$\times 10^{-3}$ sec.[7] The ultraviolet catalyzed reaction proceeds *via* an excited state of PTD with a lifetime of 8.4×10^{-7} sec. as computed from the observed value of α.

The probability of the dye peroxide DO_2 reacting with unexcited dye is 414 times greater than with PTD. If we regard the former reaction as one in which every encounter is effective, then the lifetime of the peroxide, namely, $1/k_7$, is given by $(k_8/k_7)(k_9/k_8)$ divided by 6.6×10^9 or 1.4×10^{-4} sec. It should be pointed out, however, that nothing in our data requires the *de facto* existence of the dye peroxide DO_2. The formation of an excited oxygen molecule would be equally compatible with our results. This possibility has been denied, however, on spectroscopic grounds (for summary of arguments, see ref. 4, p. 68).

Our scheme differs from that of Livingston[16] in certain respects. In that study, the chlorophyll-photosensitized autoxidation of allylthiourea, the spontaneous decay of the long-lived state (our step 4) was not considered. Furthermore, the fluorescence of chlorophyll unlike that of proflavine is quenched by small amounts of oxygen. Hence we have not included the step involving the direct attack of oxygen on D*, as did Livingston. Since the concentrations of PTD employed do not appreciably quench the fluorescence of proflavin, we can neglect this contribution. The decline in rate at very high PTD concentrations (10^{-2} *M*) would be due to this step. Our scheme also differs in the early steps for the formation of the long-lived state from that proposed for proflavine photoreduction.[5] There it was found that with increasing dye concentration the quantum yield of photoreduction increased and the fluorescence yield decreased even at concentrations of dye below 10^{-4} *M*. In the present study the quantum yield of photoöxidation decreased with increasing dye concentration. Furthermore, the fluorescence yield is independent of dye concentration up to 10^{-4} *M* in dye. We attribute these differences to salt effects which become important for low buffer concentrations but which are suppressed in the present work by operating in a medium of 0.1 *M* buffer.

The inhibitors for the reaction are all characterized by the fact that they are easily autoxidized. Thus very weak reducing agents such as glucose are ineffectual, but ascorbic acid which is more readily autoxidized than is PTD is a good inhibitor. Some substances such as PTD are good quenchers for the long-lived state as shown by their retarding effect in photoreduction of dyes.[14] In the presence of oxygen, however, reaction of the long-lived state with oxygen is much more highly favored than reaction with PTD. In fact, the form of the rate data on PTD concentration seems to rule out this latter step as being of any consequence in photoöxidations.

We are at a loss to understand why the proflavine sensitized photoöxidation is diminished on binding the dye to polymer since the rate of photoreduction is enhanced under these conditions. This anomaly in behavior is also reflected in the results of our studies on the photodynamic action using various biological substrates.[8] Proflavine is exceptional in that despite its powerful photosensitizing effect when it is free in solution, it is ineffectual in mediating photodynamic action on, for example, desoxyribonucleic acid (transforming principle), suggesting that it is in the bound state in the presence of this substrate.

BROOKLYN, N. Y.

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

Photoreduction of Dyes in Rigid Media. II. Photoredox Properties of Thiazine Dyes[1a,1b,1c]

BY BARRET BROYDE AND GERALD OSTER

RECEIVED MARCH 19, 1959

Thiazines undergo photoreduction to their leuco forms when incorporated into high viscosity glasses of polyhydroxy compounds. The rate of photoreduction is proportional to the square root of the diffusion coefficient suggesting a diffusion-controlled process in which stationary state conditions are not achieved. Illumination of highly concentrated dye glasses containing an added mild reducing agent yields an intermediate color which reverts to the original dye on softening the glass. This species is an entrapped dimer of the normal dye. Near ultraviolet light irradiation of the leuco glass yields the normal dye and other colored species. In acid glasses a red form is produced and in basic glasses a yellow form is the result, both forms reverting to the leuco species on softening the glass. The ratio of red to blue forms increases when the viscosity of the medium is increased. These intermediate species are believed to be a semiquinone and a diradical, or a molecule in the triplet state entrapped in the rigid medium.

Introduction

Thiazine dyes in solution are readily photoreduced in the presence of mild reducing agents[2] and certain chelating agents.[3] The rate of photoreduction was found to decrease when the viscosity of the medium was increased, suggesting that a

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[1] (a) Presented before the 135th National Meeting of the American Chemical Society, Boston, April 9, 1959; (b) this paper represents a part of the dissertation to be submitted by Barret Broyde to the faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degee of Doctor of Philosophy; (c) this work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Force Research and Development Command under Contract No. AF 49(638)-293 and by the U. S. Atomic Energy Commission, Contract No. AT(30-1)-2206.

(2) M. Mudrovcic, *Z. wiss. Photo.*, **26**, 171 (1928); K. Weber, *Z. physik. Chem.*, **B15**, 18 (1931); G. Holst, *ibid.*, **B169**, 9 (1934); J. Weiss, *Trans. Faraday Soc.*, **32**, 1331 (1936); E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940); M. Pestemer, *Z. Elektrochem.*, **58**, 121 (1954); H. Hardwick, THIS JOURNAL, **80**, 5667 (1958).

(3) G. Oster and N. Wotherspoon, *ibid.*, **79**, 4836 (1957).

diffusion-controlled process is involved.[4] We have found, however, that despite the extremely high viscosities of glucose glasses (as high as 10^{13} poise) the photoreduction of thiazines in this medium proceeds with a rate of the same magnitude as that in water. Here the glucose itself serves as the reducing agent and being the medium is always in contact with the dye molecules.

The role of the viscosity of the glass in the photoreduction of the thiazines is different from that in the photoreduction of the triphenylmethane dyes. In the case of triphenylmethane dyes, the high viscosity medium hinders internal rotation and hence suppresses internal conversion to the ground state thereby making a greater proportion of excited dye molecules available for reduction.[5] With the thiazine dyes, however, the molecules are already planar and the viscosity has little influence on intramolecular processes.

Photoreduction of concentrated solutions of thiazine dyes in rigid media has permitted the isolation of the pure dimer form of the dye for the first time.

The reduced (leuco) forms of the thiazine dyes can be photoöxidized by near ultraviolet light.[4] In fluid media this yields only the normal form of the dye. By employing highly viscous media we have trapped new colored species which are stable only as long as the viscosity of the medium remains high.

It is the purpose of the present paper to elucidate the kinetics and mechanism of the photoreduction of thiazine dyes, particularly azure A, and the photoöxidation of the leuco forms in extremely viscous media.

Experimental

Materials.—All the dyes were Histological Grade, obtained from Fisher, as were the other materials. The polyvinyl alcohol was Elvanol 52-22 Grade obtained from Du Pont.

Preparation of the Glasses.—Polyvinyl alcohol films were made by casting a film of a 10% aqueous solution containing dye on a glass plate and allowing it to dry. Glasses made with different sugars were prepared by heating the appropriate sugar-water mixture in a KNO_3–$NaNO_2$ bath at 210° with rapid stirring until melting was complete. This procedure, if carried out quickly, gives a glass relatively free of yellow-brown coloration which would seriously interfere with spectral determinations. The viscosity of the glass is determined essentially by the water content of the original mixture. In order to suppress dark reduction of the dye, the dye is added with stirring at 130° as the glass is cooling. Likewise, in those cases where base is added, in order to suppress browning of the glass which is particularly severe at high *p*H values, the base is introduced while the glass is cooling.

The glasses with higher water content crystallize the most rapidly at room temperature. Thus a glass containing 70% glucose crystallizes in about 3 hours while one containing 90% glucose is stable for two days. In any case, crystallization is suppressed by storing the glasses at −20° in the freezing compartment of a refrigerator. All experiments described in the present paper were carried out with glasses exhibiting no crystallinity.

The temperature dependence of the viscosity of the glucose glasses was determined using a Brookfield rotating viscometer (type HBF) capable of measuring viscosities up to 3 × 10^5 poise. In those cases (*e.g.*, 90% glucose glass, below 40°) where the viscosity exceeded this value the data were extrapolated. For relatively low viscosities (less than 10^2 poise) the type LVF Brookfield rotating viscometer was employed.

Optical Measurements.—The absorption and fluorescence spectra were determined with the recording spectrophotometer described elsewhere[6] using the glass without the dye as the blank. The photoreductions were followed by setting the monochromator at a wave length corresponding to the absorption maximum of the original dye and illuminating with a 500-watt TDC slide projector, using a red filter, Corning No. 2-59. The sample was immersed in a glass water-bath whose temperature was controlled by an Aminco circulating liquid thermostat. For the photooxidations of the leuco dyes the samples were cross illuminated in the water-bath with a 100-watt AH 4 mercury lamp, using a glass filter combination (Corning No. 7-83) which isolates the 365 mμ lines and white light was used to follow the production of the colored species.

Results

Thiazine dyes do not obey Beer's law in most solvents. In water the spectra are considerably concentration-dependent, but the position of the long wave length maximum is constant.[7] This is also true in glucose glass, except that here the positions of the long wave length maxima are slightly different from those in water (compare Fig. 1 and Table I with ref. 6).

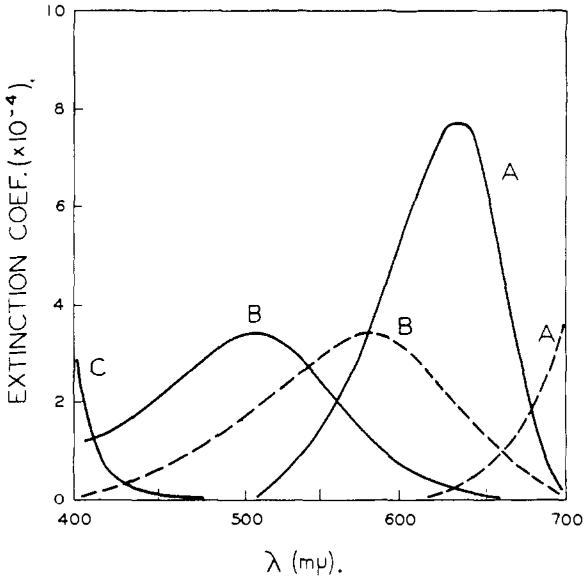

Fig. 1.—Absorption spectra (solid lines) and fluorescence spectra (dashed lines-relative intensities) of 10^{-5} *M* azure A in 80% glucose glass at 25°: A, blue form; B, red form; C, leuco form.

In the presence of a mild reducing agent thiazine dyes are photoreduced in water. Photoreduction also occurs in glucose glass but here no added reducing agent is necessary. Part of the spectrum of the resultant leuco dye is shown in Fig. 1. The complete spectra of the leuco form are not obtainable since the media employed absorb strongly in the near ultraviolet region. The initial rates of photobleaching of the blue form in two glucose glasses are given in Fig. 2. In this figure the rates of photoreduction for glasses containing 75 and 90% glucose are shown over the range from 5 to 45°. Intermediate results, obeying the same functional relationship as those shown in the

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[4] G. Oster and N. Wotherspoon, *J. Chem. Phys.*, **22**, 157 (1954).

[5] G. Oster, J. Joussot-Dubien and B. Broyde, This Journal, **81**, 1869 (1959).

[6] N. Wotherspoon and G. Oster, *ibid.*, **79**, 3992 (1957).

[7] E. Rabinowitch and L. F. Epstein, *ibid.*, **63**, 69 (1941); D. R. Lemin and T. Vickerstaff, *Trans. Faraday Soc.*, **43**, 491 (1947).

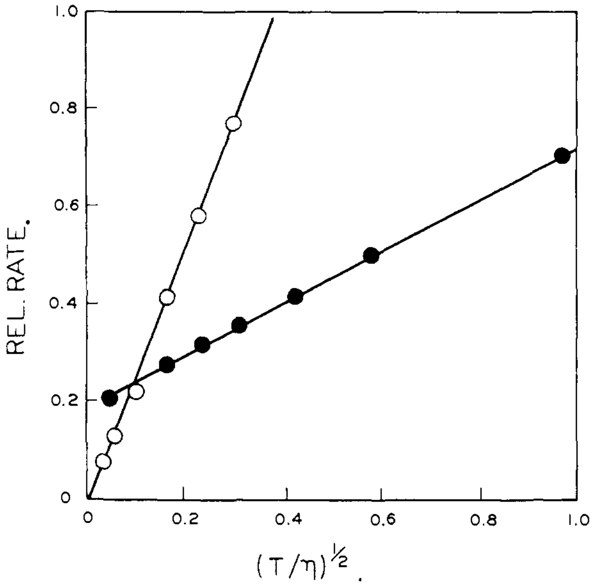

Fig. 2.—Rate of photoreduction of azure A (5×10^{-6} *M*) in glucose glasses (open circles, 90% glucose; filled circles 75% glucose). Viscosity (η) in poise and *T* in °K.

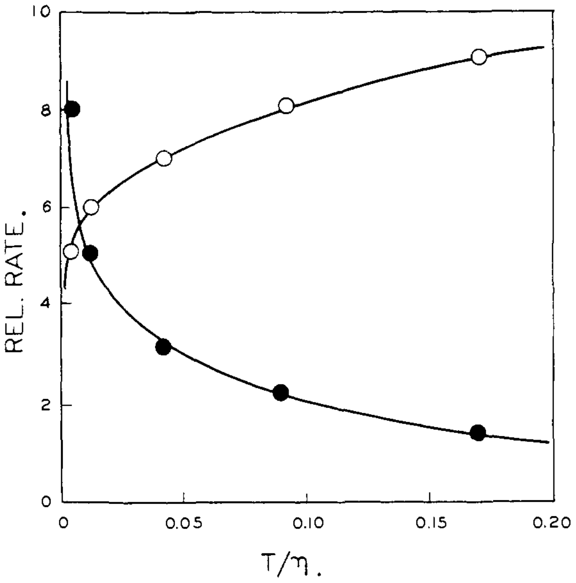

Fig. 3.—Rate of formation by ultraviolet light of red form (filled circles) and of blue form (open circles) from 10^{-4} *M* leuco azure A in 85% glucose glasses.

graph, were obtained for 80 and 85% glasses. A 70% glass has a lower slope but cannot be represented using the same abscissa scale. Other glasses made from polyhydroxy compounds (sucrose, maltose, raffinose, galactose, fructose and polyvinyl alcohol) give qualitatively similar results.

TABLE I

ABSORPTION MAXIMA (mμ) OF PHOTO PRODUCTS

Dye	Blue form	Red form
Thionine	590	520
Azure C (monomethylthionine)	620	500
Azure A (u-dimethylthionine)	630	510
Azure B (trimethylthionine)	640	520
Methylene blue (tetramethylthionine)	660	560

Illumination with near ultraviolet light of the leuco form in water and in other low viscosity solvents yields only the normal blue form.[4] In extremely viscous glasses a red form is also obtained, the absorption and fluorescence spectra of which are illustrated in Fig. 1 (see also Table I). The red form is stable only in highly viscous media and reverts to the leuco form when the glass is softened either by heating or by moistening. The red form also can be produced in the other polyhydroxy glasses mentioned above, but the absorption maxima differ slightly from each other. The red form obeys Beer's law up to at least 2×10^{-4} *M*. This conclusion was obtained by fading glasses containing various known amounts of the blue dye and irradiating the colorless glasses with ultraviolet light. Irradiation by ultraviolet light yields both the red and blue forms. The blue form is faded with visible light leaving the red form unaffected, since under these conditions the red form is not photosensitive. The leuco form is again irradiated with ultraviolet light and so on until all the dye is present as the red form. The ratio of red to blue form increases as the viscosity is increased, either by lowering the temperature (Fig. 3) or by decreasing the amount of water in the glucose glass. Changes in temperature *per se* do not alter the ratio in the temperature range shown in Fig. 3 (5 to 45°). In rigid glucose glasses at low temperatures (about −10° or lower) the leuco form is not photosensitive (see ref. 4).

Glucose glass is somewhat acid (about *p*H 3). Illumination of the leuco dye with near ultraviolet light in neutral glass (neutralized with KOH) yields a yellow form (absorption maximum at 470 mμ with a molal extinction coefficient of 1.5×10^4) as well as the red form, but now the red form is photosensitive. In basic conditions (*p*H 8) only the yellow form is produced and exists as long as the high viscosity is maintained. The yellow form is highly fluorescent (fluorescence maximum at 560 mμ) but is not photosensitive. The yellow glass becomes colorless on softening.

Glasses with comparatively high concentrations of dye (greater than about 2×10^{-4} molal) in the presence of large amounts (about 10%) of allylthiourea appear purple after irradiation with deep red light (Fig. 4). On prolonged illumination, particularly with yellow light, this purple species eventually disappears to give the leuco glass. The purple color changes to blue when the glass is softened.

Discussion

The fact that photoreduction occurs at all in such rigid media indicates that the excited dye reacts with molecules in its immediate environment. The process is obviously diffusion controlled, since the rate depends on the viscosity of the medium (Fig. 2). The flux Φ of molecules of initial concentration c_0 diffusing into a sphere of radius *R* (the "reaction sphere") is given by the relation[8]

$$\Phi = 4\pi DRc_0\left(1 + \frac{R}{\sqrt{\pi Dt}}\right) \qquad (1)$$

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[8] M. Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917); S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).

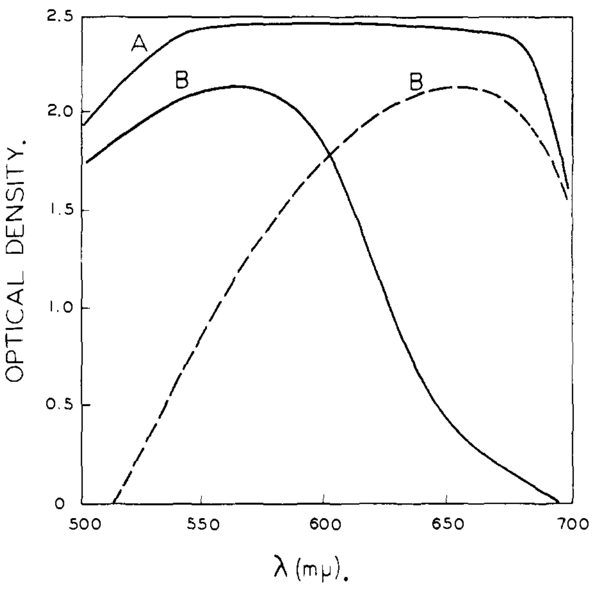

Fig. 4.—Absorption spectra (solid lines, one cm. path length) and fluorescence spectra (dashed lines, relative intensities) of 8 × 10^{-4} M azure A in glass containing 70% glucose, 10% allylthiourea and 20% water: A blue, form; B, dimer.

where D is the sum of the translational diffusion constants of the reacting species. For most diffusion-controlled processes, *e.g.*, fluorescence quenching in water,[9] the transient term is negligible compared with unity and the reaction rate is proportional to D, *i.e.*, proportional to T/η. For higher viscosities, the time dependent term becomes appreciable[10] and when the viscosity is extremely high, as in our case, the transient term dominates the reaction rate. Hence, for the glucose glasses the rate is proportional to the square root of the diffusion constant, *i.e.*, proportional to $(T/\eta)^{1/2}$ (see Fig. 2).

The higher the concentration of glucose in the glass, the greater should be the number of reducing molecules surrounding the dye molecules. This increases the chance of a light excited molecule reacting within its lifetime and is equivalent to increasing the concentration c_0 of a reactant as described in eq. 1. However, the rate increases much more rapidly than simple proportionality to c_0. It appears, therefore, that the effective size of the reaction sphere increases with increasing glucose concentration.[11] The net effect in any case is that increasing the glucose content increases the proportionality constant between the reaction rate and $(T/\eta)^{1/2}$.

The purple species remaining after irradiation of concentrated azure A glass containing allylthiourea is probably the dimer of the dye. Although dimers have been postulated to account for the variations with concentration of absorption spectra of the thiazines in water,[7] no one has heretofore been able to isolate the pure dimer. The monomer form is much more readily photoreducible than is the dimer. In highly viscous glasses the monomer–dimer equilibrium is achieved only very slowly so that photochemical elimination of the monomer leaves the pure dimer. Some of the pure dimer form will of course revert to the monomer form when the glass is softened. Hence, warming of the purple glass gives a bluish glass. The dimer formed in low-viscosity liquids is nonfluorescent, but in high viscosity media this species is fluorescent, probably because internal rotational conversion is suppressed.[12,5] The dimer cannot be isolated by merely irradiating the concentrated dye glass without added reducing agent. Concentration quenching of long-lived states will lower the quantum yield of photoreduction[13] and the introduction into the glass of large concentrations of stronger reducing agents counteracts this effect. High concentrations of the added reducing agent are required since bimolecular encounters between non-nearest neighbors are suppressed in such highly viscous media. If the added reducing agent favors the photoreduction of the monomer while the dimer is relatively stable, then the dimer will remain after irradiation with light which overlaps the absorption spectra of both species.

The photorecovery of the dye from its leuco form by ultraviolet light is, of course, a photooxidation. In low viscosity media, photoöxidation occurs by the expulsion of an electron from the excited leuco dye and is followed immediately by the loss of a hydrogen atom, to give the normal dye. This process also occurs in viscous media but as the viscosity is increased, another process yielding the red form becomes more favored. This latter process could involve the direct expulsion and entrapment of a proton from the central nitrogen atom of the leuco thiazine molecule giving a diradical, the red species. Although this expulsion could also occur in low viscosity media the proton would immediately recombine with a molecule. Softening the red glass allows recombination of the expelled proton and the diradical to give the leuco molecule. Colored intermediate species formed by irradiating glasses at very low temperature containing leuco methylene blue have been attributed to being semiquinones.[14] These do not appear to be the same species which we found since they did not obey Beer's law and no fluorescence was reported, whereas in our case it is very pronounced. The yellow intermediate form obtained in basic glasses may be a semiquinone probably similar to yellow semiquinone obtained by chemical reduction.[15] The reason given for the stability of the semiquinone in only acid media[15] is probably incorrect since the first proton adds to the central nitrogen and not to an amino nitrogen.[16] This species would arise by the expulsion of an

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(9) B. Sveshnikoff, *Acta Physiochim. U.R.S.S.*, **4**, 452 (1935); J. Q. Umberger and V. K. LaMer, THIS JOURNAL, **67**, 1099 (1945).

(10) E. J. Bowen, A. W. Barnes and P. Holliday, *Trans. Faraday Soc.*, **43**, 27 (1947).

(11) Compare, F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, **4**, 425 (1949), and *Ind. Eng. Chem.*, **41**, 2551 (1949).

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

(13) See, for example, G. Oster and A. H. Adelman, *ibid.*, **78**, 913 (1956).

(14) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2419 (1943).

(15) L. Michaelis, M. P. Schubert and S. Granick, *ibid.*, **62**, 204 (1940).

(16) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 1144 (1943).

electron from the leuco dye. It would not react further to give the blue form since basic glucose is a strong reducing agent. Any diradical (red species) formed could be converted easily to leuco dye in such strongly reducing environment.

Alternatively, the red species could be an entrapped excited triplet state of the leuco form. The absorption and fluorescence then would arise from triplet–triplet transitions. Extremely high viscosities would favor the stability of the triplet by inhibition of configurational changes necessary for conversion to the singlet ground state of the leuco dye. The stability of the triplet state would be even further enhanced by interaction with the medium as is indicated by the small shifts in absorption spectra of the red species in the different glasses. Recently we found that leuco dye glasses give only the blue form when exposed to ionizing radiation.[17] It is known that triplet states of aromatic compounds produced by ultraviolet light cannot, however, be produced by ionizing radiation in analogy with our system.

One might also postulate that the colored forms arise from expulsion of electrons yielding a different type of semiquinone and an electron trapped in the medium. We have not, however, found the near infrared absorption considered to be characteristic of entrapped electrons.[18]

[17] G. Oster and B. Broyde, details to be published.

[18] H. Linschitz, M. G. Berry and D. Schweitzer, THIS JOURNAL, **76**, 5833 (1954).

BROOKLYN, N.Y.

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

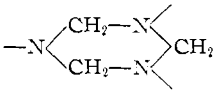
The Cyclic Structures of Methylene Aniline and Methylene-*p*-toluidine. A Dipole Moment Study

BY ROBERT A. FLORENTINE AND JOHN G. MILLER

RECEIVED APRIL 16, 1959

The electric moments of trimeric methylene-aniline and trimeric methylene-*p*-toluidine have been measured in benzene, carbon tetrachloride and ligroin. The former has an average moment of 1.17 *D*, and the latter, 0.89 *D*. These moments support the assignment of a *sym*-triazane ring configuration to these trimers and indicate that the rings are of the chair form. The pyramidal arrangement of the valence bonds of the nitrogen atoms appears to be flattened greatly in these rings.

Reaction of aniline with formaldehyde in water or alcohol at 0° produces nearly exclusively trimeric methylene aniline, $(C_6H_5NCH_2)_3$. Similarly, *p*-toluidine gives trimeric methylene-*p*-toluidine, $(CH_3C_6H_4NCH_2)_3$. These polymeric compounds appear to possess fixed cyclic structures containing the *sym*-triazane ring



as revealed by the definiteness of their molecular weights and melting points and by their reduction-cleavage into amine, methylated amine and dimethylated amine.[1]

This paper presents further evidence for the cyclic structures of these trimers. This evidence comes from measurement of their dipole moments and shows that the molecules are probably in strainless chair forms, with the pyramids of valence bonds of the nitrogen atoms flattened nearly to a coplanar arrangement.

Experimental

Solvents.—C.P. benzene was refluxed over sodium for 30 minutes and then distilled through a 16-inch packed column (glass helices) under high reflux. The product was stored over sodium until used; b.p. 80.2° cor., n^{30}_{D} 1.4983, d^{30} 0.8737. C.P. carbon tetrachloride was distilled through the same column; the fraction boiling at 76.2° was collected and stored over $MgSO_4$; d^{30} 1.5850, n^{30}_{D} 1.4574. "High boiling" ligroin, a mixture of hydrocarbons boiling from 68 to 105°, was stored over sodium, a single stock being used throughout any dipole moment determination. Transfer of solvent and solutions to the measuring equipment was carried out under dry air pressure in all-glass apparatus to prevent evaporation and contamination.

Other Materials.—Baker C.P. aniline was freshly refluxed over zinc dust and distilled under reduced pressure. The formaldehyde was Baker C.P. grade (36% solution in water). Matheson C.P. *p*-toluidine was crystallized from cold anhydrous ethanol. The samples used melted at 44.5° cor.

Preparation of the Trimers.—The preparation of the crystalline trimers of methylene aniline and methylene-*p*-toluidine followed essentially the method of Miller and Wagner.[1] The purification of the methylene aniline was accomplished by a series of extractions and crystallizations with absolute ethanol. The recrystallized trimer was kept in a vacuum desiccator, m.p. 141.0° cor. The methylene-*p*-toluidine was recrystallized from ligroin, m.p. 128.1° cor.

Measurements.—The dielectric constants were determined by use of a radiofrequency bridge over a range of frequencies from 0.5 to 1.5 megacycles, the measurements and calculations being made according to the procedures outlined previously.[2] The values of refractive index were determined[3] with a Pulfrich refractometer, using the Na_D, H_α and H_β lines. The Drude function $1/\phi = (n^2 + 2)/(n^2 - 1)$ was calculated for each of the frequencies and then extrapolated linearly to zero frequency, whereby n^2 was obtained for infinite wave length for each solution. Densities were measured with a pycnometer of approximately 25-cc. volume. A large oil-bath kept at 30 ± 0.005° was used to control the temperature for all the measurements. Each trimer was measured at five different concentrations in each solvent. In benzene and CCl_4 these concentrations lay in the mole fraction range from 0.001 to 0.01. In ligroin, methylene aniline was studied at weight fractions from 0.0003 to 0.0012 and methylene-*p*-toluidine from 0.0002 to 0.0025.

Calculation of the Dipole Moment Values.—The dielectric constant ϵ_{12}, density d_{12}, and square of the refractive index for infinite wave length n_{12}^2, for the solutions were treated as linear functions of the mole fraction of the solute N^2, for the benzene and CCl_4 solutions and as linear functions of the weight fraction of the solute w_2, for the ligroin solutions. The least squares values are shown in Table I. The slope

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[1] J. G. Miller and E. C. Wagner, THIS JOURNAL, **54**, 3698 (1932).

[2] J. G. Miller, *ibid.*, **60**, 42 (1938); **64**, 117 (1942).

[3] J. G. Miller, *ibid.*, **56**, 2360 (1934).