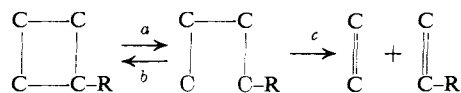


### Appendix III

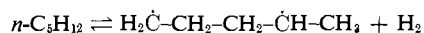
**Carboxylic Resonance Energy.** Carboxylic resonance energy of 4 kcal./mole is deduced from results of Roquette and Walters<sup>29</sup> on the pyrolysis of cyclobutane aldehyde and more recent work (in press) of the same group on the pyrolysis of cyclobutane ethyl ketone. The observed activation energy of  $\sim 54$  kcal./mole for each of the above compounds compares with a value of  $\sim 62$  kcal./mole for the pyrolysis of methylcyclobutane. Assuming the mechanism



$E_{\text{obsd}} = \Delta H_{a,b}^{\circ} + E_c$ . When R is a methyl group,  $\Delta H_{a,b}^{\circ}$  is calculated from the heats of formation of methylcyclobutane and the 1,4-*n*-pentane biradical. The heat of formation of methylcyclobutane is  $\sim -1$

(29) B. C. Roquette and W. D. Walters, *J. Am. Chem. Soc.*, **84**, 4049 (1962).

kcal./mole (estimate based on the affect of methyl group on larger rings) and the heat of formation of the biradical is obtained from considering the following reaction.



$$\begin{aligned} \Delta H_{1,2}^{\circ} &= D(\text{primary C-H}) + D(\text{sec-C-H}) - D(\text{H-H}) \\ &= 98 + 94.5 - 104 = 88.5 \text{ kcal./mole} \\ &= \Delta H_f^{\circ}(\text{biradical}) - \Delta H_f^{\circ}(n\text{-pentane}) \end{aligned}$$

$$\Delta H_f^{\circ}(\text{biradical}) = 88.5 - 35 = 53.5 \text{ kcal./mole}$$

$\Delta H_{a,b}^{\circ} = 54.5$  kcal./mole. If this value is corrected up to the temperature range of the pyrolysis measurements, it will be  $\sim 56$  kcal./mole. This means the activation energy for step *c* is  $\sim 6$  kcal./mole. Assuming that when R is  $-\text{C}(=\text{O})\text{H}$  or  $-\text{C}(=\text{O})\text{R}'$ , the activation energy of step *c* is down to as little as  $\sim 2$  kcal./mole; the value for the over-all activation energy of  $\sim 54$  kcal./mole means that the carbonyl group has at least a  $\sim 4$  kcal./mole resonance energy.

## Catalysis of the *cis* $\rightarrow$ *trans* Isomerization of 2-Hydroxy-5-methylazobenzene

Gunnar Wettermark,<sup>1a</sup> Margaret E. Langmuir,<sup>1b</sup> and Daniel G. Anderson

Contribution from the Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Massachusetts. Received August 17, 1964

The *cis*-*trans* isomerization of 2-hydroxy-5-methylazobenzene in water and ethanol solutions was studied by flash photolysis. In aqueous acetate buffer the thermal *cis*  $\rightarrow$  *trans* conversion of the neutral *cis* molecule HC follows the rate law  $-d[\text{HC}]/dt = (k_S + k_{H^+}[\text{H}^+] + k_{\text{HOAc}}[\text{HOAc}] + k_{\text{OAc}^-}[\text{OAc}^-])[\text{HC}]$ , with  $k_S = 4 \times 10^2 \text{ sec.}^{-1}$ ;  $k_{H^+} = 1.5 \times 10^7$ ,  $k_{\text{HOAc}} = 3.8 \times 10^4$ , and  $k_{\text{OAc}^-} = 6.0 \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  at  $30.0^\circ$ . The mechanism for the proton catalysis proceeds with the *cis*  $\rightarrow$  *trans* conversion of the cation as the rate-determining step; rate constant  $= 2.1 \times 10^4 \text{ sec.}^{-1}$  at  $30.0^\circ$ . The anion in water also undergoes *cis*-*trans* isomerization. Above pH 12, the thermal relaxation of the *cis* anion  $\text{C}^-$  follows the rate law  $-d[\text{C}^-]/dt = k_{H^+}[\text{H}^+][\text{C}^-]$ , with  $k_{H^+} = 2.0 \times 10^{13} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . The rate-determining step appears to be the solvent-catalyzed *cis*  $\rightarrow$  *trans* conversion of the neutral species, with rate constant  $= k_S$ . *pK* values of 2.9 and 10.7 were deduced for the *cis* cation and *cis* neutral species, respectively, as compared to  $-1.5$  and  $9.4$  determined for the *trans* species. The same general results for the *cis*  $\rightarrow$  *trans* conversions were obtained in acetate buffered ethanol and sodium ethoxide solutions. An additional, faster transient, probably the hydrazone tautomer, was observed under weakly acidic conditions. Activation energies were estimated for all transformations.

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### Introduction

The investigation described herein deals with the isomerizations of 2-hydroxy-5-methylazobenzene. Our interest in the isomerizations of a compound having a hydroxyl group *ortho* to the azo bond stemmed from recent investigations in this laboratory of structurally similar anils.<sup>2</sup> It was found that light induces two different isomerizations in *o*-hydroxyanils: (a) *cis*-*trans* about the carbon-nitrogen double bond and (b) a tautomeric hydrogen shift from the hydroxyl group to the nitrogen of the  $\text{C}=\text{N}$  bond. 2-Hydroxy-5-methylazobenzene possesses the possibility of two corresponding isomerizations, *i.e.*, *cis*-*trans* about the  $\text{N}=\text{N}$  bond and azo-hydrazone tautomerism.

Generally the *trans* isomer of an azo compound is the more stable form in solution. The equilibrium may be shifted toward *cis* by photoexcitation and in the dark undergo thermal relaxation to *trans*. This conversion has been shown to be catalyzed by both electrophilic and nucleophilic agents.<sup>3</sup> Only a few systematic studies<sup>3-7</sup> are reported on the catalysis and almost

(2) (a) G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40**, 1486 (1964); (b) D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, in press.

(3) D. Schulte-Frohlinde, *Ann.*, **612**, 131 (1958).

(4) G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

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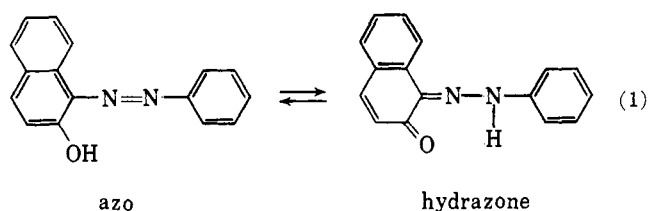
(6) S. Ciccone and J. Halpern, *Can. J. Chem.*, **37**, 1903 (1959).

(7) R. Lovrien and J. C. B. Waddington, *J. Am. Chem. Soc.*, **86**, 2315 (1964).

all of these have been on azobenzene. Catalysis by hydrogen ion is generally agreed to be due to the azo nitrogens functioning as bases, the rate-determining step being the isomerization of the *cis* cation.<sup>5-7</sup> On the other hand, for catalysis by hydrazobenzene, thiophenol, and thiourea, it has been assumed that the formation of an addition complex is the rate-determining step.<sup>5</sup>

The *cis* → *trans* isomerization of hydroxyazo compounds has been shown to be extremely fast in polar solvent.<sup>8</sup> For this reason, kinetic data have been obtained only at low temperatures in polar solvent and only for compounds of the hydroxy(phenylazo)-naphthalene type.<sup>9,10</sup> For these compounds, hydrogen bonding in the transition state<sup>9</sup> and the presence of a hydrazone intermediate<sup>10</sup> have been invoked as reasons for the unusually low activation energy in polar solvent.

Azo-hydrazone tautomerism of the type



has been shown for naphthalene compounds with a phenylazo and a hydroxyl group in the 1,4- or 1,2-positions.<sup>10-17</sup> In such cases the hydrazone peak around 470 m $\mu$  increases in intensity and the azo peak, around 390 m $\mu$ , shows a corresponding decrease in intensity when solvent polarity is increased. Fischer and Frei estimated a difference in enthalpy of  $2 \pm 0.2$  kcal. mole<sup>-1</sup> between the two tautomers of 1-hydroxy-4-(phenylazo)naphthalene from the temperature dependence of the equilibrium in methylcyclohexane.<sup>10</sup>

In the solid state, infrared and electronic spectra indicate that the naphthalene derivatives exist either as pure phenylhydrazones or as mixtures of both tautomeric forms whereas *o*- and *p*-hydroxyazobenzenes exist as the azo tautomer.<sup>16</sup> This is also the case in solution as shown by Kuhn and Bär.<sup>11</sup> Nuclear magnetic resonance studies in carbon tetrachloride solutions of 2-hydroxyazobenzene and 1-phenylazo-2-hydroxynaphthalene and some of their derivatives showed that considerably stronger hydrogen bonds occur for the benzene compounds than for the naphthalene compounds.<sup>18</sup>

In view of the above-mentioned differences between the benzene and naphthalene analogs, one cannot make *a priori* decisions as to the mechanism of the *cis* → *trans* reaction of hydroxyazobenzenes in polar solvent.

(8) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952).

(9) G. Gabor and E. Fischer, *J. Phys. Chem.*, **66**, 2478 (1962).

(10) E. Fischer and Y. F. Frei, *J. Chem. Soc.*, 3159 (1959).

(11) R. Kuhn and F. Bär, *Ann.*, **516**, 143 (1935).

(12) J. N. Ospenson, *Acta Chem. Scand.*, **4**, 1351 (1950).

(13) A. Burawoy and Y. T. Chamberlain, *J. Chem. Soc.*, 3734 (1952).

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(18) L. W. Reeves, *Can. J. Chem.*, **38**, 748 (1960).

## Experimental

**Flash Apparatus.** The flash apparatus<sup>19</sup> was used as specified in a previous investigation<sup>20</sup> except that the cutoff filter solution was 10% acetic acid, circulated through a thermostat and regulating the test solution to  $\pm 0.2^\circ$ . All measurements except the activation energy studies were performed at  $30.0^\circ$ .

**Materials.** 2-Hydroxy-5-methylazobenzene was purified by repeated recrystallization from ethanol and then from petroleum ether, m.p.  $108-109^\circ$ . Other chemicals were all reagent grade; standard buffer solutions were obtained from Fisher Scientific Co. The absolute ethanol, U.S.P., contained less than 0.04% water.

**Aqueous Solutions.** The aqueous test solutions were  $2.57 \times 10^{-6}$  M in azo compound with ethanol (2% by volume) added to facilitate solution.

The pK values of the *trans*-azo compound were determined spectrophotometrically using a Cary Model 11 spectrophotometer. For pH values in the interval 2-12, standard buffer solutions were used and the pH was recorded on a Beckman Model G pH meter. At pH < 2 and > 12, titration with standard base or acid, respectively, was used to determine the acidity. For acid concentrations above 0.1 M the  $H_0$  values given by Paul and Long<sup>21</sup> were used to express acidity.

Solutions in which  $H_0$  values were  $-5.0$  to  $1.0$  were prepared with HCl; pH 1.1 to 3.6 with perchloric acid; pH 3.7 to 6.0 with acetate buffer; pH 6.0 to 8.0 with phosphate buffer; pH 8.0 to 10.0 with borate buffer; pH 9.3 and above with sodium hydroxide.

Acetate buffer solutions were prepared in the molarity ratios [HOAc]:[NaOAc] of 1.00, 0.100, and 10.0, hereafter called 1:1, 1:10, and 10:1. Borate and phosphate buffers were prepared according to the method of Clark and Lubs.<sup>22</sup>

**Ethanol Solutions.** The dye concentration in ethanol solutions was  $5.14 \times 10^{-6}$  M except where otherwise specified.

Sodium ethoxide solutions were standardized against primary standard potassium acid phthalate. Acetate buffer was prepared in a ratio of [HOAc]:[NaOAc] of 0.99, hereafter called 1:1.

**Determination of Transient Spectra and  $k_{\text{exptl}}$ .** The change in light absorption was recorded at wavelength intervals of 10 m $\mu$ . Log ( $I_\infty/I_t$ ) was plotted vs. wave length for the same value of  $t$  to determine the difference spectrum of the transient (shown as  $\Delta\text{O.D.}$  in Figure 1).  $I_t$  is the intensity of the light transmitted through the solution at time  $t$  during the decay of the transient, and  $I_\infty$  is the intensity transmitted after completion of the reaction. When  $\Delta\text{O.D.}$  is negative, the transient absorbs less than the initial species.

The first-order rate constant,  $k_{\text{exptl}}$ , equals the slope of a straight line fitted to a plot of ln  $\Delta\text{O.D.}$  vs. time according to the method of least squares. Units are reciprocal seconds.

(19) L. Lindqvist, *Rev. Sci. Instr.*, **35**, 993 (1964).

(20) G. Wettermark and R. Ricci, *J. Chem. Phys.*, **39**, 1218 (1963).

(21) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(22) I. M. Kolthoff and H. A. Laitinen, "pH and Electro Titrations," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 35.

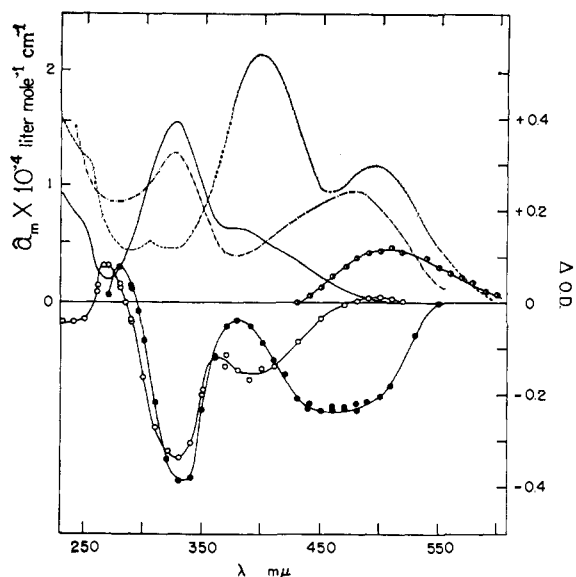


Figure 1. Spectra of 2-hydroxy-5-methylazobenzene. Left ordinate, in molar absorptivity. Absorption spectrum in aqueous solution: ----, cation in 6 *M* perchloric acid; —, neutral molecule in 1:1 acetate buffer; - · - · -, anion in 0.01 *M* sodium hydroxide. Right ordinate in  $\Delta O.D.$  Difference spectrum from flashed ethanol solutions (*t* is the time after initiation of flash): O, in acetate buffer, [HOAc]:[OAc<sup>-</sup>] of 1.42:1.00, [HOAc] =  $6.7 \times 10^{-4}$  *M*, *t* = 0.1 sec. ([azo] =  $5.14 \times 10^{-6}$  *M*); O ·, in unbuffered ethanol, *t* = 1.2 msec. ([azo] =  $2.51 \times 10^{-6}$  *M*); ●, in 1.08 *M* sodium ethoxide, *t* = 0.06 sec. ([azo] =  $5.14 \times 10^{-6}$  *M*).

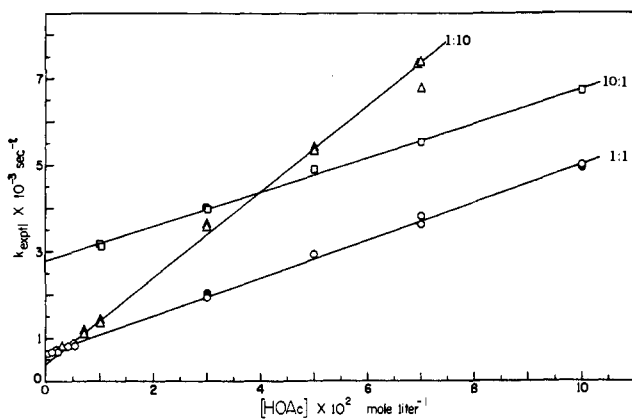


Figure 2. Catalysis in aqueous acetate buffer: plot of  $k_{\text{exptl}}$  at 30.0° vs. acetic acid concentration for the buffer ratios [HOAc]:[OAc<sup>-</sup>], 10:1, 1:1, and 1:10.

## Results

**Aqueous Solutions. *pK* Determination.** 2-Hydroxy-5-methylazobenzene shows two *pH* equilibria with *pK* values at -1.5 and 9.4. The spectra of the cationic, neutral, and anionic species are shown in Figure 1.

**Photolysis of the Neutral Molecule.** Solutions of 2-hydroxy-5-methylazobenzene in the *pH* range 1.1–6.0 yielded transient absorption changes upon flashing, with difference spectra which were essentially the mirror image of the absorption spectrum of the neutral molecule from 300–475 *mμ* (of the type obtained in acetate buffered ethanol solutions; *cf.* Figure 1). Solubility limits prevented an accurate determination of the difference spectrum in water in regions of small response (wave lengths <300 and >475 *mμ*).

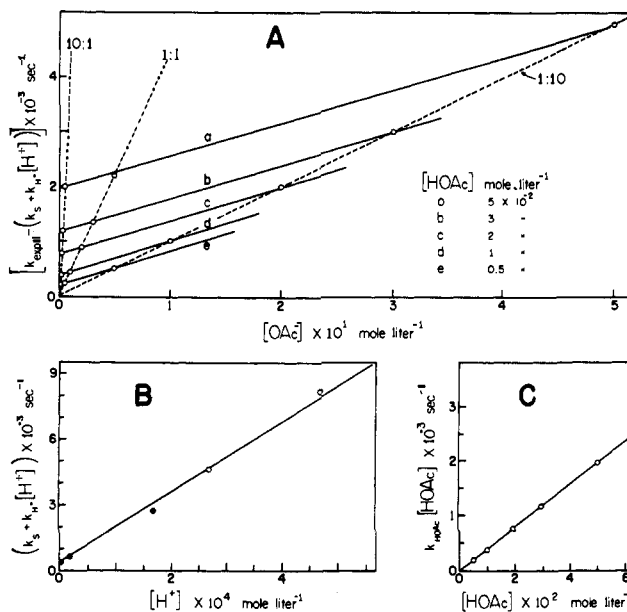


Figure 3. Separation of rate constants from aqueous acetate buffer. A: —, for constant [HOAc], ( $k_{\text{exptl}} - \text{intercept}$ ) from Figure 2, vs. [OAc<sup>-</sup>]; the slope equals  $k_{\text{OAc}^-}$  and the intercept  $k_{\text{HOAc}}[\text{HOAc}]$ ; mean value of  $k_{\text{OAc}^-} = 6.0 \times 10^3$  l. mole<sup>-1</sup> sec<sup>-1</sup>; - · - · - connects values obtained from the same buffer ratio. B: ●, plot of the intercept from Figure 2 vs. [H<sup>+</sup>]; O,  $k_{\text{exptl}}$  from perchloric acid solutions (*cf.* Figure 4); intercept,  $k_s = 4 \times 10^2$  sec<sup>-1</sup>; slope  $k_{\text{H}^+} = 1.5 \times 10^7$  l. mole<sup>-1</sup> sec<sup>-1</sup>. C: plot of intercept from Figure 3A vs. [HOAc]: slope,  $k_{\text{HOAc}} = 3.8 \times 10^4$  l. mole<sup>-1</sup> sec<sup>-1</sup>.

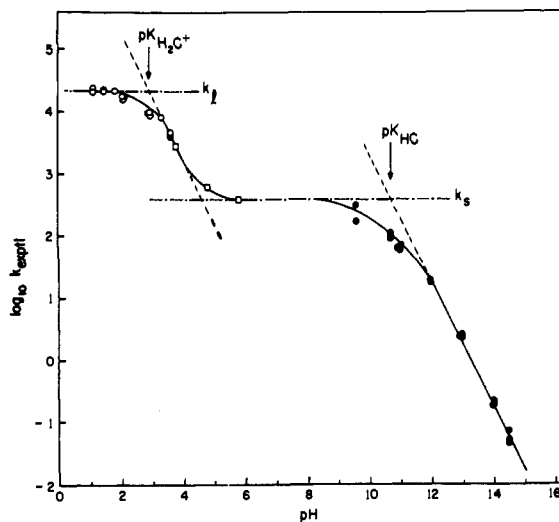


Figure 4. *pH* dependence of rate constant in aqueous solutions. Plot vs. *pH* of: O,  $\log k_{\text{exptl}}$  from perchloric acid solutions; □, intercepts from Figure 2; ●,  $\log k_{\text{exptl}}$  from sodium hydroxide solutions; - · - · -, drawn with a slope of minus unity (the units for  $k_{\text{exptl}}$  are sec<sup>-1</sup>).

The thermal relaxation of any flashed solution followed first-order kinetics. The rate constants observed in acetate buffered solutions are plotted vs. acetic acid concentration for three buffer ratios (see Figure 2). Extrapolation to zero buffer concentration gave the dependence of rate on hydrogen ion above *pH* 3.8. Above *pH* 3.3 the rate is linearly dependent on the hydrogen ion concentration (Figure 3B) while at lower *pH* the rate approaches a limiting value (see Figure 4).

**Table I.** Activation Energy Data for *cis-trans* Isomerization of 2-Hydroxy-5-methylazobenzene

	$k_{\text{exptl}}$ (30.0°), sec. <sup>-1</sup>	Pre-exp. factor <sup>a</sup> $A$ , sec. <sup>-1</sup>	$E_a$ , <sup>a</sup> kcal. mole <sup>-1</sup>	Std. error of estimate <sup>b</sup>	Temp. range, °C.
Aqueous Solutions					
Perchloric acid pH 1.8	$1.7 \times 10^4$	$1 \times 10^{11}$	9	0.1	11-30
Sodium hydroxide pH 13.0	$2.4 \times 10^9$	$2 \times 10^{11}$	15	0.08	14-60
Ethanol Solutions					
Unbuffered	$2.8 \times 10^9$	$1 \times 10^8$	10	0.07	15-60
1:1 acetate buffer					
Buffer independent portion <sup>c</sup>	$3.3 \times 10^9$	$1 \times 10^7$	9	..	15-60
Buffer catalyzed portion <sup>d</sup>	$1.0 \times 10^4$ <sup>e</sup>	$2 \times 10^{11}$ <sup>e</sup>	10	..	15-60

<sup>a</sup>  $k_{\text{exptl}} = A \exp(-E_a/RT)$ . <sup>b</sup> Root mean square of  $\ln k$  deviations about Arrhenius plot ( $\ln k$  vs.  $T^{-1}$ ). <sup>c</sup> Arrhenius equation applied to the intercepts from isothermal plots of  $k_{\text{exptl}}$  vs. buffer concentration. <sup>d</sup> Arrhenius equation applied to the slopes from isothermal plots of  $k_{\text{exptl}}$  vs. buffer concentration. <sup>e</sup> Units of l. mole<sup>-1</sup> sec.<sup>-1</sup>.

No transient was observed from pH 6.0 to 8.0 in phosphate buffer. A reaction appeared to occur, however, since the test solution became turbid after repeated flashing.

**Photolysis of the Anion.** Flashing of solutions containing predominantly the anionic species, pH 9.4 to 14.5, causes a decreased absorption of the solution from 300 to 530 m $\mu$ , the difference spectrum being essentially the same as for the ethanol solution with sodium ethoxide (*cf.* Figure 1). The rate constant was found to be strongly dependent on sodium hydroxide concentration, the reaction being slower in stronger base (Figure 4). When the logarithm of the rate constant is plotted vs. pH, the data follow a straight linear relationship with a slope of minus unity at pH values above 11.5, showing that the rate constant is directly proportional to hydrogen ion concentration in this interval with the proportionality constant  $k_{\text{H}^+} = 2.0 \times 10^{13}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. At pH < 11.5 the rate appeared to approach a limiting value. Furthermore, in this region the response to the flash gradually tapered off with decreasing concentration of base, and, below a sodium hydroxide concentration of about  $10^{-5}$  M, no transient could be observed. Using borate buffer, pH 10.0, the amount of transient produced from a given flash increased with increasing buffer concentration, all other factors being kept constant. Varying the total concentration of boric acid and borate from  $3.2 \times 10^{-3}$  to  $4 \times 10^{-2}$  M resulted in a change of  $\Delta\text{O.D.}_0$  at 350 m $\mu$ , from -0.006 to -0.049.  $\Delta\text{O.D.}_0$  designates the initial change in optical density upon flashing.

**Activation Energies.** Arrhenius plots were constructed for the neutral species in perchloric acid and acetate buffer and for the anionic species in hydroxide solutions. The lines were fitted according to the method of least squares. The data appear in Table I.

**Ethanol Solutions. Unbuffered Ethanol.** Two transients were observed upon subjecting an unbuffered solution of 2-hydroxy-5-methylazobenzene to flash. One transient having the shorter half-life,  $k_{\text{exptl}} \approx 10^3$  sec.<sup>-1</sup> at 30.0°, was observed through a weak increased absorption at wave lengths near 510 m $\mu$  (*cf.* Figure 1). The longer-lived transient,  $k_{\text{exptl}} \approx 2.8$  sec.<sup>-1</sup> at 30.0°, also had increased absorption near this wave length but produced, in addition, a difference spectrum with reduced absorption at shorter wave

lengths similar to that obtained for the acetate buffered ethanol solution (*cf.* Figure 1). Both transients followed first-order kinetics in their decay. It was not possible to obtain reproducible kinetic data for the short-lived transient in unbuffered ethanol, but the activation energy was estimated to be 5-7 kcal. mole<sup>-1</sup>.

**Acetate-Buffered Solutions.** In dilute acetate buffer, two transients of the type found in unbuffered solutions also were found. The rate of decay of the shorter-lived transient increased rapidly on addition of small amounts of acetate buffer and reached the time resolution of our equipment at an acetic acid concentration of about  $10^{-4}$  M. The longer-lived transient also showed buffer sensitivity as shown by isothermal plots of  $k_{\text{exptl}}$  vs. buffer concentration at 15, 30, 45, and 60°. Both the log of the intercepts (at zero buffer concentration) and the log of the slopes (buffer dependent) give straight lines when plotted vs. °K.<sup>-1</sup>. Arrhenius free energies,  $E_a$ , are given in Table I.

**Photolysis in Base.** In 1.08 M sodium ethoxide the compound gave the spectrum of the anion. Flashing this solution yielded the transient difference spectrum shown in Figure 1. The decay followed first-order kinetics with a rate constant of 0.20 sec.<sup>-1</sup> at 30.0°. The rate constant decreased with increasing ethoxide concentration over the entire range studied ( $10^{-4}$  to 1 M). Below  $10^{-2}$  M ethoxide, the rates were faster than in unbuffered ethanol, and log  $k$  decreased slowly (slope  $\approx -0.2$ ) with increasing log [OEt<sup>-</sup>]. Above  $10^{-2}$  M, the rates were slower than in unbuffered ethanol and log  $k$  decreased more rapidly (slope  $\approx -0.8$ ) with increasing log [OEt<sup>-</sup>].

**Activation Energies.** Rate parameters are collected in Table I.

## Discussion

A series of *o*-hydroxyazobenzenes, including 2-hydroxy-5-methylazobenzene, yielded the same spectra in several solvents of different polarity, and it was judged that they existed in solution as true phenols.<sup>8,13</sup> Therefore, we assume from previous data that in aqueous or ethanolic solutions prior to excitation, 2-hydroxy-5-methylazobenzene exists in the azo form rather than the hydrazone form, and, in addition, an intramolecular hydrogen bond is present which requires a *trans* configuration with respect to the N=N bond.

In the difference spectrum in buffered ethanol (Figure 1), the transient shows a weak absorption band at longer wave length than the *trans* species and bands of much lower extinction than the *trans* at shorter wave lengths. These spectral characteristics are typical of the *cis* isomers of azo compounds.<sup>2,3</sup> As extinction coefficients were not obtainable for the transient *cis*, it was impossible to determine the exact location of the absorption bands. Furthermore, because of the lower response in water due to lower solubility of the azo compound, it was not possible to conclude whether different *cis* species were formed at different pH on the basis of spectral evidence alone. The kinetic data presented below support our conclusion that all transient changes in water and the longer-lived transients in ethanol were due to the formation of *cis* species.

**Aqueous Solutions.** Figure 2 indicates that in acetate buffered solutions the thermal *cis-trans* reaction is catalyzed by the solvent and hydrogen ions as well as acetic acid and acetate ions. It was assumed that the catalyses by the various agents are additive, *i.e.*, the experimentally observed rate constant,  $k_{\text{exptl}}$ , could be resolved as

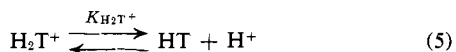
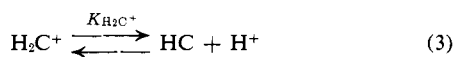
$$k_{\text{exptl}} = k_s + k_{\text{H}^+}[\text{H}^+] + k_{\text{HOAc}}[\text{HOAc}] + k_{\text{OAc}^-}[\text{OAc}^-] \quad (2)$$

This assumption appeared justified as seen by the successful separation of rate constants accomplished graphically in Figure 3. The various rate constants obtained are tabulated in Table II.

**Table II.** Rate Constants at 30.0° for the Thermal *cis-trans* Isomerization of Neutral 2-Hydroxy-5-methylazobenzene, pH 3.3–5.8

$k_s$	$= 4 \times 10^2 \text{ sec.}^{-1}$
$k_{\text{H}^+}$	$= 1.5 \times 10^7 \text{ l. mole}^{-1} \text{ sec.}^{-1}$
$k_{\text{HOAc}}$	$= 3.8 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$
$k_{\text{OAc}^-}$	$= 6.0 \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$

In the case of *p,p'*-dimethoxyazobenzene, Schulte-Frohlinde observed the decay of the *cis* cation to the *trans* neutral molecule spectrophotometrically and assumed that the *cis-trans* isomerization of the cation was the rate-determining step followed by a rapid dissociation of the *trans* cation.<sup>3</sup> Our data for the proton catalysis are consistent with the decay of the *cis* cation to the *trans* cation (eq. 4) as the rate-determining step, the two acid-base equilibria being faster.



HC and HT are neutral *cis* and *trans* molecules, respectively.  $K_{\text{H}_2\text{C}^+}$  and  $K_{\text{H}_2\text{T}^+}$  represent the two equilibrium constants, and  $k_1$  is the rate constant.

At low pH, when  $[\text{H}_2\text{C}^+] \gg [\text{HC}]$ ,  $k_{\text{exptl}}$  approaches the limiting value,  $k_1 = 2.1 \times 10^4 \text{ sec.}^{-1}$  (see Figure 4). At higher pH, in the interval 3.3–5.8,  $k_{\text{exptl}}$  shows linear

(23) M. N. Inscoc, J. H. Gould, and W. R. Brode, *J. Am. Chem. Soc.*, 81, 5636 (1959).

dependence on hydrogen ion concentration (see Figure 3). For these solutions  $[\text{H}_2\text{C}^+] \ll [\text{HC}]$ , and one obtains

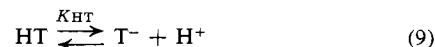
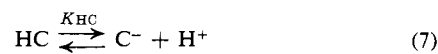
$$k_{\text{H}^+} = k_1/K_{\text{H}_2\text{C}^+} \quad (6)$$

Using the value of  $k_1$  obtained above and  $k_{\text{H}^+}$  from Table II,  $K_{\text{H}_2\text{C}^+}$  equals  $1.4 \times 10^{-3} \text{ mole l.}^{-1}$  ( $\text{p}K_{\text{H}_2\text{C}^+} = 2.9$ ).

The values of  $A$  and  $E_a$  ( $1 \times 10^{11} \text{ sec.}^{-1}$  and 9 kcal. mole<sup>-1</sup>) obtained from a  $1.6 \times 10^{-2} M$  perchloric acid solution (Table I) seem reasonable for the monomolecular reaction 4.

The above mechanism of specific acid catalysis implies that the concurrent catalyses by solvent, acetic acid, and acetate ions take place *via* other paths. It is possible that these catalyses proceed through addition complex formation as proposed for the catalysis of azobenzene by hydrazobenzene, thiourea, thiophenol, and undissociated hydrochloric acid.<sup>5,6</sup> Concurrent catalyses by acetic acid and acetate have also been shown by Lovrien and Waddington<sup>7</sup> for other azo compounds. It is interesting to note that acetic acid was ineffective as a catalyst for the *cis-trans* conversion of azobenzene<sup>6</sup> in 50% ethanol.

For 2-hydroxy-5-methylazobenzene the *cis-trans* rate was retarded by increasing sodium hydroxide concentration, and we propose the following mechanism for the pH dependence in alkaline solutions



with reaction 8 as rate determining and no direct conversion of  $\text{C}^-$  to  $\text{T}^-$ . In hydroxide solutions above pH 12, where  $[\text{HC}] \ll [\text{C}^-]$

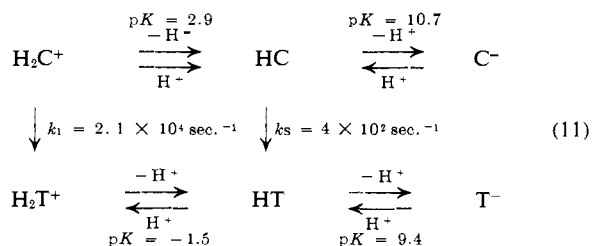
$$k_{\text{exptl}} = k_{\text{H}^+}[\text{H}^+] = k_s[\text{H}^+]/K_{\text{HC}} \quad (10)$$

and  $k_s/K_{\text{HC}}$  equals  $2.0 \times 10^{13} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ .

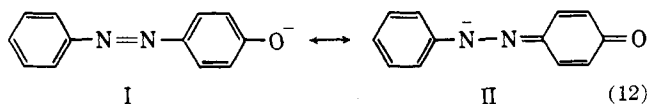
Below pH 12,  $k_{\text{exptl}}$  approaches the limiting value  $k_s$ . The limit could not be determined in base because of decreased photochemical production of *cis* isomer, but was obtained from acetate buffered solution (see Table II and Figure 4). With this value for  $k_s$ , one obtains  $K_{\text{HC}} = 2.0 \times 10^{-11} \text{ mole l.}^{-1}$  ( $\text{p}K_{\text{HC}} = 10.7$ ).

Assuming that  $[\text{H}^+]/K_{\text{HC}}$  has a very low temperature coefficient, the activation energy of 15 kcal. mole<sup>-1</sup> determined in basic solution (Table I) refers primarily to step 8, the solvent-catalyzed reaction of neutral *cis* to *trans* (see eq. 10).

The pH dependence of the *cis-trans* relaxation is summarized in the following diagram (data refer to 30.0°).



The apparent lack of direct *cis* → *trans* isomerization of the anion cannot be accommodated by the mechanism proposed by Hartley<sup>4</sup> for the catalysis of the *cis*-*trans* isomerization of *p*-hydroxyazobenzene in benzene by piperidine. He attributed the increased rate to formation of anion in which the N=N double bond character was decreased by a significant contribution of the canonical form II.<sup>24</sup> However, it is possible that piperidine catalysis in benzene does not



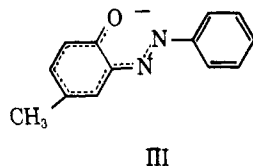
involve anion formation at all, but acts similarly to hydrazobenzene and other nucleophilic agents.<sup>3</sup>

For the anions of *p*- and *o*-hydroxyanils where direct decay of C<sup>-</sup> to T<sup>-</sup> has been postulated, the -O<sup>-</sup> group acts like other electron-donating groups; *i.e.*, it decreases the rate of the thermal *cis* → *trans* reaction.<sup>2b,25</sup> It therefore seems plausible that the -O<sup>-</sup> group so greatly retards the direct C<sup>-</sup> to T<sup>-</sup> reaction of 2-hydroxy-5-methylazobenzene, by increasing the electron density around the N=N bond, that transfer of a proton from solvent to the *cis* anion and subsequent conversion of the neutral *cis* molecule is the kinetically preferred path.

The observed dependence of ΔO.D.<sub>0</sub> on borate buffer concentration at pH 10 as well as on sodium hydroxide concentration in the pH region 12-9 indicates that the quantum yield of the *trans* (*hν*) → *cis* may be dependent on acid-base reactions in the excited state. This may also be responsible for the absence of any intermediate in phosphate buffer.

**Ethanol.** The effect of 1:1 acetate buffer on the *cis* → *trans* decay was of the same order of magnitude in ethanol as in water. Contrary to the large effect of proton in water, there appeared to be no appreciable proton catalysis in ethanol. This was evidenced by the fact that the intercepts of the isothermal

(24) In the anion of 2-hydroxy-5-methylazobenzene, rotation may be hindered for the C=N bond, the N=N bond, or both (III), owing to delocalization of the electrons. In the latter case there is a possibility



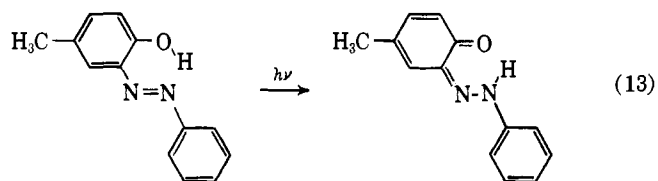
of four geometrical isomers. Since isomerization appears to take place through a neutral species, isomerization around the C=N and N=N bonds could take place through the neutral hydroxyazo and the neutral hydrazone tautomer, respectively. The fact that the hydroxyazo form is the stable neutral tautomer in the dark suggests easy rotation for the C=N bond and thus we favor representation of the observed transformation of the anion as a light induced *cis* → *trans* about the N=N bond. For such a representation of the anion, a canonical form similar to II would have little importance.

(25) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Am. Chem. Soc.*, submitted.

plots of  $k_{\text{exptl}}$  vs. buffer concentration were the same as the rates in unbuffered ethanol within experimental error.

The acceleration of the rate in solutions containing 10<sup>-4</sup> to 10<sup>-2</sup> M ethoxide over that in unbuffered ethanol finds analogy with catalyses by other anions, *e.g.*, phthalate and acetate.<sup>7</sup> At concentrations greater than 10<sup>-2</sup> M ethoxide, however, the anion becomes the predominant species, and the ethoxide inhibition can be explained in the same manner as the hydroxide inhibition in water discussed above.

The short-lived species has characteristics similar to those observed for the quinoid tautomer produced in the flash photolysis of *o*-hydroxyanils.<sup>2</sup> It shows long wave-length absorption in the visible ( $\lambda_{\text{max}} \sim 510$  m $\mu$ ); it is the more rapid of the two observed transformations; its relaxation is strongly accelerated by increasing buffer concentration and possesses an activation energy of 5-7 kcal. mole<sup>-1</sup>. This second transient is therefore postulated to be the hydrazone tautomer produced by a photoinduced intramolecular hydrogen transfer from the hydroxyl group to the nitrogen atom. Reaction 13 appears to have a low quantum



yield. The high susceptibility of this species to acid catalysis is probably responsible for the fact that it was not observed in water.

**Activation Energies.** The activation energies for the *cis*-*trans* isomerization of 2-hydroxy-5-methylazobenzene are low compared to the 20-23 kcal. mole<sup>-1</sup> activation energies generally obtained for substituted azo compounds.<sup>5</sup> They are consistent, however, with values for other hydroxyazo compounds reported as 12-14 kcal. mole<sup>-1</sup> for 2-hydroxy-3-(phenylazo)naphthalene and 11-13 kcal. mole<sup>-1</sup> for 1-hydroxy-4-(phenylazo)naphthalene in alcohol solvent.<sup>9,10</sup> In the latter case, the hydrazone acts as an intermediate and the activation energies for the two steps, *cis*-azo → hydrazone, and hydrazone → *trans*-azo are almost equal. In the former case, where hydrazone formation was judged improbable, the low value was attributed to hydrogen bonding in the transition state. For the 2-hydroxy-5-methyl compound, the rapid decay of the photoproduct hydrazone tautomer to the *trans*-hydroxyazo tautomer does not preclude its participation as an intermediate in the *cis* → *trans* reaction. It is thus not possible to tell whether either of the aforementioned factors are responsible for the low activation energy reported here.

**Acknowledgment.** The authors wish to thank Dean Smiley for synthesizing 2-hydroxy-5-methylazobenzene.