

## Transient Species in the Photolysis of Anils

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Two photoinduced isomerizations occur in the photolysis of ethanol solutions of the anil, *o*-hydroxybenzylidene-aniline in the temperature interval 15°–70°C. One isomerization involves the formation of a visible absorption band,  $\lambda_{\text{max}}$  470 m $\mu$ , which fades in the dark with a lifetime in the millisecond region. The fading is buffer catalyzed and yields an activation energy of 3.5 kcal/mole for this catalysis. The second isomerization, which is observed as a change in the near ultraviolet spectrum, is about a thousand times more long-lived and not catalyzed by the presence of buffer, activation energy: 15.0 kcal/mole. The two isomerizations are identified as (1) a hydrogen transfer from the *ortho* hydroxyl group to the nitrogen atom forming an *ortho* quinoid structure, (2) a *cis-trans* isomerization around the C=N double bond.

IN their recent review<sup>1</sup> Brown and Shaw list about 200 anils which change color on exposure to light and revert back in the dark. Attempts have been made to characterize the structural requirement for photochromism in anils by reacting different aldehydes and amines and testing for photochromism. Many of the earlier tests were performed on the crystalline compounds and it became evident from this screening that a great number of the photochromic anils were derivatives of *o*-hydroxybenzaldehyde. Several anils derived from *o*-hydroxybenzaldehyde have recently been investigated<sup>2</sup> in rigid glass solutions at about –100°C and it was found that they invariably change color on exposure to light whether or not they show photochromism in the crystalline state. Using flash photolysis techniques it has now been possible to observe short-lived transients in solutions of anils at room temperatures, the behavior of one characteristic derivative, *o*-hydroxybenzylidene-aniline is illustrated in the following:

*o*-Hydroxybenzylidene-aniline, A, exhibits photochromism, turning from yellow to red both in the crystalline state and in solution at temperatures below –40°C.<sup>1,2</sup> At room temperature the compound is yellow in any common solvent such as ethanol, acetone, ether, benzene, or heptane, with several absorption maxima in the ultraviolet. Subjecting such solutions to a high-intensity pulse of ultraviolet light creates a new absorption band with a maximum around 470 m $\mu$ , Fig. 1. This band disappears with a lifetime in the millisecond region and was found to be almost identical in the different solvents used indicating the presence of a transient species A\*. The kinetics of fading of A\* followed first-order kinetics in polar solvents such as methanol, ethanol, and acetone but was of higher order in nonpolar solvents such as benzene, *n*-heptane, and cyclohexane.

The existence of another transient species B\* was

evident from changes in optical absorption around 385 m $\mu$ . In this region the solution became more transparent on flashing and the original optical density was restored in a reaction being about a thousand times slower than the fading of A\*. The data did not provide enough information to determine whether A\* and B\* are both formed in a primary reaction or if B\* is a subsequent product of A\*.

A solution could be recycled at least thirty times without showing any significant change in response indicating the entire photochemical reaction to be essentially reversible. Deaerating the solutions did not show any measurable effect.

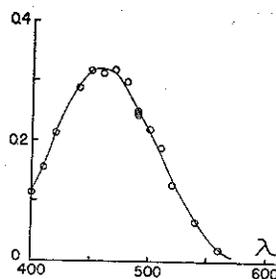


FIG. 1. Visible absorption spectrum of short-lived transient in *n*-heptane recorded as the optical density increase upon flash excitation for a 20-cm layer of a  $6.3 \times 10^{-5} M$  *o*-hydroxybenzylidene-aniline solution as a function of wavelength, m $\mu$ .

The addition of small amounts of acid or base had a drastic effect on the rate of disappearance of A\* but affected the rate of disappearance of B\* to a much smaller extent. A somewhat detailed study of this effect was carried out for ethanol as the solvent (absolute ethanol with 0.04% water). Using an acetic acid buffer with a constant ratio of 1.402 between concentration of acetic acid and sodium acetate, it was observed that the rate of fading of A\* increased with increased buffer concentrations, whereas the decay of B\* showed no apparent dependence on buffer concentration over the same range. Figure 2 shows a plot of the rate constant for the fading of A\* as a function of acetic acid concentration for three different temperatures. It is seen that at these concentrations a linear relation between rate constant and buffer concentration satisfies the data. Choosing the acetic acid concentration as

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

<sup>2</sup> M. D. Cohen and G. M. J. Schmidt, J. Phys. Chem. **66**, 2442 (1962).

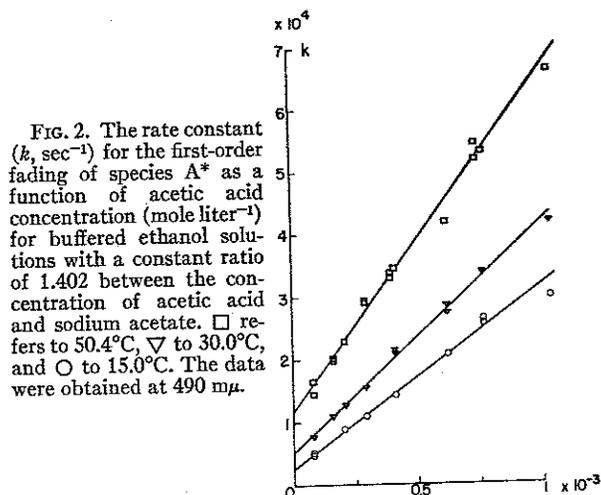


FIG. 2. The rate constant ( $k$ ,  $\text{sec}^{-1}$ ) for the first-order fading of species  $A^*$  as a function of acetic acid concentration ( $\text{mole liter}^{-1}$ ) for buffered ethanol solutions with a constant ratio of 1.402 between the concentration of acetic acid and sodium acetate.  $\square$  refers to  $50.4^\circ\text{C}$ ,  $\nabla$  to  $30.0^\circ\text{C}$ , and  $\circ$  to  $15.0^\circ\text{C}$ . The data were obtained at  $490 \text{ m}\mu$ .

reference it is thus possible to assign second-order rate constants,  $k_1$ , to a catalysis (1) by using the slopes of the straight lines in Fig. 2:



An Arrhenius plot for the rate constants thus obtained yields an activation energy of  $3_5 \text{ kcal/mole}$ , Fig. 3.

As mentioned above the life time of  $B^*$  did not show

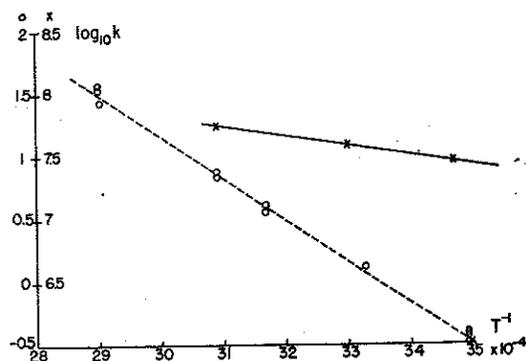
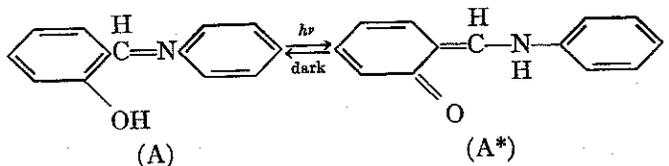


FIG. 3. Plots of the decadic logarithm of the rate constant as a function of the inverse absolute temperature ( $^\circ\text{K}^{-1}$ ).  $\circ$  refers to the disappearance of species  $B^*$  as recorded at  $385 \text{ m}\mu$ ,  $\times$  refers to the buffer catalyzed fading of species  $A^*$  with  $k_1$  values obtained from the slopes of the lines in Fig. 2.

any dependence on buffer concentration. Using the rate constants obtained from first-order plots at several buffer concentrations, an Arrhenius plot, Fig. 3, gives an activation energy of  $15_0 \text{ kcal/mole}$ .

It has been proposed<sup>1,2</sup> that the red photochromic species observed in low-temperature solutions or in the crystalline state is a quinoid isomer of the anil produced in a proton transfer from the hydroxyl group to the nitrogen atom



The spectrum observed for the red form in rigid glass and in the solid<sup>3</sup> is very similar to the spectrum of  $A^*$  observed in the present experiments and it is thus assumed that  $A^*$  is the quinoid isomer. The acid catalysis of the fading reaction suggests a rate determining step for the fading of  $A^*$  to be of the type proposed for *o*-nitro-toluene derivatives.<sup>4</sup>

It is believed that the stable yellow isomer represents the *trans* form around the  $\text{C}=\text{N}$  double bond: x-ray diffraction has shown that in the crystal the molecules are packed in the *trans* configuration<sup>2</sup> and in solution the *trans* form, which is essentially planar, is stabilized

by strong hydrogen bonding,<sup>5</sup> the *cis* form being strongly folded lacking this ability to form a stabilizing hydrogen bond. At  $-40^\circ\text{C}$  and below, Fischer and Frei<sup>6</sup> have observed reversible changes in the absorption spectrum upon irradiation of compounds containing a  $\text{C}=\text{N}$  double bond, which they attribute to *cis-trans* isomerization. The kinetics of the thermal reversion was measured in the temperature range  $-70^\circ$  to  $-40^\circ\text{C}$  and an activation energy of  $16\text{--}17 \text{ kcal/mole}$  was estimated for this first-order reaction. It is likely that light induced rotational isomerization with regard to the  $\text{C}=\text{N}$  bond should occur for *o*-hydroxybenzylidene-aniline. It is concluded that  $B^*$  is the *cis* isomer of  $A$  and that the decay of  $B^*$  involves the reformation of the stable *trans* species.

<sup>3</sup> M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, in *Hydrogen Bonding*, edited by D. Hadzi (Pergamon Press, Ltd., London, 1959), p. 293.

<sup>4</sup> G. Wettermark and R. Ricci, *J. Chem. Phys.* **39**, 1218 (1963).

<sup>5</sup> H. H. Freedman, *J. Am. Chem. Soc.* **83**, 2900 (1961).

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