

Photoinduced Isomerizations in Anils

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Reversible photochemical isomerizations have been observed in ethanol solutions of the anils, *N*-(*o*-hydroxybenzylidene)aniline (I), *N*-(*o*-hydroxybenzylidene)- β -naphthylamine (II), *N*-(*p*-hydroxybenzylidene)aniline (III), and *N*-benzylideneaniline (IV). In each of these compounds there appears to be a light-induced formation of *cis* isomer from the more stable *trans* isomer. The thermal *cis* \rightarrow *trans* decay has an activation energy of 14 to 17 kcal. mole⁻¹ and a half-life of about 1 sec. at room temperature. Under similar conditions, *N*-benzohydrylideneaniline (V) gave rise to no transient species. I, II, and III yield anions which also show *cis*-*trans* isomerization. In acidic solutions, I and II exhibit an additional isomerization to a shorter lived species having a half-life of the order of 1 msec. These species are proposed to be quinoid isomers formed through an intramolecular hydrogen transfer from the *o*-hydroxyl group to the nitrogen of the C=N bond. The reverse thermal reaction is buffer catalyzed and has an activation energy of 3 to 4 kcal. mole⁻¹.

Introduction

Some anils derived from salicylaldehyde have been found to display photochromism in the crystalline phase as a transformation from yellow to red under the action of light.² Generally, anils from aromatic aldehydes possessing an *o*-hydroxyl group develop similar red colors on exposure to ultraviolet light in a low temperature glass.³⁻⁵ These color phenomena have been attributed to a photochemical tautomerization involving a hydrogen transfer from the *o*-hydroxyl group to the nitrogen atom of the carbon-nitrogen double bond.

It has also been found that light produces *cis*-*trans* isomerizations about the carbon-nitrogen double bond of anils at Dry Ice temperatures.⁶ Measurements at room temperature showed *N*-(*o*-hydroxybenzylidene)aniline to undergo two different photoinduced isomerizations.⁷ In ethanol buffered with acetic acid-sodium acetate, one isomerization was observed as a transient, increased absorption with maximum around 470 m μ . The disappearance of this band in the dark was found to follow first-order kinetics and was accelerated by increasing buffer concentrations. The half-life was of the order of 1 msec. The second isomerization was evidenced by a decreased absorption at wave lengths near 385 m μ . In the dark, the reverse

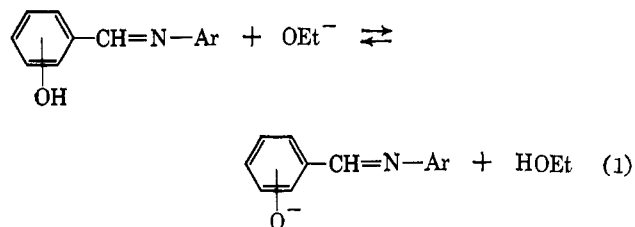
reaction had a half-life of approximately 1 sec. The decay followed first-order kinetics but was not catalyzed by the buffer. The two transformations were postulated to be due to the hydrogen transfer mentioned above and *cis*-*trans* isomerization, respectively.

The present investigation deals with the photochemical behavior of the following compounds: *N*-(*o*-hydroxybenzylidene)aniline (I), *N*-(*o*-hydroxybenzylidene)- β -naphthylamine (II), *N*-(*p*-hydroxybenzylidene)aniline (III), *N*-benzylideneaniline (IV), and *N*-benzohydrylideneaniline (V).

Results

Absorption Characteristics and Acid-Base Equilibria. Although most anils are rapidly hydrolyzed by water,⁸ the rate of hydrolysis can be suppressed by maintaining a sufficiently low water concentration in the system. In this investigation it was found that reproducible results for the isomerizations could be obtained using ethanol containing only 0.04% water.

The absorption spectrum of each of the compounds, I through V (Figure 1), in ethanol remained unchanged upon addition of the different acetate buffers used in this study. When sodium ethoxide in ethanol was added, a different spectrum developed for the compounds containing hydroxyl groups, I, II, and III, whereas the spectra of IV and V remained unchanged. The changes in I, II, and III are reversible in that the original spectra were reobtained after neutralization of the basic solutions. For two characteristic wave lengths, the extinction coefficients (based on initial anil concentration) are plotted as a function of the concentration of ethoxide; see Figure 2. These curves indicate acid-base equilibria, and defining the equilib-



rium constant for (1) as

$$K = \frac{[\text{conjugate base}]}{[\text{anil}][\text{OEt}^-]} \quad (2)$$

the p*K* values are -3.4, -3.7, and -4.3 for I, II, and III, respectively. The ethoxide concentration was computed from the amount added disregarding any side reactions that might reduce its concentration, such as neutralization by acids such as water or carbon dioxide in the system. Even though water (0.04%) is present in concentrations of the same order of magni-

(1) Plastics Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del.

(2) G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, **11**, 1 (1961).

(3) M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press Ltd., London, 1959, p. 293.

(4) M. D. Cohen and G. M. J. Schmidt in "Reactivity of Solids," J. H. de Boer, Ed., Elsevier Publishing Co., Amsterdam, 1961, p. 556.

(5) M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962).

(6) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

(7) G. Wettermark and L. Dogliotti, *ibid.*, **40**, 1486 (1964).

(8) H. von Euler, H. Hasselquist, and O. Ceder, *Arkiv Kemi*, **6**, 287 (1953).

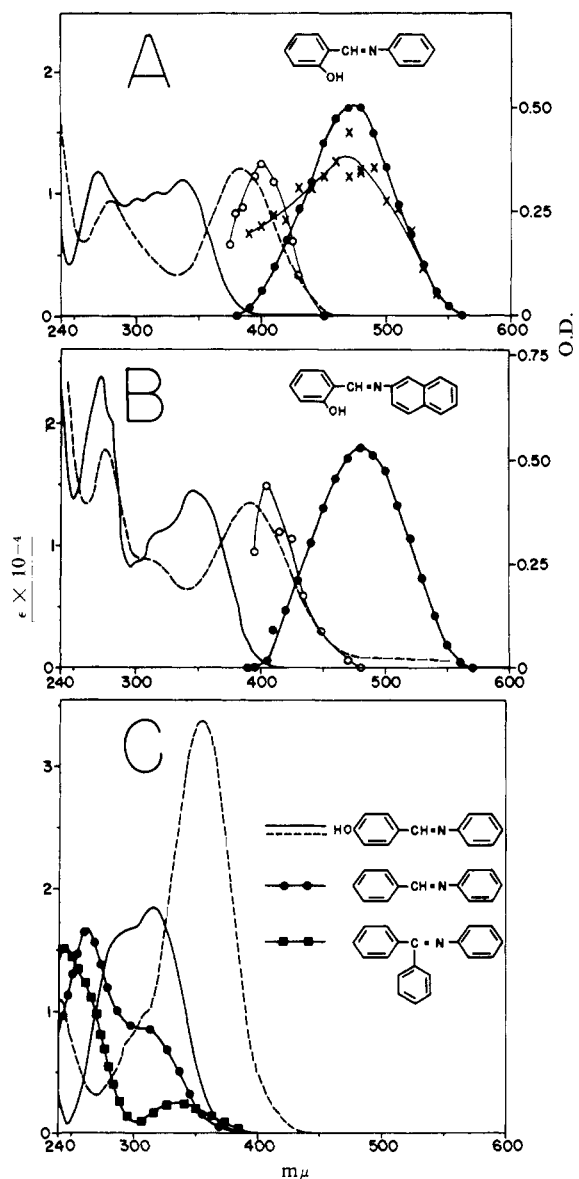


Figure 1. Spectra. A: *left ordinate*, absorption spectra of I in ethanol, ϵ = extinction coefficient ($M^{-1} \text{ cm}^{-1}$); —, anil in acetate buffer; ---, conjugate base. *Right ordinate*, difference spectra for "millisecond transients" from I; O.D. = optical density (arbitrary units); ●, I in 7:1 and 1.4:1 acetate buffer; ×, I in 1:5 acetate buffer; ○, I in half-neutralized solutions. B: *left ordinate*, absorption spectra of II in ethanol; ϵ = extinction coefficient ($M^{-1} \text{ cm}^{-1}$); —, anil in acetate buffer; ---, conjugate base. *Right ordinate*, difference spectra for "millisecond transients" from II; O.D. = optical density (arbitrary units); ●, II in 7:1 and 1.4:1 acetate buffer; ○, II in half-neutralized solutions. C: absorption spectra of III, IV, and V in ethanol; —, III in acetate buffer; ---, conjugate base of III; ●—●—, IV in acetate buffer; ■—■—, V in acetate buffer.

tude as the anil, its effect upon equilibrium 1 was neglected since the acidities of water and ethanol do not appear to differ by more than a power of ten.^{9,10}

N-(o-Hydroxybenzylidene)aniline (I). Photolysis in Buffered Acid. The investigation of I referred to in the Introduction⁷ was extended to include two additional acetate buffer ratios and several alkaline solutions, one with an ethoxide concentration sufficient to cause approximately half-conversion of the anil to

(9) E. F. Caldin and G. Long, *J. Chem. Soc.*, 3737 (1954).

(10) A. Koivisto, *Acta Chem. Scand.*, 8, 1218, 1223, 1229 (1955).

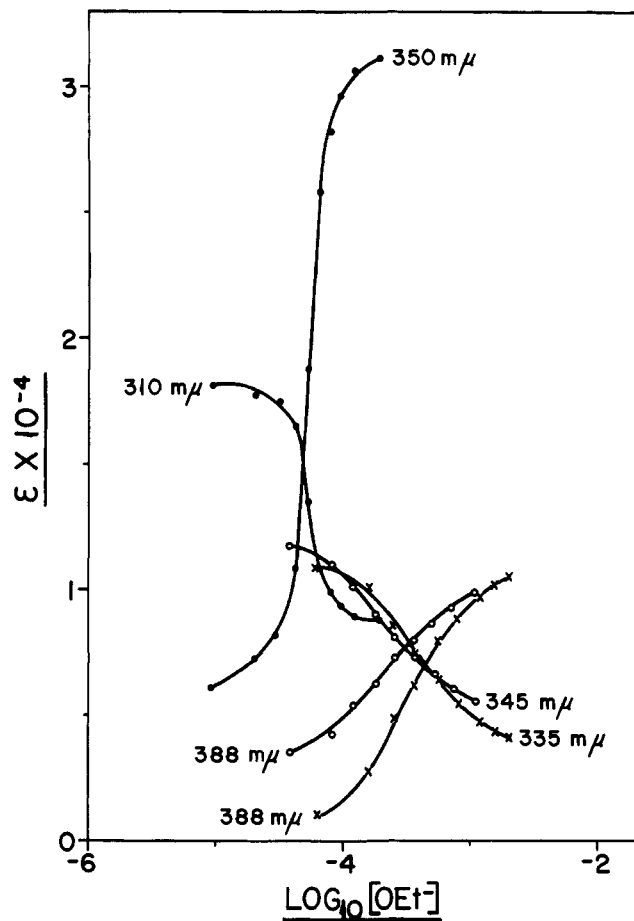


Figure 2. Titration curves for compounds I, II, and III: ×, I; ○, II; ●, III.

its conjugate base and others in which the anil is converted essentially completely into its conjugate base.

Flashing of ethanol solutions in acetate buffer generated a long-lived species observed through a decreased absorption at wave lengths below 400 $m\mu$. The species decayed following first-order kinetics; *cf.* Table I. The concentration of buffer appeared to have no effect on reaction rate, nor did the rate constants show any significant difference for the two higher buffer ratios as indicated in the Arrhenius plots given in Figure 3A. (For the buffer ratio 1:5, measurements were made only at 30.0°.)

A shorter lived species was also observed and displayed maximum absorption around 470 $m\mu$. The difference spectra were the same in 7:1 and 1.4:1 buffer but significantly different in 1:5 buffer; *cf.* Figure 1A. The species faded in the dark following first-order kinetics. To determine buffer catalysis, the experimentally determined rate constants, k_{expt} , were plotted as a function of acetic acid concentration, Figures 4A and B. Activation energies were obtained for the buffer catalysis from the slopes of the lines of Figures 4A and B and for the nonbuffer catalyzed portion of the reaction from the intercepts. Arrhenius plots are shown in Figure 5, and the values of the pre-exponential factors and activation energies are shown in Table II.

Photolysis at Half-Neutralization. Ethanol solutions of I with sufficient sodium ethoxide to establish a 1:1 ratio between anil and its conjugate base were

Table I. Absorption Characteristics and Kinetics for the Thermal Relaxation of Flash-Perturbed Equilibria of I-V in Acetic Acid-Sodium Acetate Buffered Ethanol (Long-Lived Transformation^a)

Anil	Spectral response of soln.	k_{exptl}^b at 30.0°C, sec. ⁻¹	$A \times 10^{-11},^b$ sec. ⁻¹	$E_a,^b$ kcal. mole ⁻¹
I	Decreased absorption, 385-400 m μ	1.67 ^c	0.3	14.2
II	Decreased absorption, 385-400 m μ	1.93 ^c	3	15.4
III	Increased absorption, 380-400 m μ	0.72	2	15.7
IV	Increased absorption, 385-395 m μ	1.46	12	16.5
V	No spectral change, 350-550 m μ

^a *cis* \rightarrow *trans* isomerization of the neutral molecule in proposed mechanism. ^b Obtained from Figure 3 using the Arrhenius equation, $k_{\text{exptl}} = A \exp(-E_a/RT)$. ^c Equal to k_{IC} in eq. 5 and 6.

exposed to a flash. Again, two transient species were observed, each with a first-order decay; the kinetic

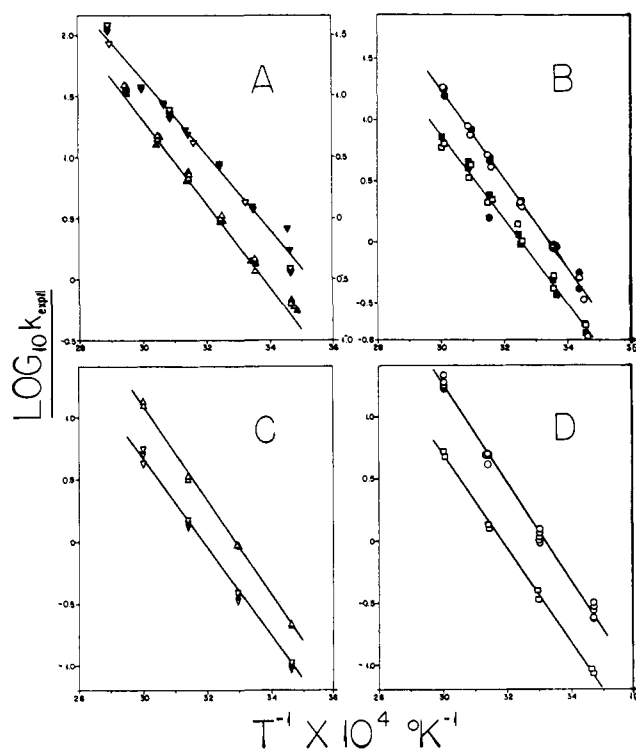


Figure 3. Arrhenius plots for the thermal *cis-trans* isomerization. A: ∇ , I in 1.4:1 acetate buffer; \blacktriangledown , I in 7:1 acetate buffer (right ordinate); \triangle , II in 1.4:1 acetate buffer; \blacktriangle , II in 7:1 acetate buffer (left ordinate). B: \square , III in 1.4:1 acetate buffer; \blacksquare , III in 7:1 acetate buffer; \circ , IV in 1.4:1 acetate buffer; \bullet , IV in 7:1 acetate buffer. C: ∇ , I in 0.040 M NaOEt; \triangle , II in 0.035 M NaOEt. D: \square , III in 0.036 M NaOEt; \circ , IV in 0.036 M NaOEt. (For A and B: longer lived relaxation; for each temperature and both buffer ratios, data were obtained for two concentrations of buffer, $[\text{HOAc}] = 2 \times 10^{-4}$ and $10^{-3} M$.)

data are given in Table III. At wave lengths longer than 450 m μ no transient change in light absorption

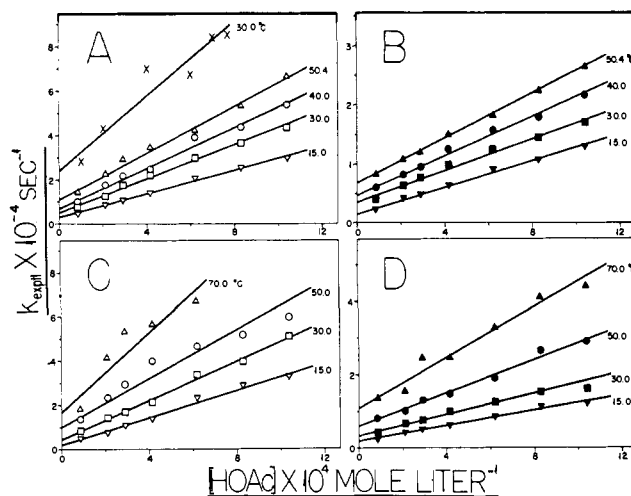


Figure 4. Rate of decay of the "millisecond transient" as a function of buffer concentration. (The concentration of acetic acid was chosen to represent buffer concentration.) A: \times , I in 1:5 acetate buffer; ∇ , \square , \circ , \triangle , I in 1.4:1 acetate buffer. B: \blacktriangledown , \blacksquare , \bullet , \blacktriangle , I in 7:1 acetate buffer. C: ∇ , \square , \circ , \triangle , II in 1.4:1 acetate buffer. D: \blacktriangledown , \blacksquare , \bullet , \blacktriangle , II in 7:1 acetate buffer.

was noticed. The difference spectrum for the species having the shorter half-life is shown in Figure 1A.

Photolysis in Strong Base. Solutions with ethoxide in the range 10^{-1} to $4 \times 10^{-3} M$ yielded only one transient, observable by a decreased absorption of the solution in the region 385 to 440 m μ . The original optical density was restored following first-order decay kinetics. Within experimental error, all solutions gave the same rate constant, 0.37 sec.⁻¹. No transient changes were observed at wave lengths longer than 450 m μ . An Arrhenius plot for the transient in a $4 \times 10^{-2} M$ sodium ethoxide solution is shown in Figure 3C.

N-(*o*-Hydroxybenzylidene)- β -naphthylamine (II).

Photolysis in Acetate Buffer. Compound II was subjected to an investigation similar to the one performed with I. The results show almost identical behavior for the two compounds. In acetate-buffered ethanol solution, two transients were generated upon flashing; see Tables I and II. As with compound I, these photoinduced changes were reversible. The absorption spectrum (difference spectrum) for the faster transient is shown in Figure 1B.

Treating the data for II in the same manner as those for I gives the plots of buffer catalysis shown in Figures 4C and D and Arrhenius plots shown in Figures 3A and 5.

Photolysis at Half-Neutralization. Flashing ethanol solutions of II, approximately half-neutralized with sodium ethoxide, gave rise to two transients (lifetime in the "millisecond region" and in the "second region"); see Table III. The difference spectrum of the short-lived transient is given in Figure 1B.

Photolysis in Strong Base. In strong base, only one transient was observed; see Table IV. Over the investigated region, 3.5×10^{-2} to $5.5 \times 10^{-3} M$ sodium ethoxide, the rate constant showed no systematic change with base concentrations. An Arrhenius plot is given for the solution containing $3.5 \times 10^{-2} M$ ethoxide; see Figure 3C.

Table II. Absorption Characteristics and Kinetics for the Thermal Relaxation of Flash-Perturbed Equilibria of I-V in Acetic Acid-Sodium Acetate Buffered Ethanol (Short-Lived Transformation^a)

Anil	Spectral response	Buffer ratio [HOAc]: [OAc ⁻]	Data obtained from intercept ^b		Data obtained from slope ^b			
			$k_0 \times 10^{-3c}$ at 30.0°, sec. ⁻¹	$A_0 \times 10^{-8d}$ at 30.0°, sec. ⁻¹	E_a, d kcal. mole ⁻¹	$k_2 \times 10^{-7e}$ at 30.0°, M ⁻¹ sec. ⁻¹	$A_2 \times 10^{-9f}$ at 30.0°, M ⁻¹ sec. ⁻¹	E_a, f kcal. mole ⁻¹
I	Increased absorption, 390-550 m μ ; λ_{max} 470 m μ	1:5	24	8.4
		1.4:1	5.0	3	6.7	3.7	10	3.4
		7:1	3.1	8	7.5	1.4	2	3.1
II	Increased absorption, 400-560 m μ ; λ_{max} 480 m μ	1.4:1	4.0	14	7.7	4.4	3	2.6
		7:1	3.2	0.6	5.9	1.5	16	4.2

^a Tautomerization in proposed mechanism. ^b Obtained from the lines in Figure 4. ^c Intercept of the lines of k_{exptl} vs. [HOAc] at 30.0° in Figure 4. ^d Obtained from Figure 5A using $k_0 = A_0 \exp(-E_a/RT)$. ^e Slope of the lines of k_{exptl} vs. [HOAc] at 30.0° in Figure 4. ^f Obtained from Figure 5B using $k_2 = A_2 \exp(-E_a/RT)$.

N-(*p*-Hydroxybenzylidene)aniline (III). *Photolysis in Acetate Buffer.* Flashing of III in ethanol buffered with acetic acid-sodium acetate produced only one transient which had essentially the same characteristics as the long-lived species from compounds I and II. This transient, observed through an increased absorption over the wave lengths 385-400 m μ , showed no apparent dependence of rate of fading on concentration of buffer or buffer ratio; see Tables I and II and Figure 3B.

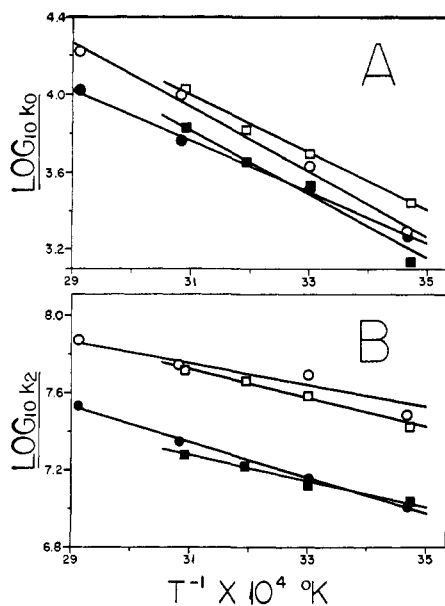


Figure 5. Arrhenius plots for the "millisecond transient." A: logarithm of the intercepts from Figure 4 vs. the inverse absolute temperature; \square , I in 1.4:1 acetate buffer; \blacksquare , I in 7:1 acetate buffer; \circ , II in 1.4:1 acetate buffer; \bullet , II in 7:1 acetate buffer. B: logarithm of the slopes from Figure 4 vs. the inverse absolute temperature; symbols defined as under A.

Photolysis at Half-Neutralization. When half-neutralized with sodium ethoxide, III yielded only one transient upon flashing; see Table III. The rate constant appeared dependent on the basicity, i.e., the ratio of anil to its conjugate base.

Photolysis in Strong Base. One transient was also observed in strong base, and the rate constant for the thermal relaxation was essentially constant over the range 9×10^{-2} to 2.5×10^{-4} M ethoxide concentra-

tion; see Table IV. An activation energy plot for a 3.6×10^{-2} M ethoxide solution is given in Figure 3D.

N-Benzylideneaniline (IV). As with III, IV gave rise to only one transient species upon flashing in acid and base; see Tables I and II. In acetic acid-sodium acetate buffer, the transient had a lifetime of about 1 sec., and, as the transient from III, it showed no dependence upon buffer concentration or ratio. Activation energy plots for an acidic and a basic solution are shown in Figures 3B and D.

N-Benzohydroxybenzylideneaniline (V). Flash photolysis of a solution of V (8.6×10^{-4} M in ethanol) produced no response at wave lengths 350, 400, 425, 450, 500, or 550 m μ , showing that there was no transient absorbing in the region 350-550 m μ having a lifetime longer than about 10 μ sec. (limit of the time resolution of the apparatus).

Discussion

cis-trans Isomerization. Acidic Solutions. A comparison of rate constants and activation energies for the transformations observed in the anils I-IV in acetic acid-acetate buffered solutions on exposure to flash indicates that I-IV all undergo a similar transformation resulting in a species of half-life of the order of 1 sec. at room temperature, whereas no change occurs in V; see Tables I and II. It is proposed that this transformation involves *cis-trans* isomerization about the carbon-nitrogen double bond with the *trans* isomer as the stable species in the dark, yielding the *cis* isomer on exposure to light. The activation energy (14.2-16.5 kcal. mole⁻¹) for this decay agrees quite well with results obtained previously by Fischer and Frei.⁶ They followed the thermal decay kinetics of irradiated solutions of IV in methylcyclohexane over the range -70 to -40° and observed an activation energy of 16 to 17 kcal. mole⁻¹. They proposed a *cis-trans* isomerization. Furthermore, the fact that V, for which *cis* and *trans* isomers do not exist, does not give rise to any observable photoinduced transients tends to support this proposition. The rate data in Tables I and II accordingly refer to the thermal conversion of the *cis* anil into the *trans* anil. It is noted that the hydroxyl-substituted compounds I, II, and III, which possess the possibility of tautomerization, have pre-exponential factors and activation energies of the same magnitude as the unsubstituted anil, IV. This indicates that the quinoid tautomer probably plays no role in the thermal *cis-trans* relaxation. This is in contrast to observa-

Table III. Absorption Characteristics and Kinetics for the Thermal Relaxation of Flash-Perturbed Equilibria of Ethanol Solutions of I-III Half-Neutralized with Base^a

Anil	[Conjugate base]: [anil]	Long-lived transformation		Short-lived transformation	
		Spectral response	k_{exptl} at 30.0°, sec. ⁻¹	Spectral response	$k_{\text{exptl}} \times 10^{-4}$ at 30.0°, sec. ⁻¹
I	Ca. 1	Increased absorption, 385-400 m μ ; decreased absorption, 410-470 m μ	0.42	Increased absorption, 365-450 m μ ; λ_{max} 400 m μ	1.0
II	Ca. 1	Increased absorption, 385-400 m μ ; decreased absorption, 410-470 m μ	0.95	Increased absorption, 385-470 m μ ; λ_{max} 405 m μ	1.0
III	Ca. 0.3	Decreased absorption, 380-420 m μ	2.2

^a Solution titrated with sodium ethoxide until approximately equal concentrations of anil and its conjugate base were obtained.

Table IV. Absorption Characteristics and Kinetics for the Thermal Relaxation of Flash-Perturbed Equilibria of I-IV in Excess Base

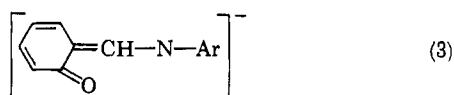
Anil	Spectral response	k_{exptl} at 30.0°, sec. ⁻¹	$A \times 10^{-12}$, ^b sec. ⁻¹	E_{a} , ^b kcal. mole ⁻¹
I	Decreased absorption, 385-440 m μ	0.37 ^a	0.2	16.3
II	Decreased absorption, 385-440 m μ	0.95 ^a	4	17.4
III	Decreased absorption, 385-430 m μ	0.40	1	17.2
IV	Increased absorption, 385-395 m μ	1.10	11	18.0

^a Equal to k_{C^-} in eq. 5 and 6. ^b Obtained from $k_{\text{exptl}} = A \exp(-E_{\text{a}}/RT)$; Figures 3C and D.

tions made with a similar azo compound, 1-hydroxy-4-(phenylazo)naphthalene, where a hydrazone tautomer appears as an intermediate in the thermal *cis* \rightarrow *trans* conversion.¹¹

Strongly Alkaline Solutions. In strong base, compounds I-IV yield a photochemical transformation similar to that observed in buffered acid; see Tables I, II, and IV. The absorption spectra showed IV to exist in the same state in the ethoxide solutions as in the acetic acid-acetate buffered solutions. The spectral changes by which the transformation was noted are similar to those in acid, and the rate constants in base were also of the same order of magnitude, indicating again a *cis-trans* isomerization.

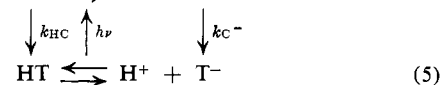
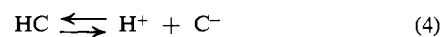
I-III exist as anions in ethoxide solution and one might have expected appreciable redistribution of electronic charge with respect to the C=N bond typified by canonical structures such as (3) and consequent changes



in the kinetic and activation energy data. Examination of Tables I and III indicates, however, that *cis-trans* isomerization does occur for the anions of I-III with an energy barrier which is comparable to that of the neutral species.

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

Half-Neutralization. The following scheme for I and II contains two acid-base equilibria, one for the *trans* species (5) and the other for the *cis* species (4) generated upon flash.



HC = *cis* acid, C⁻ = *cis* anion, HT = *trans* acid, and T⁻ = *trans* anion for I and II. It seems reasonable to assume that these equilibria are established in a time much shorter than the time required for the thermal *cis-trans* transformation characterized by the first-order rate constants k_{HC} and k_{C^-} .

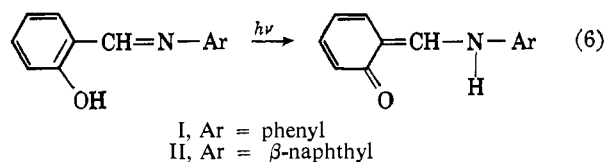
With HT and T⁻ present in equal amounts, the rate constants for the long-lived relaxation, believed to be the *cis-trans* isomerization, are close to the ones observed in strong base, Tables III and IV. If it is assumed that HC is decaying to HT with the rate constant k_{HC} obtained in buffered acid, and C⁻ to T⁻ with rate constant k_{C^-} obtained in strong base, it appears that, at a basicity equal to the pK for the *trans* species, the *cis* species exist principally as C⁻; i.e., HC is a stronger acid than HT. Spectral evidence supports this conclusion. In the region investigated, the *cis* species, both anil and anion, have lower extinction than the corresponding *trans* species; see Tables I and IV. However, when solutions with equal concentration of *trans* anil and anion were flashed, a decreased absorption was noticed only between 410 and 470 m μ , but there was an increased absorption between 385 and 400 m μ . An increased population of the anion in the *cis* equilibrium (4) in relation to the *trans* equilibrium (5) would explain this observed crossover in the absorption spectra if the extinction of *cis* anion (although smaller) is sufficiently close to that of the *trans* anion in the region 385-400 m μ .

III shows a different behavior in that the rate constant for the decay of the long-lived transient is higher at half-neutralization than in either acid or base media. This indicates that the simple scheme, eq. 4 and 5, for the *cis* \rightarrow *trans* isomerization cannot apply in this case.

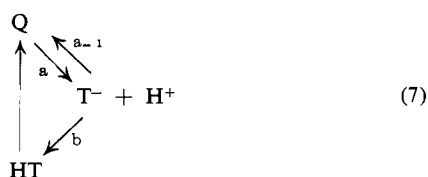
Hydrogen Migration. In acetate-buffered ethanol and in half-neutralized solutions, I and II give rise to a second transient with a half-life of the order of 1 msec.; see Table II and Figure 1. Different transient spectra

were obtained dependent on the acidity of the solution; *i.e.*, the spectra obtained in acetate buffer were different from those in half-neutralized solutions. For I, the spectrum obtained at an intermediate acidity, 1:5 acetate buffer, can be regarded as a composite of the spectrum in 7:1 or 1.4:1 acetate buffer and that in half-neutralized solution.

The acid-base dependence of the spectrum is indicative of an equilibrium between an acid and a base form of the transient. The acid spectrum is similar to that produced in the solid and in low-temperature glass on irradiation of anils derived from salicylaldehyde. It is, therefore, postulated that the acid form is the *o*-quinoid isomer arising from the transfer of the hydrogen from the hydroxyl group to the nitrogen of the C=N bond.¹²

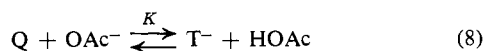


It is suggested that the "millisecond transient" at half-neutralization is the *trans* anion since subtraction of the spectrum of the anil from that of its conjugate base yields essentially the observed spectrum; *cf.* Figure 1. Therefore, it appears that, even though light produces the quinoid species, Q, from the anil, HT, Q forms an equilibrium with the *trans* anion, T⁻, this equilibrium being established faster than the time resolution of our equipment. The rate-determining step in the observed decay may accordingly be the neutralization of T⁻ to form HT (reaction b),¹³ consistent with the low activation energies obtained.



At half-neutralization the solvent, HSol, is the neutralizing acid, and the decay can be described as T⁻ + HSol ⇌ HT + Sol, with $k_{\text{HSol}}[\text{HSol}] = 1.0 \times 10^4 \text{ sec.}^{-1}$ for both I and II; *cf.* Table III.

In acetate-buffered ethanol, both solvent and acetic acid act as neutralizing acids and assuming equilibrium 8 establishes rapidly the rate law may be expressed as



$$\frac{-d([\text{Q}] + [\text{T}^-])}{dt} = (k_{\text{HSol}}[\text{HSol}] + k_{\text{HOAc}}[\text{HOAc}])(\text{T}^-) \quad (9)$$

(12) In solution, the photochemical process most likely involves an intramolecular hydrogen transfer through a six-membered ring since compound III, for which a *p*-quinoid structure is possible, does not yield a similar species.

(13) It is possible that in the dark Q and HT are in equilibrium through the common conjugate anion, T⁻, with the equilibrium shifted toward HT (Q being a slightly stronger acid than HT). Light perturbs this equilibrium. For II, two tautomers have been isolated, one yellow and one red, likely HT and Q: C. V. Gheorghiv and B. Arrventieu, *Bull. soc. chim. France*, **47**, 195 (1930).

Substituting for [Q], one obtains eq. 10 for an expression of the rate constant.

$$k_{\text{exptl}} = \left(\frac{[\text{HOAc}]}{K[\text{OAc}^-]} + 1 \right)^{-1} (k_{\text{HSol}}[\text{HSol}] + k_{\text{HOAc}}[\text{HOAc}]) \quad (10)$$

Estimates of the constants in eq. 10 for 30.0° can be made by plotting the reciprocal of slope and intercept from Figure 4 vs. the buffer ratio. For I: $k_{\text{HSol}}[\text{HSol}] \approx 1 \times 10^4 \text{ sec.}^{-1}$, $k_{\text{HOAc}} \approx 7 \times 10^7 \text{ l. sec.}^{-1} \text{ mole}^{-1}$, and $K \approx 2$. For II: $k_{\text{HSol}}[\text{HSol}] \approx 4 \times 10^3 \text{ sec.}^{-1}$, $k_{\text{HOAc}} \approx 8 \times 10^7 \text{ l. sec.}^{-1} \text{ mole}^{-1}$, and $K \approx 2$. k_{exptl} follows eq. 10 only semiquantitatively, and large errors are contained in the estimated values. It is possible that the rates of a and b become of the same order of magnitude in acetate buffer. It is noted, however, that the values of $k_{\text{HSol}}[\text{HSol}]$ do agree fairly well with those obtained from the half-neutralized solutions. In the case of compound I, slopes and intercepts in Figure 4 lead to essentially the same K value, ~ 2 , but for II, while the slope yields a K value of 2, the intercept leads to the unreasonable value 20. It should be emphasized that the estimates for II are based on only two buffer ratios.

Experimental

Measurement Procedure. A brief description of the flash apparatus and the general measuring procedure has already been given,¹⁴ and a more complete explanation of the equipment has been published recently by Lindqvist.¹⁵ The spectra of the unexcited solutions were recorded on a Cary 11 spectrophotometer.

Materials. Anils were prepared by stirring equimolar quantities of aldehyde and amine in ethanol solution and were purified by repeated recrystallization from ethanol. In the case of compound V, the preparation was performed in refluxing xylene, water being removed by the use of a Dean-Stark trap.

Chemicals used were: sodium, J. T. Baker, reagent grade; acetic acid, J. T. Baker, glacial reagent grade; sodium acetate, Merck, anhydrous, reagent grade; ethanol, U.S.P. (containing 0.04% water).

Sodium ethoxide was prepared by dissolving sodium metal in ethanol under anhydrous conditions.

Test solutions for the flash experiment were approximately $10^{-4} M$ in anil and contained buffer or sodium ethoxide in ethanol as specified. The buffer ratios referred to in the text as 1.4:1, 7:1, and 1:5 contained acetic acid and sodium acetate in molarity ratios of 1.402:1, 7.010:1, and 0.200:1, respectively.

Titrations of the anils I, II, and III were made under dry argon atmosphere, and the samples were transferred to the spectrophotometer without atmospheric contact.

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

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