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[CONTRIBUTION FROM THE BIOCHEMISTRY DEPARTMENT, MEDICAL SCHOOL, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN.]

### Photoresponsive Systems. I. Photochromic Macromolecules<sup>1</sup>

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Azo dyes bearing acrylamide groups were synthesized and copolymerized with acrylic and methacrylic acids to yield photochromic polyelectrolytes. The optical behavior of the isomerizing side chains was qualitatively studied, especially the *cis* → *trans* isomerization process, and compared with that of corresponding alkylamide dyes (copolymerized monomer dye models), which are also photochromic and moderately soluble in water. Preliminary comparison of adsorption bound dyes was made. The geometry of the various dyes can be switched at will by irradiation, but the relaxation processes vary with environment of the dye, so that three distinct types of dye are defined: free dyes, adsorption bound dyes, and covalently bound (or tethered) dyes. All these behave reversibly and react with nucleophilic catalysts. In the case of the tethered dyes, irradiation response and dark relaxation behavior are linked to the charge and conformation of the copolyelectrolyte.

Photoresponsive systems are systems which respond to light energy beyond merely absorbing and releasing it as heat. Storage of the light energy for varying lengths of time, to reappear as fluorescence, phosphorescence, and chemical or even mechanical energy, are properties of photoresponsive systems. In this work, systems have been studied which utilize photochromic<sup>2,3</sup> azo dyes as the absorbing chromophores. In the attendant absorption process, light energy becomes stored up in what is probably best called chemical energy, since the chromophores become isomerized. The processes observed so far are reversible.

Photochromic macromolecules are macromolecules which have covalently connected photochromic dye side chains. These dyes shall be called tethered dyes, to distinguish them from adsorption bound dyes, which in turn are in labile equilibrium with free dyes. In all the work on photochromism here, *cis* ⇌ *trans* isomerism about the diazo bond is assumed to be responsible for the *immediate* optical properties observed, especially the absorption spectra. Brode<sup>4</sup> and Zollinger<sup>5</sup> have given general discussions about the evidence which links the stereoisomeric and optical properties to each other.

The solvent most useful for our purposes is water. Fortunately, the dyes discussed in this paper are photo-

(1) Presented in part at 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963; Abstracts, p. 40U.

(2) In the older literature photochromism and phototropism were sometimes used interchangeably; the term photochromism is now preferred; see ref. 3a.

(3) General reviews are: (a) R. Dessauer and J. Paris, in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 275-321; (b) G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, **11**, No. 1 (1961); (c) G. M. Wyman, *Chem. Rev.*, **55**, 625 (1955); (d) L. Chalkley, Jr., *ibid.*, **6**, 217 (1929).

(4) W. R. Brode in "Roger Adams Symposium," John Wiley and Sons, Inc., New York, N. Y., 1955.

(5) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, Chapters 4 and 13.

chromic in water: these are N-amide substituted 4-azobenzene derivatives. Water photochromic dyes—*i.e.*, dyes which are slowly photochromic in water<sup>6</sup>—are of considerable intrinsic interest. In 1959, Inscoc, Gould, and Brode<sup>8</sup> discovered a series of water photochromic azo dyes, which all have methoxy groups as ring substituents. Previous to that, chrysophenine, an ethoxy-substituted dye, was the only azo dye which fell in this class (see ref. 7 for earlier references). Although in this work methoxy-substituted azobenzene derivatives were used to a considerable extent, the absence of an alkoxy substituent does not preclude photochromism in water.

One of the aims of this research is to examine macromolecular systems which contain flexible dyes, and correlate the observations with chain conformation changes. For example, collapse of a macromolecular coil might exclude solvent from around a chromophore and introduce steric hindrance around it. Conversely, study of the optical properties of tethered dye systems might lead to information about the interior of the macromolecule. When bound dye systems are used for similar studies the complications are: (1) Corrections for free dye have to be made, requiring more treatment of the data, and also binding experiments. (2) As experimental conditions vary, the systems probably continually readjust so that the dyes which remain bound change their locale in the domain.

(6) In general, hydroxylic solvents or solvent mixtures destroy photochromism in the sense that the *cis* → *trans* conversion rate is usually accelerated very markedly in these solvents. This was studied by Gould and Brode<sup>7</sup> using equipment which could follow processes having half-times of the order of milliseconds. For purposes of this paper, in which our methods only allow following processes lasting several seconds at the least, dyes such as *p*-aminoazobenzene are "not slowly photochromic in water," whereas they are photochromic on a millisecond time scale.

(7) J. H. Gould and W. R. Brode, *J. Opt. Soc. Am.*, **42**, 380 (1952).

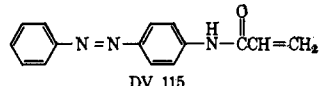
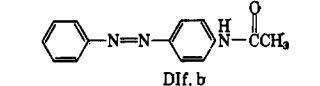
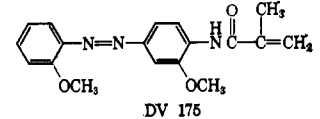
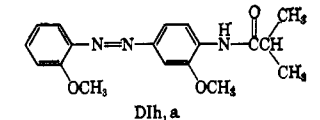
(8) M. Inscoc, J. H. Gould, and W. R. Brode, *J. Am. Chem. Soc.*, **81**, 5634 (1959).

As it happens, the photochromic processes in simple azo dye systems are complicated by a number of factors, especially catalysis by molecules and ions in addition to  $H^+$  and  $OH^-$ . Therefore, in making comparisons between the photochromism of free and tethered (and also bound) dyes, it is necessary to account for these factors in addition to macromolecule conformation states. Nevertheless, the marked effects wrought by chain conformation control over processes internal to the macromolecule are reflected in the photochromism of tethered dyes.

### The Dyes and Macromolecules Used in This Research

Table I lists the dyes used as monomers for copolymerization. Since the vinyl derivatives become saturated and branched at the carbon  $\alpha$  to the amide carbonyl after polymerization, DIh,a and DI f,b are assumed to be reasonable replicas of the vinyl derivatives after copolymerization. These will be called "copolymerized dye models." They may be studied in solution as free dyes, or adsorption bound to form bound dye systems. The DV dyes after copolymerization cannot leave the macromolecular domain. These latter dyes—tethered dyes—are assumed to be distributed uniformly along the macromolecular chain and to act independently.

TABLE I

Dye	M.p., °C. (uncor.)	$\lambda_{max}$ , Å, <sup>a,b</sup> 1st absorption band	$\epsilon^{a,b}$
 DV 115	166-167	3530	32,700
 DI f, b	143-145	3490	28,800
 DV 175	96	3780	25,700
 DI h, a	107-108	3760	23,800

Copolymer systems: P94, copolymer of DV175 with acrylic acid (3.6% dye); P176, copolymer of DV175 with methacrylic acid (1.2% dye).

<sup>a</sup> Solvent: 0.64 M  $NH_3$  in 90% ethanol. <sup>b</sup> In the dark stationary or steady state.

The solvent used for determining the extinction coefficients for the dyes was an ethanol-water mixture, over 90% in ethanol and 0.64 M in  $NH_3$ . Without the  $NH_3$ , decidedly different extinction coefficients were observed; these were usually about 20% lower and are likely due to isomer presence.

The kinetic experiments for the free dyes used saturated water solutions of the dye crystals as the initial stock, and no organic solvents were present.

Experiments were performed in which DIh,a was made up to a constant concentration (about saturated in dye), with varying amounts of KCl, to see if dye precipitated upon standing for several days. Since it did not, using as criteria retention of constant optical den-

sity (O.D.), we assume that our observations on these free dyes in 100%  $H_2O$  solvent are not affected by aggregation.

The copolymers containing tethered dye are highly soluble in water over the whole pH range of interest as might be expected from the solubility of the corresponding homopolymers, polymethacrylic acid (PMA), and polyacrylic acid (PAA). However, these copolymers are solubilizing agents for nonpolar compounds like benzene (see Experimental section) and are akin to polysoap systems studied by Strauss and co-workers.<sup>9</sup>

### Photochromism

The mechanisms of photoisomerization are the subject of research by several groups of workers.<sup>10</sup> For this paper, no attempt will be made to give a detailed discussion in this area, but there are some points which might become important in the future.

There is a strong possibility that conformational<sup>11</sup> isomerism leading to "single bond isomerism" can occur in dyes which are axially asymmetric; this interesting point is raised by Robin and Simpson.<sup>12</sup> They also give energy magnitudes involved in this type of isomerization for two azo dyes. These magnitudes are not too far from ambient thermal energies, at least for the cases they discuss. *cis*  $\rightleftharpoons$  *trans* isomerism about the C-N bond in the amide section can exist and is probably labile in the absence of nearby strong hydrogen bond donors and acceptors.<sup>13</sup> Therefore for some tethered dye systems moderate spectral shifts could originate from single bond isomerism, especially when macromolecule shrinkage occurs and causes crowding of the chromophores. Presumably this type of isomerism could also operate in adsorption binding. Separation of this isomerism from absorption spectral effects wrought by changes in dielectric environment accompanying conformation changes cannot clearly be made at the moment. However, it remains clear that geometric isomerism about double bonds is plainly distinguishable from minor geometry changes because of the energies involved in the irradiation processes with the attendant major changes in the absorption spectrum.

Extension of studies of photochromism in solvents like water should become useful for at least three reasons: First, water has a much higher dielectric constant than the average organic solvent, so that electrostatic contributions to the transition states involved in the isomerization process might be accentuated. Secondly, the unusually high internal pressure of water compared with that of most organic solvents<sup>14</sup> gives another parameter which probably would affect the kinetics of isom-

(9) U. P. Strauss and E. G. Jackson (Paper I), *J. Polymer Sci.*, **6**, 646 (1951).

(10) Papers from the Intern. Symposium on Reversible Photochemical Processes held at Duke University, April, 1962, are published in *J. Phys. Chem.*, **66**, 2423-2579 (1962); included are papers outlining the theories of geometric photoisomerization about double bonds.

(11) Somewhat unfortunately, there are difficulties in terminology. In macromolecular chemistry, the term conformation is now preferred in describing main chain arrangements. Configuration needs to be reserved for side chain and small molecule stereochemical descriptions; however, conformation is already heavily used in referring to the shapes of small molecules, e.g., steroids. Furthermore, binding of substrates to macromolecules is an important process, and it appears that geometry and volume changes for both components in those systems accompany the binding process. We therefore will rely partly on context in this and future papers to make clear what is meant by conformation and associated terms.

(12) M. Robin and W. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

(13) H. Morawetz and P. Otaki, *J. Am. Chem. Soc.*, **85**, 467 (1963).

(14) W. J. Moore, "Physical Chemistry," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1955, p. 424.

erization besides the position of equilibrium, parallel to what has been found for other reactions in various solvents, *e.g.*, solvolyses.<sup>15</sup> Third, water is, of course, the best solvent in which to carry out variations in pH and ionic catalyst concentration; these quantities will be dealt with in this paper.

Other factors which need be accounted for in a detailed treatment of *cis*  $\rightleftharpoons$  *trans* isomerizations for azo dyes are symmetry changes which must occur somewhere in the formation of the transition states for these isomerizations; Benson<sup>16</sup> treated this problem, and Dyck and McClure<sup>17</sup> did so for azobenzene and stilbene photoisomerization processes.

### Experimental

The dyes were synthesized by condensing amine group-bearing azo dyes (the parent dye) with appropriate acid chlorides in acetonitrile. All necessary chemicals are commercially available (Eastman, Matheson Coleman and Bell, Monomer-Polymer Inc.). The parent dyes were recrystallized to literature m.p.'s before use; acid chlorides were distilled. Usually the product precipitated in acetonitrile, or readily did so on addition of aqueous base to neutralize the HCl reaction product. Recrystallization (ethyl alcohol-water) of the vinyl derivatives was performed only once, yielding m.p.'s which were reasonably sharp and different from those of the parent dye.

Structures of the dyes (Table I) follow from: (1) expected chemistry of the synthesis, (2) elemental analysis, (3) infrared and ultraviolet absorption spectra, (4) copolymerization of the DV dyes.

Carbon, hydrogen, and nitrogen analyses results (Univ. of Minn. Microanalytical Lab.) were, respectively: DV115, calculated and found (%), 71.70, 71.87; 5.23, 5.53; 16.75, 16.89; DV175, 66.44, 65.49; 5.86, 5.88; 12.92, 13.19; DIh,a, 66.04, 65.95; 6.47, 6.52; 12.84, 12.49.

Infrared spectra of some dyes were compared with those of compounds having groups common with those of expected structure; *e.g.*, DIh,b and DV115 were both compared with azobenzene, *p*-aminoazobenzene, acetanilide, and acrylamide, all in chloroform with the same instrument. This method, plus use of the literature,<sup>18</sup> identified the amide II band and the strong band characteristic of the  $\text{—C=C—H}$  out-of-plane vibration for vinyl groups (990  $\text{cm.}^{-1}$ ) for the DV dye.

Near-ultraviolet spectra of the dyes in Table I yield extinction coefficients which compare reasonably well with those of the parent dyes, indicating molecular weight increases by the derivatives.

Monomers were recrystallized and vacuum distilled. The polymerization solvent was a 50:50 (by volume) mixture of water and purified<sup>19</sup> methyl alcohol. A typical polymerization mix is: 0.03 g. of azobisisobutyronitrile initiator, 0.30 g. of DV dye, 25 ml. of main chain monomer, and 60 ml. of solvent.

The mix, in a medium wall tube, was frozen and thawed twice, and sealed under vacuum (1–2 mm.). It was rotated in boiling alcohol vapor for 1 hr. (at which temperature the mix is homogeneous), opened, and the contents poured into water.

About half the polymer was neutralized with KOH, and the solution shaken with benzene until the top layer was quite clear (about four times), thus removing nonpolymerized dye. With systems containing very much tethered dye, emulsification of benzene occurred; in that case, salt addition aided separation.

The aqueous layer was then treated with acetone, precipitating the polymer, which was then redissolved in water. This was repeated several times. The polymer was next deionized with mixed bed exchange resin and dialyzed a few times *vs.* H<sub>2</sub>O. It was then filtered through medium and fine fritted filters and freeze dried. Dye content was obtained spectrophotometrically, and, as might be expected for vinylamide monomers, the propor-

tion of dye in the final product was within about 30% that in the original mix. Polymers containing up to about 8% dye have been made; therefore it is unlikely that DV dyes are chain transfer or terminating agents. Furthermore, the viscosity average molecular weights<sup>20,21</sup> in 2.0 M KOH are in the 50,000 to 200,000 mol. wt. range.

Salts were A.R. grade, water glass distilled. Viscosity measurements, pH measurements and standardization, and glass electrode calibrations were made as before,<sup>22</sup> except that a Beckman G pH meter was used, so pH measurement precision and accuracy are both *ca.* 0.01 unit. Calibration of the electrode (standard HCl and carbonate-free KOH) enables use of the apparatus to obtain free acid and base concentration at the ends of the pH range.

Temperature was held at 25.0° by closely fitting metal jackets around the spectrophotometer cells during irradiation and monitoring of the solutions. The spectrophotometer was a Zeiss PMQ II. To avoid isomerization by the spectrophotometer light source, samples were removed from the light path when not being read.

Irradiation employed a 100-w. Hanovia mercury-quartz arc, filtered through a Corning CS7-51 filter, which passes the 3650 Å. line with reasonable exclusion of energy at other wave lengths. As Table I shows, this falls well within the first absorption band of all the dyes, since these are fairly broad. Irradiation times from 200 to 2000 sec. were ordinarily used to reach the photo-stationary state.

No effects by oxygen on free dye rates were observed when comparison was made with nitrogen; direct saturation of the solutions by commercial gases (*ca.* 99% purity) was employed.

Reversibility was studied by achieving the dark steady state, irradiating, and confirming return of the optical properties to the original state. For slowly relaxing systems, this sometimes required 2 or 3 days, but reversibility under a variety of conditions for all dyes was always finally achieved when sought.

### Free Dyes<sup>23</sup>

Typical absorption spectra of one of the dyes, DIh,b, a copolymerized dye model, is illustrated in Fig. 1. The vinyl derivatives possess quite similar absorption spectra. There is a broad peak in the 3700 Å. region for the dark steady state, independent of pH within reasonable limits (pH 1 to 13). This spectral curve is sometimes called the dark spectrum. At neutral pH, the optical density at the original peak drops considerably upon irradiation and new peaks occur, which must be assigned to the *cis* form of the dye.

The lower absorption spectrum, for the irradiated steady state ("irradiated spectrum," for short), was always taken in the dark, immediately after irradiation. After taking the irradiated spectrum, kinetic data for the *cis*  $\rightarrow$  *trans* isomerization were also taken with no further irradiation, so that all kinetics for this isomerization refer only to the dark reaction.

The irradiated spectrum in contrast to the dark spectrum is sharply dependent on pH, buffer, and interval and intensity of irradiation. Hydrogen and hydroxyl ions are catalysts for the *cis*  $\rightarrow$  *trans* conversion, so that for high acid and base concentrations rapid conversion occurs; at extreme pH values, the shape of the irradiated spectrum becomes dependent on the length of time used for its measurement, and errors in isomerization rate constant measurement become large.

*cis*  $\rightarrow$  *trans* conversion kinetics are apparent first order in all dye systems studied for this paper, so that  $k_{APP}$  is defined:  $-d(C)/dt = k_{APP}(C)$ , where (C) equals *cis* form concentration. Assuming H<sup>+</sup> is in rapid

(15) G. Clarke and R. Taft, *J. Am. Chem. Soc.*, **84**, 2295 (1962).

(16) S. Benson, *ibid.*, **80**, 5151 (1958).

(17) R. Dyck and D. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(18) R. N. Jones and C. Sandorfy in W. West and W. Weissberger, Ed., "Technique of Organic Chemistry," Vol. 9, Interscience Publishers, Inc., New York, N. Y., 1956.

(19) L. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath & Co., Boston, Mass., 1957, p. 289.

(20) A. Katchalsky and H. Eisenberg, *J. Polymer Sci.*, **6**, 145 (1951).

(21) I. Kagawa and R. Fuoss, *ibid.*, **18**, 535 (1955).

(22) R. Lovrien, *J. Am. Chem. Soc.*, **85**, 3677 (1963).

(23) In this and subsequent papers, this means all dye is free, *i.e.*, no macromolecules are present.

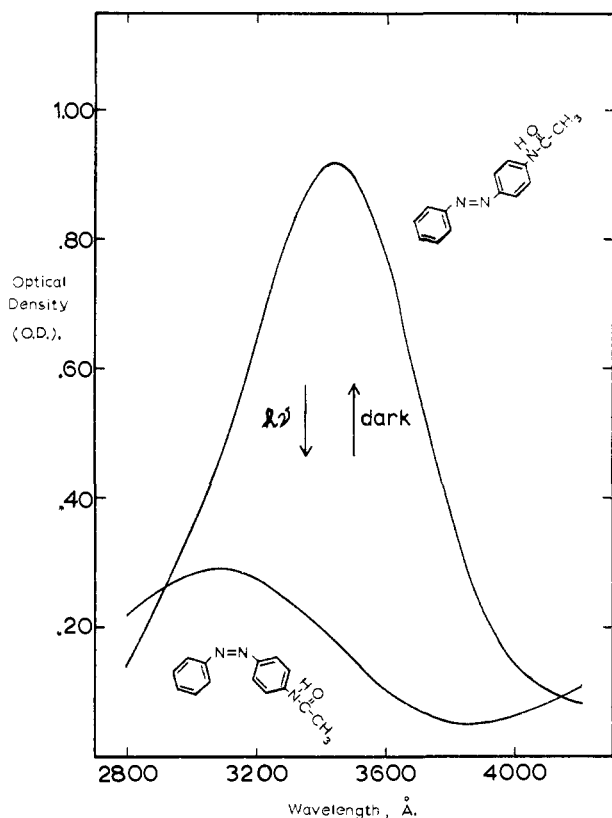
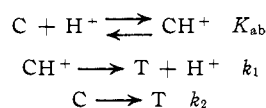


Fig. 1.—Photochromism of DIh,b in 0.01 *M* Tris buffer, pH 8. In concentrated buffer, the lower absorption spectrum reverses rapidly to the upper one. Crossing points of the spectra are isobestic points.

equilibrium with the *cis* form characterized by equilibrium constant  $K_{ab}$  then a mechanism consistent with the data is



in which the  $k$ 's are rate constants. In the  $k_1$  step, the reverse step (rate constant  $k_{-1}$ ) is not included because addition of  $H^+$  or other catalysts to a solution of dye in the *trans* form (T) does not cause a discernible absorption spectral shift by the free dye toward that of the *cis* form. It is to be emphasized that this is true only in the dark, in water. For other conditions it is not true.

The same situation holds for the  $k_2$  step; that is, the back reaction  $k_{-2}$  may well be important under different solvent and temperature conditions than those employed in this work. This step is probably not a simple one-step reaction as noted by several others for nonaqueous systems. It is likely that water molecules themselves are catalysts; in connection with this Brode, Seldin, Spoerri, and Wyman<sup>24</sup> gave absorption spectral evidence that addition of water to azo dyes in other solvents forms a new species. They believe it is a complex of water and the dye, with a hydrogen bond between the azo group and a water molecule. For the present, we assume that activity of water is a constant at 25°, and is a factor in  $k_2$ .

From this simplified mechanism there follows

$$k_{APP} = k_1 K_{ab} (H^+) + k_2 \quad (1)$$

(24) W. R. Brode, I. L. Seldin, P. E. Spoerri, and G. M. Wyman, *J. Am. Chem. Soc.*, **77**, 2762 (1955).

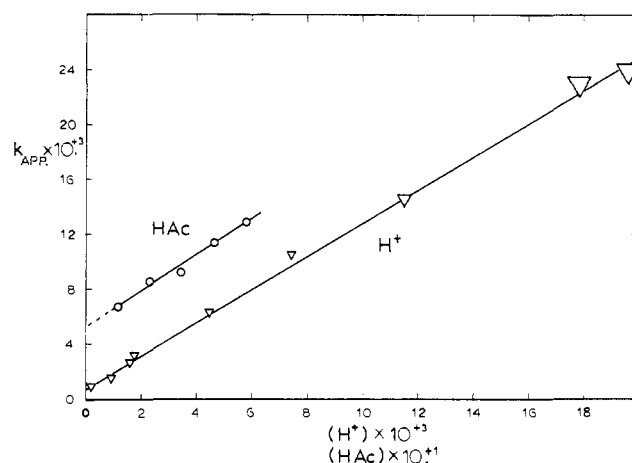


Fig. 2.—Test of eq. 2. For acetic acid catalysis, pH 2.41 ± 0.02 (adjusted with HCl); slope =  $k_3$  value.

Inserting steps to include the catalytic effect of various ions and molecules, in which  $k_3$  is the attendant rate constant and (B) the catalyst concentration (often a buffer component), yields

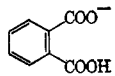
$$k_{APP} = k_1 K_{ab} (H^+) + k_2 + k_3 (B) \quad (2)$$

again with a similar expression for  $OH^-$  catalysis. If more than one B catalyst is present, we would have the concomitant rate constants,  $k_4, k_5$ , etc.

Tests of eq. 2 are illustrated in Fig. 2. At intermediate pH's, for the free dye systems, it is necessary to control pH with buffers. In the limit, at (B) = 0, the plots yield  $k_1 K_{ab} (H^+) + k_2$  and  $k_1' K'_{ab} (OH^-) + k_2$ , as the case may be. These limiting  $k_{APP}$  values, called  $k_L$ , thus are functions of  $(H^+)$ ,  $(OH^-)$ ,  $H_2O$  activity, and presumably temperature. Compensating salt was not added to the buffers, so that in the limit the ionic strength is also zero. The  $k_L$  values are probably dominated by  $k_2$  in the neutral pH region, but further dissection of  $k_L$  need not be made for our immediate purpose. In order to present the data for the various dyes,  $k_L$  values were converted to half-times:  $t_{1/2} = 0.693/k_L$ .

The slopes equal  $k_3$  and are a measure of the effectiveness of the B species as a catalyst. Since 0.20 *M* KCl had virtually no effect on the rates for the DIh,a system at low pH,  $K^+$  and  $Cl^-$  are not good catalysts. Table II lists values for  $k_3$  which enable comparison of some ions and molecules as catalysts. Since ionic

TABLE II  
CHARACTERISTIC RATE CONSTANTS FOR DIh,a  
*cis* → *trans* ISOMERIZATION CATALYSIS

Species	Rate constant $k_3$ , sec. <sup>-1</sup>	Species	Rate constant $k_3$ , sec. <sup>-1</sup>
$H^+$	1.25		0.0143
$OH^-$	0.80	$NH_3$	.039
$CH_3COO^-$	.0046	$NH_4^+$	.0014
$CH_3COOH$	.013		

strength varied with buffer concentration, some error in  $k_3$  obtains from that, as well as errors due to pH variations, etc.; the effect of these errors is of the same order of magnitude as the last significant number in the  $k_3$  values.

Internal consistency of some of the numbers in Table II was checked by using them to predict rates of cata-

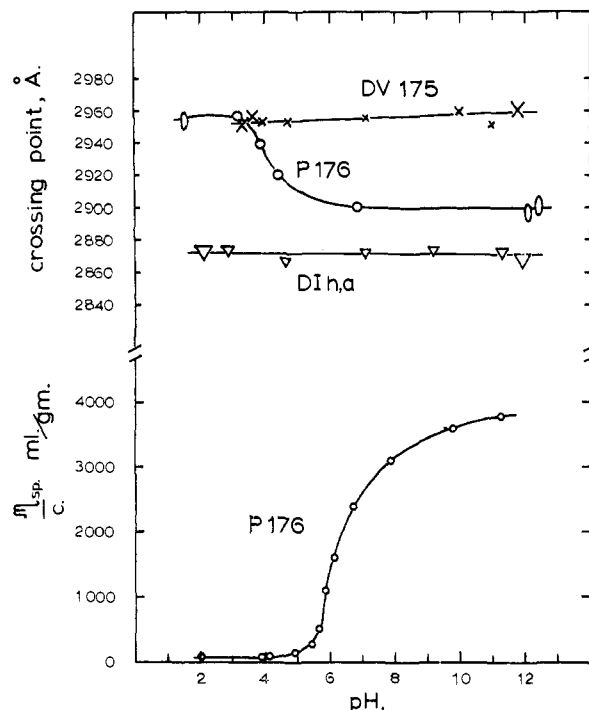


Fig. 3.—Upper section: crossing point wave length dependency on pH; lower section: pH dependent viscosity behavior of P176 polyelectrolyte (ionic strength 0.03).

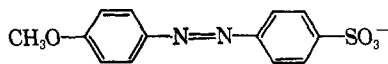
lyzed isomerizations of DIh,a for cases in which more than one catalyst was present. These were within a few per cent of the observed values, so the effects by the catalysts seem to be reasonably additive.<sup>25</sup>

There are some comparisons of the numbers in Table II which may be made with those from detailed studies of organic mechanism in which the same catalysts operate, reported by others. Our efforts aim at varying the dye structures to limn some of the more obvious features bearing on azo dye isomerization catalysts.<sup>27</sup> Catalysis of the light-energized *trans* → *cis* isomerization—the photoisomerization process—is also observed, as required by theory (of microscopic reversibility). This aspect bears on photoisomerization of azo dye systems in water and probably partly governs some of the results discussed below.

(25) The effects by mixtures of catalysts are not always additive if they can act in concert; in that case multiplicative expressions of the type proposed by Swain<sup>26</sup> might be best employed. This may apply to the case of zwitterionic catalysts like glycine, which are considerably more effective than the corresponding monovalent group catalysts (*i.e.*, separate amine and carboxyl group catalysts) in Table II. The origin of this behavior may lie in the ability of such molecules to act as polyfunction catalysts (in the Swain sense), or to act on more than one barrier, if such are involved, in formation of the final transition state. These points are germane to studies involving protein molecule catalysis of *cis* ⇌ *trans* isomerization, and also in the work in this paper, in which synthetic polyelectrolytes with their high density of side chains qualify as polyfunction catalysts.

(26) C. G. Swain, *J. Am. Chem. Soc.*, **72**, 4578 (1950).

(27) *E.g.*, extension of studies of the catalysts to isomerization of charged dyes have been started. We find that a dye we call D50



is photochromic in water, as expected on the basis of studies by Inscoc, *et al.*,<sup>8</sup> who studied the 3-sulfonate homolog. In common with the dyes listed in Table I, protons are catalysts for the *cis* → *trans* reaction. But NH<sub>3</sub> even at high concentration is not a catalyst, in contrast to the case for dyes listed in Table I. Either the catalysts can interact with more centers on the Table I type dyes than on D50 (all in the ground state), or else the catalysts interact rather specifically with either the ground or excited state in the case of the Table I dyes, which in turn depends on the ring substituents (*e.g.*, amide linkages). At any rate, presence of the azobenzene moiety does not of itself render the systems sensitive to nucleophilic catalysis.

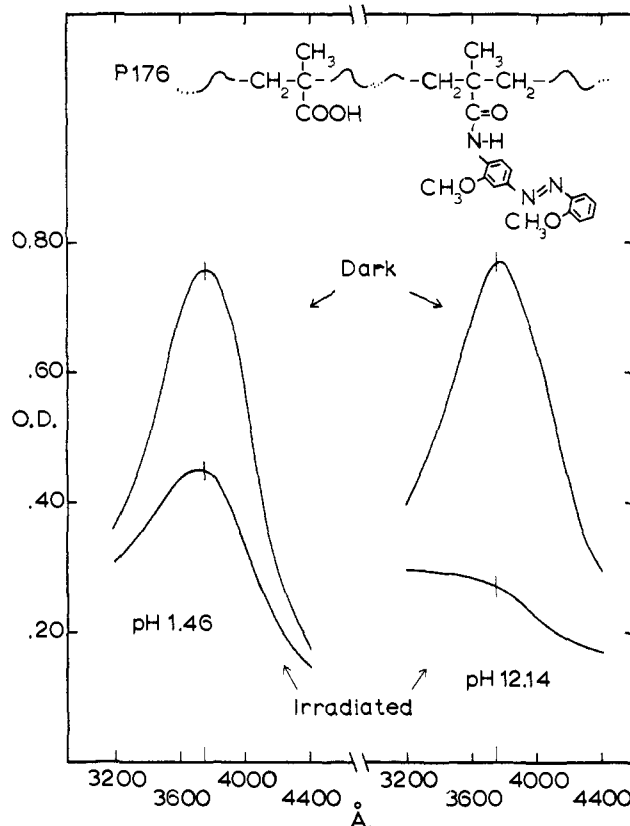


Fig. 4.—Absorption spectra of P176 in its steady states. Kinetics of *cis* → *trans* isomerization are slow enough at the extreme pH's such that the lower (irradiated) absorption spectra can be obtained before extensive distortion has occurred; ionic strength 0.03.

#### Photochromic Behavior of Tethered Dyes Compared with Free Dyes. Results

Upon achievement of a steady state, either the dark or the irradiated one, the free dyes are still some mixture of *cis* and *trans* isomers. With only two discrete species, the crossing points in the absorption spectra (Fig. 1) should be isosbestic points. This condition is illustrated in Fig. 3, in which: (1) the crossing points are isosbestic points; (2) H<sup>+</sup> and OH<sup>-</sup> do not titrate either isomer of the free dye in the pH range shown. Hence optical effects by the tethered dye systems may not be assigned to simple titration of the chromophores.

In the latter systems, the crossing points are not invariant with pH. Since the chromophores do not titrate, the effect is probably an environmental one, somehow linked to titration of the macromolecule, with its major conformation change, *viz.*, an expansion and extension in the pH range where the carboxyl groups titrate. As expected, the latter shows up vividly as a viscosity dependency on pH (Fig. 3, lower section). Detailed viscosity studies of the corresponding homopolymers were made by Silberberg, Eliassaf, and Katchalsky<sup>28</sup>; Tanford<sup>29</sup> has covered the subject in general. Also, as expected from the general treatment, the viscosity plot is asymmetric and broadened in the pH region corresponding to  $\alpha > 0.3$ , in which  $\alpha$  = degree of ionization.

Absorption spectra for P176 are shown in Fig. 4. In the dark, the spectra are essentially independent of pH,

(28) A. Silberberg, J. Eliassaf, and A. Katchalsky, *J. Polymer Sci.*, **23**, 259 (1957).

(29) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 489-523.

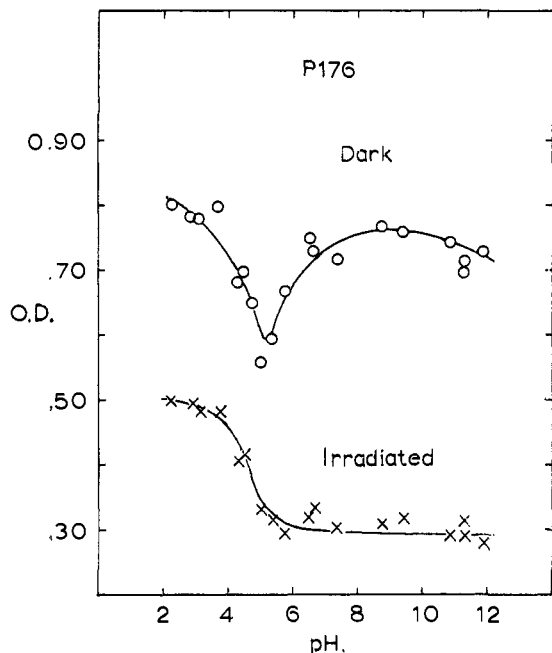


Fig. 5.—O.D. of P176 at 3750 Å., from steady states.

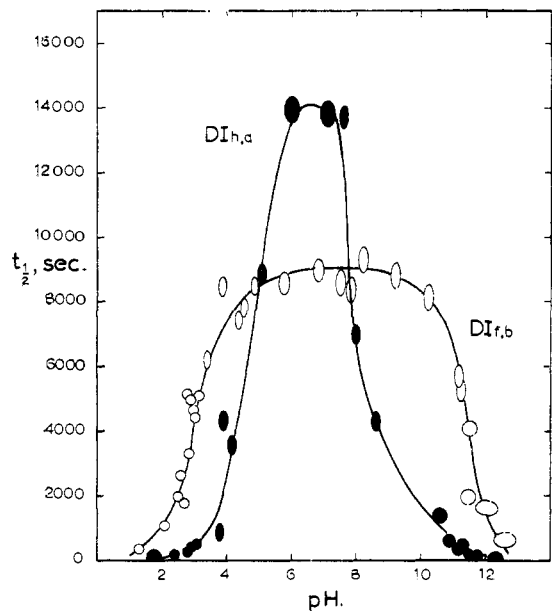


Fig. 6.—Characteristic half-time of isomerization,  $t_{1/2}$ , of copolymerized model dyes obtained from  $k_L$  values at intermediate pH's, and from direct measurement at pH < 3.5 and pH > 10.5.

at least at the extremes. Using constant polymer concentration, plotting the dark steady-state optical density at the absorption peak reveals a distinct minimum in the pH 5 to 7 region (Fig. 5). For the irradiated state, a monotonic change occurs in the same region. This pH region corresponds to large changes in titration and coil conformation.

The data in Fig. 5 are assigned to changes in the proportions of the amounts of *cis* and *trans* isomers, as discussed above. The P176 photochromism is reversible, insofar as it has been tested for a few cycles. The irradiation times necessary to achieve the irradiated steady state are much shorter (a factor of *ca.* 10) than the characteristic half-time of *cis*  $\rightarrow$  *trans* return; hence the data in Fig. 5 are not distorted much by competing *cis*  $\rightarrow$  *trans* return processes.

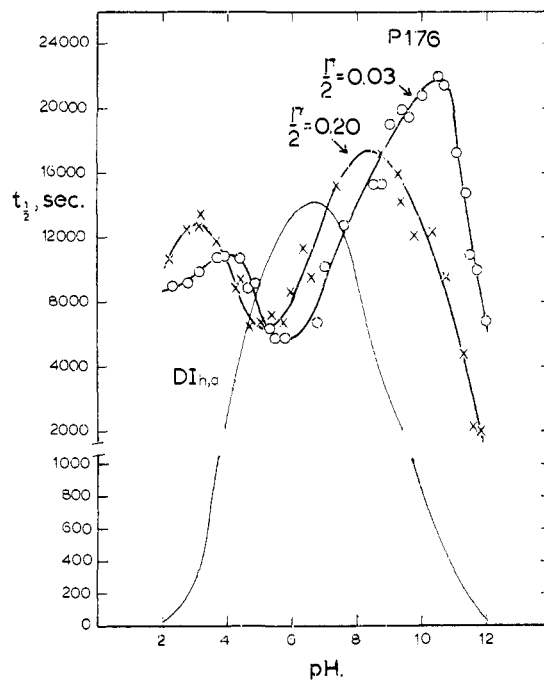


Fig. 7.—Isomerization of tethered dye in polymethacrylic acid, and the effect of ionic strength;  $DI_{h,a}$  plot reproduced from Fig. 6.

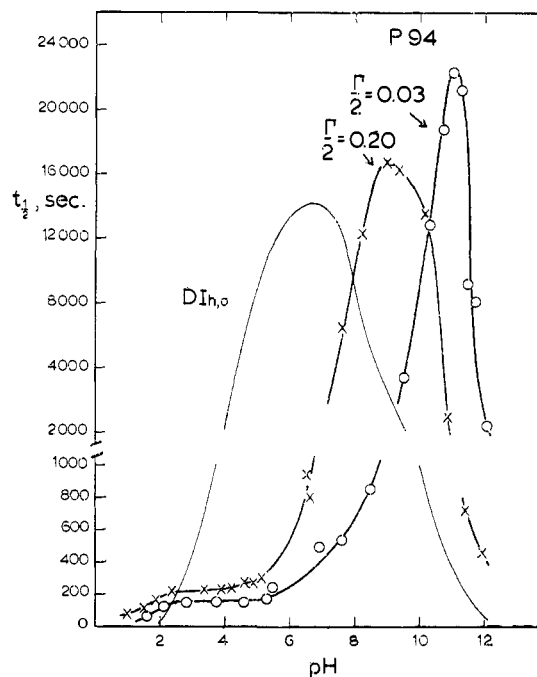


Fig. 8.—Isomerization of the same tethered dye as in Fig. 7, but with polyacrylic acid backbone.

Results for kinetics of the isomerization return process for two copolymerized monomer model dyes are summarized in Fig. 6. They are independent of the buffer species catalytic processes, since the ordinates in the intermediate pH region are half-times obtained from  $k_L$  quantities.

In order to compare the kinetic aspect of the behavior of free dyes with tethered dyes (Fig. 7 and 8), dye  $DI_{h,a}$  is assumed to be a suitable model for DV175 when it is copolymerized with methacrylic acid to form P176, and with acrylic acid to form P94. Buffers were not used to control pH for the polymers, since the titration curve for both these macromolecules is so broad.

The ionic strength contribution mostly comes from added salt (KCl).

### Tethered Dye-Free Dye Comparison. Discussion

Although the dyes DIf,b and DIh,a may not be ideal copolymerized model dyes (if there be such), two points emerge: (1) The kinetic behavior of the two dyes is roughly similar in that both respond to the catalysts  $H^+$ ,  $OH^-$ , and  $H_2O$ . Figure 6 shows that there is not a whole order of magnitude difference between the  $H_2O$ -catalyzed *cis*  $\rightarrow$  *trans* rates, but a difference by a factor of less than two, at pH  $\sim 7$ . This is not highly significant in most kinetic processes. At pH 3.5 and 10.5 there is a significant difference between the isomerization rates of the two dyes, catalyzed by  $H^+$  and  $OH^-$ , respectively. Now it seems likely that these catalysts attack somewhere around the amide section (*cf.* footnote 27), yet the considerably more sterically hindered DIh,a molecule responds most easily to these catalysts. Hence a rather large variation in volume of the alkyl group does not *ipso facto* eliminate their use as model for copolymerized dyes. (2) When chain conformation and side-chain catalysis effects are taken into account (below), isomerization kinetic behavior of the free and tethered dyes is again similar. Therefore if other models with say a neopentyl or long linear group attached to the amide group were synthesized, it is unlikely that they would differ much from the models at hand.<sup>30</sup> The differences observed between the latter, with respect to other water phototropic dyes studied here (*e.g.*, *p*-azobenzene semicarbazide and some of its derivatives) seem to stem mainly from electronic properties. Hence variation of the substituents on the insulating carbon (so long as it is saturated) is diminished in effect. On the other hand, it is unlikely that any small molecule model even approximates the behavior of the macromolecular coil, especially if the coil interacts physically or chemically with the whole chromophoric section of the dye. In sum, small molecules serve in this work as models for intragroup electronic behavior (as they have in many studies by others), but less successfully so for intergroup behavior, if a macromolecular coil is involved.

Comparison of the data in Fig. 7 with that in Table II indicates that the pendant carboxyl and carboxylate groups in P176 (polymethacrylic acid backbone) are not very effective intramolecular catalysts, even though their local concentration is very high. Presumably there exists stringent orientation requirements which the catalyst must meet; when the catalysts and the dye are tethered in the same chain, steric constraints may operate.<sup>31</sup> However, the acceleration of isomerism in the acid region, for P94 (polyacrylic acid backbone), is consistent with the supposition that intragroup catalysis can operate.

Although the plots for tethered dye in Fig. 7 appear more complex than for the bell-shaped curve for the free dye, the optical behavior of the former may be

(30) DIf,b is also a model for copolymerized DV115 (Table I), which copolymerizes to yield water-soluble phototropic terpolymers with acrylic acid and acrylamide. Research on these, together with that for systems including cross links besides tethered dye, will be reported in a separate paper.

(31) The polymers are probably atactic. Backbone stereoregularity, as it affects the rate of side-chain ester catalysis, was studied by Morawetz and co-workers<sup>32</sup>; they conclude that interaction between side chains does indeed depend on polymer stereoregularity.

(32) *E.g.*, E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.*, **83**, 1738 (1961).

linked in a reasonably simple way with conformation and titration behavior of the macromolecule, keeping in mind the intrinsic effect of pH on the free dye.

For P176, beginning at pH about 6, the tethered dye decreases in its rate of *cis*  $\rightarrow$  *trans* conversion and continues this trend until pH  $\sim 10$ , whereas in the same range the free dye's rate of conversion rapidly increases due to  $OH^-$  catalysis. But in that range, the tethered dye finds itself inside an increasingly charged macroanionic environment, and if the pendant carboxylate groups may not act as very good catalysts, it is probable that no other catalyst is very available, because  $OH^-$  would probably be excluded due to electrostatic interaction. At pH 10 the polyelectrolyte is extended as much as it can, the dye is exposed as much as possible, and on further increase in pH the very large  $OH^-$  concentration takes over, until finally the tethered dye conversion rate is markedly increased, with an attendant decrease in  $t_{1/2}$  as shown.

The effect of ionic strength is what would be expected for a solvent penetrable coil, including the abscissal difference of the maximum  $t_{1/2}$  values in the alkaline region: As ionic strength increases, penetration of the macroanion by  $OH^-$  would be aided, and then there occurs in the high alkaline region (pH  $> 10$ ) a large increase in the conversion rate (decrease in  $t_{1/2}$ ).

Below pH  $\sim 6$ , both  $H^+$  and  $-COOH$  catalysis of the process might be expected to operate, according to the case for the free dye (Table II). Instead the opposite occurs, and it is in just this region, as pH decreases, that the macromolecule is rapidly coiling up, somehow protecting *cis* dye from catalysis, or else sterically hindering the conversion. The effect of salt is diminished as expected, and not until the pH is quite low ( $\sim 3$ ) does  $H^+$  seem to have much effect. It never does make its presence felt so effectively as  $OH^-$  at high concentration, when comparison is made with the symmetry of the free dye curve, perhaps due to  $H^+$  (and  $Cl^-$ ) exclusion from the coil domain.

The data in Fig. 7 and 3, both for P176, are similar in that both sets of data undergo large changes in the conformation transition region. However, Fig. 5 indicates that, except for the hiatus in the pH 5–6 region, P176 influences the dye to remain in the *trans* form when the macromolecule is coiled, even on irradiation. When it uncoils, exposing the side chains, the chromophore can act more like a free dye, so the difference between the proportions in the steady states in the alkaline pH region is greater. This would not have been guessed from Fig. 7, in that the rates of *cis*  $\rightarrow$  *trans* return in the alkaline region for P176 are not so very different from the acid region case. These comparisons for P176 would all seem to be consistent with the idea that P176 is probably a rather stiff coil with considerable internal steric hindrance. Moreover, polymethacrylic acid is thought to hypercoil<sup>28</sup> (and polyacrylic acid probably does not). Thus once the tethered dye becomes *cis* inside P176, it does not return in a normal way (as judged by the free dye case) to the *trans* form, over a considerable range of conformation states of this macromolecule.

The case for P94 seems simpler: there is a shoulder in the pH 3 to 5 region which probably reflects the coil conformation transition, in the plot on Fig. 8. The general fast rate of *cis*  $\rightarrow$  *trans* return here corresponds

to effective catalysis by the side chains. Then if allowance is made for the fact that the chromophore is confined to a polyelectrolyte coil, the remainder of the reasoning used for the P176 case in the other pH regions indicates that tethered dye in P94 behaves like that of free dye in the *cis* → *trans* isomerization.

### Bound Dye Systems

Completion of the trilogy of dye systems requires mention of the case for bound dyes. Since these systems are more complicated than the free and tethered dye systems, details will be covered separately.<sup>33</sup>

For the moment, we note that in general the *cis* → *trans* return rates of bound photochromic dye are much more rapid over the whole pH range, when polycarboxylic acids are employed, than for either of the other two types of systems.

This stems from two main factors: (1) Adsorption bound dye may be in a different sort of environment

(33) Preliminary report: ref. 1, p. 68C.

than is tethered dye. Perhaps it is not even distributed evenly throughout the macromolecular domain. (2) There are two paths for isomerization of bound dye: (a) it may isomerize while bound; (b) it may unbind, isomerize out in solution, and rebind.

Besides these factors, the rate at which binding processes occur may enter, and the binding equilibrium constants for both isomers certainly do. Rates at which the macromolecule undergoes conformation changes are perhaps superimposed.

From the data in Table II, it is obvious that both polycarboxylic acids should act as effective catalysts; this is in fact the case, but with a pH dependency which reflects the broadened titration curve of a macroion.

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## Polymerization in the Crystalline State. VI. Electron Spin Resonance Study of the Propagating Species in a Polymerizing Single Crystal of Barium Methacrylate Dihydrate<sup>1a</sup>

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Single crystals of barium methacrylate dihydrate were irradiated at  $-196^\circ$  with  $\gamma$ -rays from a  $\text{Co}^{60}$  source. The e.s.r. spectrum recorded at the irradiation temperature was isotropic and consisted of seven lines spaced at 23 gauss. This spectrum was assigned to the species  $(\text{CH}_3)_2\dot{\text{C}}\text{COO}^-$  formed by the addition of a hydrogen to the double bond of a methacrylate ion. On warming to  $20^\circ$  a new and anisotropic spectrum appeared which had 9 lines when observed with the magnetic field parallel to the *a*- or *b*-axis of the pseudo-orthorhombic monomer crystal but 13 lines when the magnetic field was parallel to the *c*-axis. This spectrum was attributed to the propagating radical  $\text{RCH}_2\dot{\text{C}}(\text{CH}_3)\text{COO}^-$ . The anisotropy of the e.s.r. spectrum of this species proves that a preferred orientation of the propagating radical in a crystallographic direction of the parent monomer is retained with at least one monomer unit added to the primary radical. When polymerization is carried to high conversion at  $50^\circ$ , the anisotropic spectrum gradually disappears, leaving an isotropic 5-line spectrum. This transformation is believed to be due to a conformational transition to a form in which one of the methylene hydrogens becomes magnetically equivalent to the hydrogen of the  $\alpha$ -methyl group, while interaction of the unpaired electron with the other methylene hydrogen becomes negligible.

### Introduction

It is a surprising fact that a variety of organic reactions may proceed in the crystalline state in spite of the restricted mobility of the reagent molecules within the crystal structure.<sup>2</sup> It is then of particular interest to determine the extent to which the geometrical arrangement of the molecules within the crystal structure of the reagent determines the characteristics of the reaction. Such "topochemical" effects may be deduced in several ways: (1) Chemically similar substances may react at very different rates in the solid state, although no corresponding differences would be expected in the liquid state.<sup>3–5</sup> (2) Different crystalline modi-

fications of the same reagent may be characterized by different reactivities.<sup>6</sup> (3) A comparison of the rates of similar reactions in the glassy and crystalline states may show that the chemical process may be either favored or hindered by the molecular arrangement in the crystal.<sup>7</sup> (4) If the reaction can proceed in alternative directions, the nature of the reaction product obtained in the solid state process may be determined by crystallographical factors<sup>5</sup> and be different from the product obtained if the reaction proceeds in the liquid state.<sup>8,9</sup> (5) The molecules of a crystalline reaction product may have a definite orientation with respect to the crystallographic directions of the reagent crystal (topotaxy).<sup>10</sup>

(1) (a) We are indebted for financial support of this study to the U. S. Atomic Energy Commission, Contract AT(30-1)-1715; (b) to whom inquiries should be addressed.

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