the basal plane of a prism having temperature as its vertical axis and consisting of a number of intersecting surfaces. The pyrophosphate solid solution surface is concave upward with its minimum a broad valley and sides of decreasing slope as the P_2O_5 content is increased. It intersects the tripolyphosphate surface; first the surface of the $Na_5P_3O_{10}$ solid solution series, then the surface of $Na_5P_3O_{10}\cdot K_5P_3O_{10}$, which is convex upward, as is shown by the curves of constant P_2O_5 content of 0.40, 0.41 and 0.425 P_2O_5, of Fig. 2, then the surface of $K_5P_3O_{10}$. The change in temperature of the intersection with K_2O content is shown in Fig. 9, and the locus of compositions is indicated in Fig. 1.

The melting surface of KPO_3 sweeps down to its intersection on the one side with the surfaces of the tripolyphosphates and on the other side with the melting surface of the compound $3NaPO_3\cdot KPO_3$, which come together at the ternary eutectic, E. The melting surface of $3NaPO_3\cdot KPO_3$ has a comparatively small temperature gradient, and intersects the surface for $NaPO_3$ from the incongruent melting point of $3NaPO_3\cdot KPO_3$ on the side $NaPO_3$–KPO_3 at 552° to the reaction point C at 517°, then intersects the surface of tripolyphosphate solid solutions from the reaction point C to the eutectic, E. The surface of $NaPO_3$ intersects the surfaces of $3NaPO_3\cdot KPO_3$ and $Na_5P_3O_{10}$, and reaches its minimum temperature at the reaction point, C.

WASHINGTON, D. C.

NOTES

Phototropic Behavior of 4-(*p*-Dimethylaminobenzeneazo)-phenylmercuric Acetate

BY M. G. HOROWITZ[1] AND I. M. KLOTZ

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In the course of investigations of the interaction of proteins with azomercurials, it was observed that exposure of the dye 4-(*p*-dimethylaminobenzeneazo)-phenylmercuric acetate, dissolved in certain organic solvents, to light led to a drop in the absorption of light in the region of 420 mμ. The absorption could be restored to its original value if the dye solution were stored in the dark. This light effect appeared to be similar to the photo-induced *trans–cis* isomerization which has been observed[2–5] with other azo dyes. The isomerization reaction in the dark was studied as a function of solvent and time, since the results have a bearing on the configuration of the azomercurial in aqueous solution.

Experimental

4-(*p*-Dimethylaminobenzeneazo)-phenylmercuric acetate was prepared by a modification of the method of Jacobs and Heidelberger.[6] The absorption spectrum of the dye was determined with a solution which had been stored in the dark overnight and also with a solution which was exposed to light before each reading. The solvents used were commercial preparations.

Optical measurements were made with the Beckman spectrophotometer, Model DU.

The rate of the *cis–trans* transformation was determined with a sample of the dye which had been dissolved in NN'-dimethylformamide (or pyridine) and exposed to illumination until the absorption at 420 mμ was at the minimum value which could be obtained with the available light intensity. The solution was then placed in the cell compartment of the spectrophotometer where it was protected from extraneous light. The increase in the optical density readings at 420 mμ was recorded at intervals. The temperature at which the reaction proceeded was controlled by water circulating from a thermostated bath through the jacket surrounding the cell compartment.

If x is the optical density at 420 mμ when the dye is all in the *trans*-form, y the lowest reading which can be obtained at 420 mμ after exposure of the solution to light, and z the reading of the solution at 420 mμ at any given time, then c_0 the initial concentration of the *cis*-dye is proportional to $(x - y)$ and c, the concentration of the *cis*-isomer at any given time, t, is proportional to $(x - z)$. Initial concentration of the *cis*-form is taken as the concentration at the moment when the solution is cut off from light.

Results and Discussion

The absorption spectrum of 4-(*p*-dimethylaminobenzeneazo)-phenylmercuric acetate dissolved in dimethylformamide is shown in Fig. 1. The spectrum of the solution maintained in the dark shows

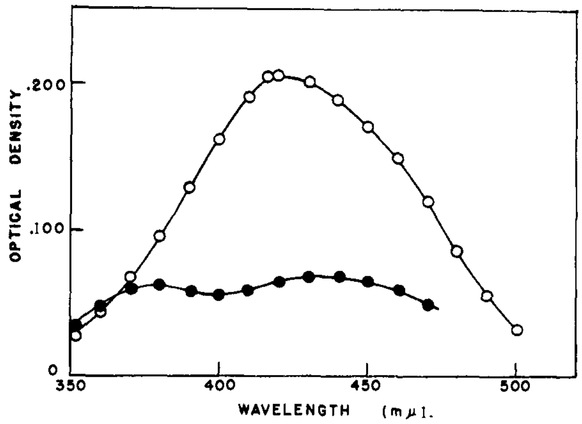

Fig. 1.—Spectrum of a 6.3 × 10^{-6} *M* solution of 4-(*p*-dimethylaminobenzeneazo)-phenylmercuric acetate in N,N'-dimethylformamide: *trans*-form, ○; steady state mixture of *cis*- and *trans*-forms after exposure to light, ●.

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[1] Fellow of the National Foundation for Infantile Paralysis, 1952–1954.

[2] G. S. Hartley, *Nature*, **140**, 281 (1937).

[3] G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

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[5] W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **76**, 1856 (1953).

[6] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **20**, 513 (1915).

a peak at 420 mμ which may be attributed to the *trans*-form of the dye, as has been suggested for other azo dyes.[3–5] The absorption at 420 mμ dropped after exposure of the solution to light and a new peak began to develop at 380 mμ. In addition, the original band shifted to somewhat longer wave lengths. These changes are due to the production of the *cis*-isomer.[3–5] The double-banded curve shown in Fig. 1 may be ascribed to the existence of both *cis*- and *trans*-forms in the steady state mixture maintained in the presence of light.

Almost identical spectra were obtained for the dye dissolved in pyridine which, like dimethylformamide, is an aprotic solvent. In contrast, in a series of primary alcohols, solvents with proton-donor character, the concentration of *trans*-isomer in the steady state (at a given light intensity) was always greater than in the aprotic solvents, and, furthermore, increased as one went downward in the series from decanol to ethanol. Such behavior is consistent with the suggestion that the catalysis of the *cis–trans* transformation is directly dependent on the proton-donor ability of the solvent and that the intermediate complex is ionic.[3,5] It also becomes apparent why this azo compound exists entirely in the *trans* form in aqueous solutions.

The kinetics of the dark reaction, the *cis–trans* isomerization, were followed quantitatively in dimethylformamide and in pyridine, respectively. In each case, a first-order rate law was followed (Fig. 2). Rate constants, k, computed from the slopes of the lines in Fig. 2, are listed in Table I. From the increase in rate with increasing temperature, the free energy $\Delta F^{\ddagger}$, enthalpy $\Delta H^{\ddagger}$, and entropy $\Delta S^{\ddagger}$, of formation of the activated complex were computed.[7] The magnitudes of these quantities are close to those observed in the *cis–trans* isomerization of other azo dyes.[3] Evidently the mechanism of the transformation is the same in all cases.

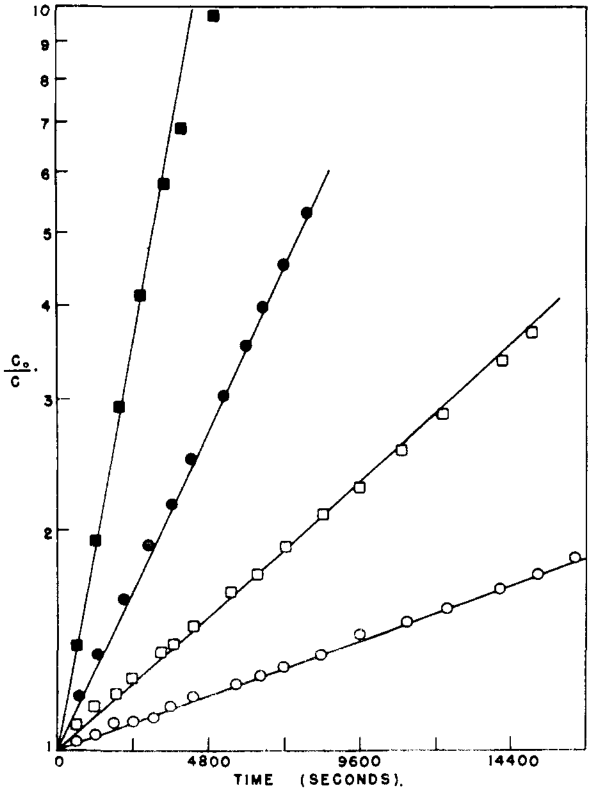

Fig. 2.—Rate of *cis–trans* conversion of 4-(*p*-dimethylaminobenzeneazo)-phenylmercuric acetate in N,N′-dimethylformamide at 19.4°; ○, in N,N′-dimethylformamide at 19.4°; ●, in N,N′-dimethylformamide at 35.4°; □, in pyridine at 19.4°; ■, in pyridine at 35.4°.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE *cis–trans* TRANSFORMATION OF 4-(*p*-DIMETHYLAMINOBENZENEAZO)-PHENYLMERCURIC ACETATE

Solvent	k, sec.$^{-1}$ × 10^5 At 19.4°	At 35.4°
Pyridine	8.81	53.3
N,N′-Dimethylformamide	3.68	21.0

TABLE II

"THERMODYNAMIC" QUANTITIES FOR THE *cis–trans* TRANSFORMATION OF 4-(*p*-DIMETHYLAMINOBENZENEAZO)-PHENYLMERCURIC ACETATE AT 19.4°

Solvent	$\Delta F^{\ddagger}$ (cal./mole)	$\Delta H^{\ddagger}$ (cal./mole)	$\Delta S^{\ddagger}$ (e.u.)
N,N′-Dimethylformamide	23,000	18,900	−14.0
Pyridine	22,500	19,600	−9.9

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[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 95.

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The Premixed Hydrogen–Fluorine Flame and its Burning Velocity

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In recent years we have studied various high temperature flames, among them the H_2–F_2 flame.[1–3] This was a diffusion type flame, with pure F_2 burning in excess H_2.

The literature data on the possibilities of premixing the two gases are conflicting. We observed a number of years ago[4] that the flame is self-igniting whenever pure fluorine gas emerges from a copper tip into a H_2 atmosphere.[2,3] Our recent attempts to mix the two gases in a steel chamber cooled to −78° at linear velocities up to 100 m./sec. invariably led to self-ignition in the chamber.[5]

On the other hand, Eyring and Kassel[6] described the ignition- and explosion-free mixing of the two gases, in the whole range of 100% H_2 to 100% fluorine at room temperature, with only occasional explosions, which they believed were initiated

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[6] H. Eyring and L. Kassel, THIS JOURNAL, **55**, 2796 (1933).