purpose of the present work to examine the detailed kinetics of the photoreduction of these triphenylmethane dyes when bound to high polymeric substrates. In particular, we are concerned with those photochemical steps characteristic of excited bound dye molecules. In contrast to their behavior in the light, the reduction of these dyes in the dark by strong reducing agents is actually inhibited when the dyes are bound.

Experimental

Materials.—Crystal violet, ethyl violet, malachite green, pararosaniline, basic fuchsin, victoria blue 4 R, were histological grade obtained from General Aniline and Film Corporation. These samples contained small amounts of inorganic salts, and were used without further purification. All other reagents used were C.P. grades. Helium (Airco) was used to flush oxygen from the solutions. Polymethacrylic acid (PMA) was prepared by polymerizing vacuum-distilled methacrylic acid (5.0% in water) under nitrogen, at 90° for 30 minutes, using 0.1% of potassium persulfate as catalyst. After polymerization the solution was dialyzed against frequent changes of distilled water for four days, and lyophilized.

Procedure.—Solutions containing dye, PMA and ascorbic acid (the hydrogen donor for the photoreduction) were made up in 0.1 *N* acetate buffer at *p*H 5.00. This *p*H was chosen because spectral shifts are large at *p*H 5. In addition, ascorbic acid is relatively more stable at low *p*H values, and yet is a sufficiently strong reducing agent at *p*H 5. The rate of fading by light of wave lengths corresponding to the absorption maximum of the solution in question was determined as previously described,[5] except that helium was used instead of nitrogen to deaerate the solutions. The probable error of the measurements of the initial rate of fading was ±6%.

The rate of reduction of the dyes by stronger reducing agents (*e.g.*, sodium bisulfite) in the dark was followed by placing 4.0 ml. of dye solution in a cylindrical cell 3 cm. in diameter and 1 cm. deep, which was provided with an inlet tube which allowed helium to pass through the solution, an outlet tube for the gas, and a third, stoppered tube through which reducing agent was added after the solution was deaerated. The change in transmission was then followed. In order to observe the transmittance, the cell was illuminated by a feeble light source. Using intermittent illumination of the solution, it was found that the incident light had no effect on the rate of fading.

Fluorescence spectra and measurements of fluorescence intensity were determined as described previously,[5,8] using an RCA 1P22 (red-sensitive) phototube. Care was taken in these observations to eliminate the effects of self-absorption of fluorescence.[8] Visual observations on the phosphorescence of the dyes dissolved in glycerol were made after flushing with helium in order to eliminate possible quenching by oxygen. The solutions were cooled to −120° by placing in pentane at its melting point. Phosphorescence was excited by illumination with the 365 mμ lines of a mercury arc, and the phosphorescence was observed visually.

Absorption spectra were determined with a Beckman model DU spectrophotometer using cells of 1.0 cm. path length.

Results

Absorption Spectra.—When PMA at *p*H 5.00 is added to a solution of ethyl violet at the same *p*H, there is a noticeable shift in color from purple to deep blue, and the solution becomes fluorescent. These changes are illustrated in Fig. 1. Similar changes occur when PMA is added, without change in *p*H, to solutions of other triphenylmethane dyes. By following the change in optical density at the wave length where these changes are largest as a function of the amount of PMA added to the system at constant *p*H, one obtains a "binding curve."[2] By employing the customary analysis,[9]

(1) (a) This paper represents a part of the dissertation to be submitted by Judith S. Bellin to the faculty of the Graduate Schol of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)1182.

(2) G. Oster, *J. Polymer Sci.*, **16**, 235 (1955).

(3) E. Rabinowitch, "Photosynthesis," Interscience Publishers, Inc., New York, N. Y., 1945.

(4) G. Oster, *Trans. Faraday Soc.*, **47**, 660 (1951).

(5) G. Oster and A. Adelman, THIS JOURNAL, **78**, 913 (1956); A. H. Adelman and G. Oster, *ibid.*, **78**, 3977 (1956).

(6) G. Oster, *Photographic Engr.*, **4**, 173 (1953).

(7) J. S. Bellin and G. Oster, to be published.

(8) G. Oster and Y. Nishijima, THIS JOURNAL, **78**, 1581 (1956).

(9) I. Klotz, "The Proteins," edited by H. Neurath and K. Bailey, Academic Press, New York, N. Y., 1953, Vol. I, Chapt. 8.

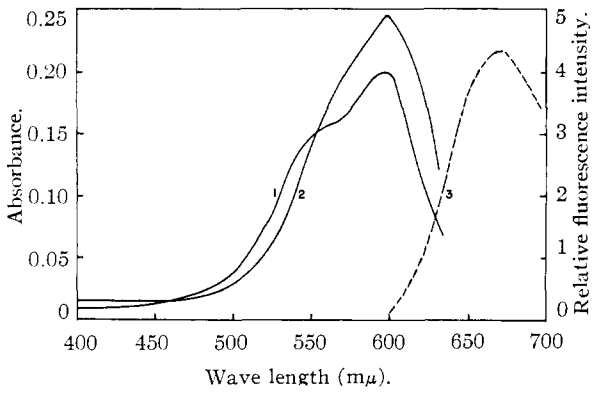

Fig. 1.—Absorption and fluorescence spectra of ethyl violet: dye concentration 2.5×10^{-6} M in 0.1 acetate buffer at pH 5.0: curve 1, absorption of free dye; curve 2, absorption and curve 3, fluorescence of dye in the presence of 0.1% polymethacrylic acid.

we find that at pH 5.00, the number of moles of crystal violet bound to 1 g. of PMA is 4×10^{-5}, while for ethyl violet, it is 0.6×10^{-5} mole per gram of PMA.

Fluorescence Spectra.—In water, at room temperature, binding of crystal violet and ethyl violet to PMA results in a red fluorescence which is very pronounced in the case of ethyl violet. At room temperature the fluorescence of both dyes, when dissolved in glycerol, is markedly enhanced by the addition of PMA. The fluorescence spectrum in both cases is an approximate mirror image of the absorption spectrum with slight overlapping and having a maximum at 620 mμ for crystal violet and at 670 mμ for ethyl violet.

Fluorescence Quenching.—Self-quenching of fluorescence of free dyestuffs in solution is usually discernible only at concentrations above $10^{-3}M$.[10] For bound ethyl violet, however, self-quenching of fluorescence is apparent at concentrations as low as $3 \times 10^{-6}M$, without any change in the absorption spectrum (Fig. 2). Due to the low fluorescence efficiency of bound crystal violet, and due to the low sensitivity of photomultiplier tubes to radiation of wave lengths longer than 600 mμ, it was not possible to obtain similar data with crystal violet. The same self-quenching effect has been noted for fluorescein-type dyes in the bound state.[7] This evidence of increased self-quenching when the molecules are bound to a polymeric substrate is reflected in the kinetics of the photoreduction (see below).

Phosphorescence.—Crystal violet and ethyl violet in rigid media and at low temperatures exhibit red phosphorescence when irradiated by green light, and green phosphorescence when excited by ultraviolet radiation.[11] These phosphorescence bands are readily observable in glycerol at $-190°$ but disappear at $-120°$ or higher. On the other hand, when PMA is added to the system, the phosphorescence is marked even at $-120°$. The phosphorescence of the bound dye

(10) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoek and Ruprecht, Gottingen, 1951, Chapt. 11.

(11) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942).

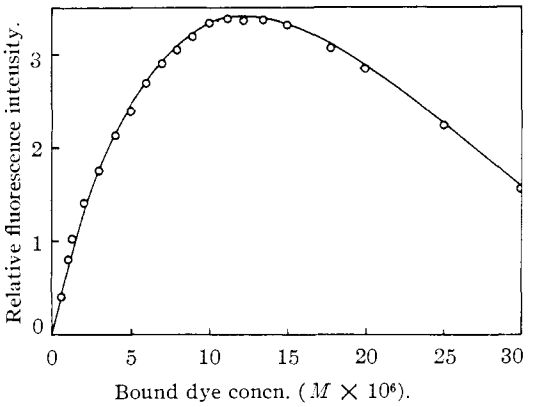

Fig. 2.—Self-quenching of the fluorescence of bound ethyl violet at pH 5.0, PMA concentration 0.6%.

in glycerol at $-120°$ is not appreciably quenched by increasing the dye concentration from 10^{-6} to 10^{-4} M, but ascorbic acid in the concentration ranges employed in our photoreduction studies does quench the phosphorescence. The phosphorescence of the bound dye is also quenched by extremely small quantities ($10^{-7}M$) of nitrobenzene.

Dark Reaction.—Triphenylmethane dyes are reduced in the dark by a wide variety of strong reducing agents (*e.g.*, sodium hydrosulfite, hydrogen and palladium, potassium borohydride, sodium bisulfite). Illumination of the solution has no effect on the rate of fading by such reducing agents. We have noted a rough relationship between the wave length of maximum absorption and the initial rate of fading in the dark: blue triphenylmethane dyes reduce more rapidly than do red triphenylmethane dyes. When PMA is added to the system, the reduction of basic triphenylmethane dyes by strong reducing agents is inhibited. For example, a concentration of as little as 5γ/ml. of PMA in a 10^{-6} M crystal violet solution completely inhibits the dark reaction. Similar data were obtained for other basic triphenylmethane dyes. In the case of acid triphenylmethane dyes, which do not bind to PMA, the addition of the polymer had no effect on the rate of reduction.

Photobleaching.—In the unbound state, triphenylmethane dyes cannot be photoreduced by ascorbic acid. When in the bound state, however, crystal violet, ethyl violet, and to some extent malachite green, are irreversibly photoreduced, giving a colorless solution with a new absorption maximum in the ultraviolet, near 360 mμ, which exhibits a strong yellow fluorescence when excited by ultraviolet light. Under the conditions of photoreduction the excited dye molecules can reduce tetrazolium salts to insoluble formazans. This fact provides evidence for the photofading reaction as a photoreduction: ascorbic acid alone does not reduce tetrazolium salts; therefore, the products of the photofading reaction (or some intermediates) are sufficiently strong reducing agents to reduce the tetrazolium salt. The photofading is inhibited by nitrobenzene in concentration as low as 10^{-7} M and by traces of benzophenone and picric acid. It is characteristic of the inhibition by nitrobenzene that after an initial period of retarda-

tion, which is directly proportional to the amount of inhibitor added, the reaction proceeds with a rate identical to that observed when no inhibitor is added (Fig. 3). Dye, ascorbic acid and light are

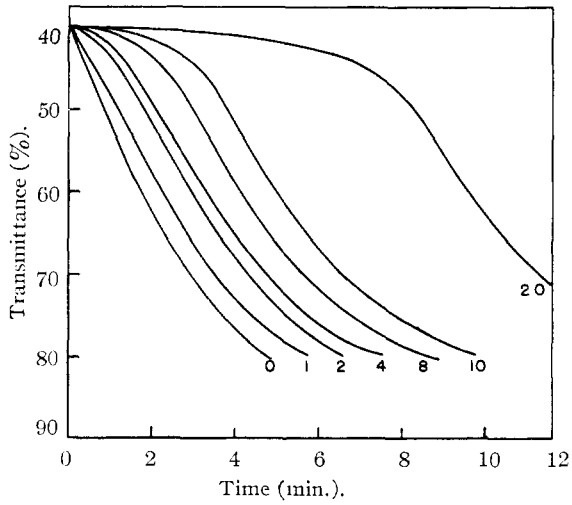

Fig. 3.—Inhibition of photoreduction of bound crystal violet by nitrobenzene; numbers on the curves refer to the molarity ($\times 10^7$) of nitrobenzene; dye 5×10^{-6} M; PMA 0.1%; ascorbic acid 3.2×10^{-3} M in pH 5.0 acetate buffer.

necessary for the destruction of the added nitrobenzene. Potassium iodide and p-phenylenediamine, usually effective quenchers of excited states, do not inhibit the reaction at concentrations of 10^{-6} molar. The fading curve (change in transmittance with time—see Fig. 3, curve 0) is linear at first, and from the initial rates of fading we have evaluated the rate of the photobleaching process. The quantum yield of fading (*i.e.*, the rate per quantum of absorbed radiation) is directly proportional to the fraction of dye molecules which are bound to the polymer. Figure 4 shows the reciprocal of the quantum yield of fading of completely bound ethyl violet plotted against the reciprocal of the ascorbic acid concentration for two dye concentrations. For a given reductant concentration, the quantum yield is directly proportional to the concentration of bound dye (Fig. 5). It was further found that the rate of fading for any of the solutions was proportional to the incident light intensity. Hence, empirically we obtain for the quantum yield ϕ in the absence of inhibitor, the expression $\phi = (A)(D)/[\alpha+\beta(A)]$ where (A) and (D) are the concentrations of ascorbic acid and bound dye, respectively, and α and β are empirical constants.

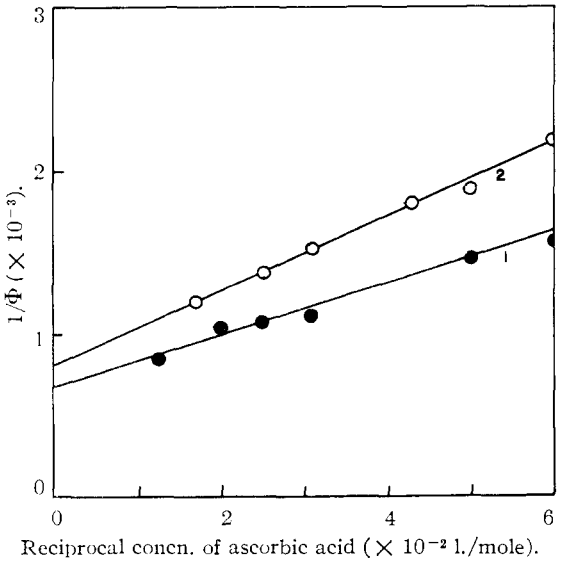

Fig. 4.—Variation of quantum yield of photoreduction of bound ethyl violet with reductant concentration: curve 1, 5×10^{-6} M dye; curve 2, 2.5×10^{-6} M dye; dye/PMA ratio 0.6×10^{-5} mole/gram.

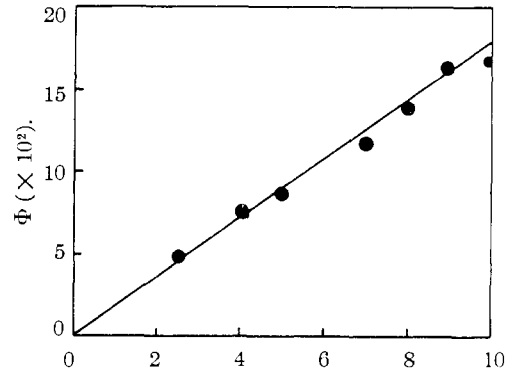

Fig. 5.—Variation of quantum yield of photoreduction with concentration of bound dye; dye/PMA ratio 0.6×10^{-5} mole/gram; ascorbic acid concentration 3.2×10^3 M.

Discussion

The alteration of absorption spectra of triphenylmethane dyes on addition of PMA is characterized by a shift of the absorption maximum to longer wave lengths, and, in the case of ethyl and crystal violet, the shoulder on the short wave length side of the absorption maximum of the free dye disappears (Fig. 1). In addition, the small absorption maximum of the free dye in the ultraviolet is increased. These changes in absorption may be attributed to binding of the dye to the polymer.[2] The addition of other polymeric acids (*e.g.*, nucleic acids) has the same qualitative effect. All the dyes examined obey Beer's law in the concentration range in question (up to 10^{-5} M), and hence the observed spectral changes cannot be attributed to a dissociation of dye aggregates.

The alteration in absorption spectra of crystal violet in various media has been attributed by Lewis, *et al.*,[11] to the existence of two possible geometrical isomers in rapid equilibrium with each other. These authors attributed the shoulder in the absorption curve of crystal violet to a "B" isomer" and the maximum to a more symmetrical "A isomer." From their observations on the fluorescence and phosphorescence exhibited by crystal violet in rigid media, the authors conclude that these phenomena arise from the "A isomer" alone. The disappearance of the shoulder in the absorption spectrum on binding (Fig. 1) is suggestive of the fact that complexing with PMA displaces the equilibrium between the two isomers, and favors

the formation of the "A isomer." The increase in fluorescence and phosphorescence on binding lead one to the same conclusion. In addition, the absorption spectrum of crystal violet in the presence of PMA resembles that of the dye in media of low dielectric constant, where the formation of the "B isomer" was shown[11] to be decreased. One could also ascribe the increased fluorescence when the dye is bound or when it is dissolved in viscous media to a more planar configuration, in which the formation of the "B isomer" (formed by means of a rotation through nearly 180° of one of the phenyl rings of crystal violet) is hindered. It was shown that in such media, or on binding to polymeric substrates, internal rotational movement of many dyes is suppressed.[8]

The change in optical density at the absorption maximum as a function of the amount of polymer added to the solution gives a measure of the degree of binding. The binding curve thus obtained has the form of a Langmuir absorption isotherm, and is not affected by changing the salt concentration of the solution. These observations, together with the fact that the greatest spectral shifts occur at a *p*H at or near the *pK* of PMA (*p*H 4.85),[12] suggest that the forces binding cationic triphenylmethane dyes to PMA are not purely electrostatic.[2] A further indication of binding is the fact that the addition of a small amount of polymer lowers the reduction potential of the triphenylmethane dyes by a large factor, so that even strong reducing agents can no longer reduce the bound dye.

By contrast, the rate of photoreduction of crystal violet, ethyl violet and malachite green is increased by the addition of PMA, so that even a mild reducing agent, such as ascorbic acid, is able to reduce these dyes in the bound state upon illumination. The dependence of the rate of the photoreduction on ascorbic acid concentration and on light intensity parallels the observations on the photoreduction of free fluorescein-type dyes in solution.[5] However, in several respects the photochemical behavior of the bound dyes is entirely different. Whereas, with the free dye, the quantum yield of photoreduction decreases with increasing dye concentration, for bound dyes the quantum yield increases with increasing dye concentration. Furthermore, nitrobenzene retards the rate of photobleaching of free dyes, while in the case of bound dyes the reaction is inhibited until all the nitrobenzene is consumed, after which the reaction proceeds at a rate equal to that for the inhibitor-free system.

We will now propose a scheme for the kinetics of the photoreduction which is compatible with our data. Throughout D, D* and D′ refer to the bound species, since the free dye is photochemically inert. On absorption of visible light, the dye in the ground state, D, is raised to its first electronically excited singlet state, D*, *i.e.*, (1) $D + h\nu \rightarrow D^*$. The excited molecule can then fall to the ground state with emission of fluorescence, or by a radiationless transition, *i.e.*, (2) $D^* \rightarrow D$ + heat (and/or $h\nu_f$). This excited species D* does not react with the reductant to give the reduced dye, since ascorbic acid does not quench the fluorescence of bound dye.

It is therefore necessary to postulate the existence of another (metastable) excited species D′ with which ascorbic acid reacts to give the colorless product. The metastable species might arise directly from the first excited state, namely, (3) $D^* \rightarrow D'$, or *via* an energy transfer between the dye molecules in the ground and those in the first excited state, namely, (4) $D^* + D \rightarrow D' + D$. The fact that the quantum yield increases with increasing dye concentration (Fig. 5) strongly favors step 4, and the linearity of the curve shows that step 3 is of negligible importance (see below). Further evidence for step 4 is the fact that self-quenching of fluorescence of bound dyes occurs at such remarkably low concentrations (Fig. 2). Energy transfer between dye molecules may be favored when their positions are fixed by the polymer chain. If we identify the metastable species as that giving rise to the low-temperature phosphorescence, step (5) $D' \rightarrow D + h\nu_p$, then, since in the presence of PMA there is no evidence of self-quenching of phosphorescence ($D' + D \rightarrow 2D$), we adduce more evidence in favor of step 4. Ascorbic acid (A) strongly quenches the phosphorescence hence the step (6) $D' + A \rightarrow D + A$ must be important.

Let us now suppose that the metastable species can also react with ascorbic acid to give colorless product, *i.e.*, (7) $D' + A \rightarrow$ product. Then assuming steady-state concentrations for the transient species D* and D′, we obtain the quantum yield ϕ of photobleaching the expression

$$\phi = \frac{k_7(A)}{k_5 + (k_6 + k_7)(A)} \times \frac{k_3 + k_4(D)}{k_2 + k_3 + k_4(D)}$$

Since ϕ increases linearly with dye concentration and goes through the origin (Fig. 5) therefore $k_2 >> k_4(D) >> k_3$. Hence, we eliminate step 3 as a mechanism for the formation of metastable dye molecules: such formation is much more likely to occur *via* step 4. From our data we calculate the following ratios for ethyl violet bound to PMA: $k_6/k_7 = 403$; $k_5/k_7 = 1.11$ mole/l.; $k_5/k_6 = 2.77 \times 10^{-3}$ mole/l. These values show that the rate of the reaction is limited by step 6, the quenching of the phosphorescent state by ascorbic acid. Since there is a parallel between the phosphorescent behavior and the photochemical behavior we identify the metastable state D′ as a long-lived state, probably triplet (see ref. 5).

The inhibition of the photoreduction by nitrobenzene might be explained by a termolecular reaction between D′, ascorbic acid (A), and nitrobenzene (X) as follows: $D' + X + A \rightarrow D +$ products. But this would give a rate equation in which the rate is inversely proportional to the amount of nitrobenzene present, *i.e.*, retardation rather than the observed inhibition. It is necessary, therefore, to postulate that step 7 really consists of two steps, namely, (7) $D' + A \rightarrow M$, where M is an intermediate complex, and (8) $M \rightarrow$ colorless products (I). The intermediate complex can react with the inhibitor resulting in its destruction and the reversion of excited dye molecules to the

(12) R. Arnold and J. T. G. Overbeek, *Rec. trav. chim. Pays-Bas.*, **T69**, 192 (1950).

ground state, *i.e.*, (9) M + X → colorless products (II) + D. If k_9 (X) > k_8 > k_7 (D) then the rate of destruction of inhibitor is dependent on the rate of formation of the intermediate complex and is independent of the concentration of the inhibitor, as is observed. Furthermore, this postulation accounts for the fact that appreciable photoreduction of the bound dye cannot take place until most of the inhibitor is destroyed.

From considerations analogous to those used to calculate the Stern–Vollmer self-quenching relation[10] we obtain for the dependence of fluorescence intensity on dye concentration (D)/[1 + k_4/k_2 (D)]. Figure 2 shows that this relation is applicable up to a concentration of about 10^{-5} *M* ethyl violet bound to PMA, from which we calculate that $k_4/k_2 = 1.95 \times 10^5$ l./mole. If the dye molecules were free in solution k_4 would be proportional to the diffusion-controlled collision frequency but since these molecules are fixed to a polymer chain, energy transfer by other mechanisms occurs. There is evidence that energy transfer takes place in pigment systems present in photosynthetic cells and is much more efficient *in vivo* than *in vitro*.[13] Chlorophyll exists in *grana* of plants at concentrations as high as 0.1 *M*. If self-quenching of the metastable state, namely, D′ + D → 2D, were to occur in plants, as it does in solution,[5,14] one would not expect any photochemical processes involving this excited state in plants. On the other hand, our data show that step 4, namely, D* + D → D′ + D is of overwhelming importance for bound dye molecules and that the quantum yield actually increases with increasing dye concentration. In an analogous manner, since photochemical processes take place in photosynthezing systems where the bound pigments are in high concentration, there must be an intimate connection between this unusual behavior and the fact that chlorophyll exists in the bound state in living systems.

(13) L. N. M. Duysens, *Nature*, **168**, 548 (1951).
(14) H. Gaffron, *Biochem. Z.*, **264**, 251 (1933).

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. III. Solutions of Sodium and Potassium Halides in N-Methylpropionamide and in N-Methylbutyramide from 30 to 60°[1a,b]

BY LYLE R. DAWSON, RICHARD H. GRAVES AND PAUL G. SEARS

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Properties of solutions of sodium and potassium chlorides and iodides and potassium bromide in N-methylpropionamide and sodium and potassium chlorides in N-methylbutyramide have been measured at ten-degree intervals from 30 to 60° for concentrations ranging from 8×10^{-4} to 0.5 molar. Kohlrausch plots for all of the systems exhibit relatively good agreement with the Onsager limiting equation to 0.01 molar or more. Modifications of the Onsager equation, which include viscosity effects describe the conductances of the systems studied to concentrations of 0.2 to 0.3 molar. Both the bulk viscosity of the solvent and short-range viscosity effects around the ions appear to influence the conductance.

The properties of solutions of several alkali halides in N-methylacetamide were described in an earlier paper.[2] Good agreement with the limiting Onsager conductance equation to concentrations of 0.01 molar or more was exhibited by these systems. At higher concentrations deviations from the pattern usually observed with strong electrolytes in water were attributed primarily to viscosity effects. The present paper describes the behavior of some of these alkali halides as solutes in N-methylamides having higher molecular weights.

Experimental

The equipment, experimental procedures and purification of the salts have been described previously.[2]

Solvents.—N-Methylpropionamide was prepared by treating monomethylamine with propionic acid. Xylene was added and the mixture was heated to crack out the water and distil off the xylene–water mixture. By this means unreacted propionic acid is removed also as a xylene–acid azeotrope. After removing the xylene the product was redistilled several times at low pressure (5 mm.) through an efficient column. This process yielded N-methylpropionamide having a dielectric constant of 164 and a conductivity of 3×10^{-6} ohm^{-1} cm.$^{-1}$ at 30°.

N-Methylbutyramide was prepared by the same procedure as for N-methylpropionamide except that the distilling column was electrically heated to lower the temperature gradient. This was done to reduce the possibility of thermal decomposition. The conductivity of the product was 10^{-6} ohm^{-1} cm.$^{-1}$; its density and refractive index indicated a high degree of purity.

Solutions.—All solutions were prepared on a weight basis with transfers made in a dry-box. Sufficient quantities of solutions were prepared so that separate portions of each could be used for conductance, density and viscosity measurements.

Dielectric Constants.—Dielectric constants of N-methylbutyramide were measured with a General Radio Type 821-A Twin-T Impedance Measuring Circuit,[3] using a General Radio Type 1001-A Standard Signal Generator as a signal source and a Hallicrafters Model S-40A multiband receiver as a null detector. All measurements were made at 10 megacycles. The cell used was a modification of the type devised by Connor, Clark and Smyth[4] which has been described by Leader.[5]

Results

Properties of the solvents are listed in Tables I and II. A plot of dielectric constant against temperature at six points between 25 and 40° for N-methylbutyramide yielded a straight line from which the values at 50 and 60° were obtained by linear extrapolation.

(1) (a) Presented at the 130th Meeting of the American Chemical Society in Atlantic City, September, 1956; (b) based in part on research performed under a contract with the U. S. Army Signal Corps.
(2) L. R. Dawson, P. G. Sears and R. H. Graves, THIS JOURNAL, **77**, 1986 (1955).
(3) D. B. Sinclair, *Proc. Inst. Radio Eng.*, **28**, 310 (1940).
(4) W. P. Connor, R. P. Clark and C. P. Smyth, THIS JOURNAL, **64**, 1379 (1942).
(5) G. R. Leader, *ibid.*, **73**, 856 (1951).