Photochromic Anils. Mechanisms and Products of Photoreactions and Thermal Reactions[1]

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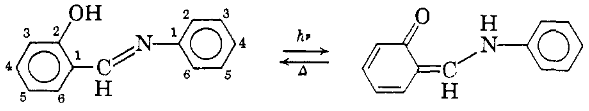
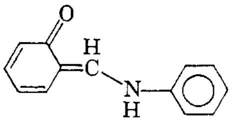
Abstract: In nonpolar, nonhydrogen-bonding solvents at 77°K most anils of salicylaldehyde exist in the enol form. However, the addition of a small quantity of an organic acid results in the conversion of some enol to *cis*-keto anil as the temperature of the solution is lowered to 77°K. The nitrosalicylidene anils show formation of the *cis*-keto species on cooling to 77°K without the addition of organic acid. The irradiation of most enol forms causes photocoloration which is the result of the formation of *trans-keto anil.* No photocoloration or eradication results from irradiation of the *cis*-keto anil. The nitrosalicylidene anils show no photocoloration even when irradiated throughout the entire region of absorption. This is most likely the result of the increased acidity and a resulting strongly intramolecularly bonded molecule. The *cis*-keto form is produced in the thermal back-reaction from the *trans*-keto form as *trans*-keto (Δ) → *cis*-keto (Δ) → enol. Emission from the enol is actually that of a species closely resembling the *cis*-keto form.

It has been found[3,4] that in rigid solution salicylideneaniline and its derivatives are photochromic and that this photochromism is confined to the anils of *o*-hydroxybenzaldehydes. It has been further noted[4] that all salicylideneanilines are photochromic in rigid solutions although we will show that several nitrosalicylaldehyde derivatives do not show this phenomenon.

It has been proposed[3,5] that action of light upon the anils causes a proton transfer to form a keto anil



Further, in the crystal[3] it has been suggested that a *trans*-keto anil may be photoproduced.



A *cis*-keto form was thought to be the form related to the thermochromic behavior of crystalline anils.[3] Despite continued study of anils of salicylaldehyde and hydroxynaphthaldehydes,[4] there has been almost no evidence concerning the definitive nature of the photocolored species, the mechanism of phototransformation, and the mechanism and nature of the species involved in the thermal back-reaction.

Very recent investigations[6–8] relative to salicylaldehyde anils, particularly that of Dudek and Dudek,[6] show that the yellow color resulting from the appearance of an absorption band in the 440-mμ region in hydrogen-bonding solvents is caused by the formation of a *cis*-keto species. Since at least for most anils the above absorption is absent (and thus, so is the *cis*-keto anil) in nonpolar, nonhydrogen-bonding solvents, it is possible to obtain the absorption, emission, and excitation spectra of the enol form. Further, in hydrogen-bonding solvents, similar spectra can be obtained for the *cis*-keto form. Finally these data can be compared with those obtained for the photoproduced species.

The purpose of this investigation is to elucidate (1) the nature of the species photochemically formed, (2) the mechanism of the photoreaction, and (3) the nature of the products and the mechanism of the thermal back-reaction for salicylaldehyde anils irradiated in rigid media at low temperature (77°K).

Experimental Section

The anils were prepared by stirring equimolar quantities of the salicylaldehyde and the aniline in methanol solution. Recrystallization involved a variety of solvents depending on the solubility properties of the particular anil; benzene and methanol were most frequently used. Purity was determined through the use of thin layer chromatography as well as melting point determinations.

The low-temperature absorption measurements were obtained on a Cary Model 15 spectrophotometer and involved a flat-windowed quartz dewar and flat-windowed quartz or Suprasil cells of 2- and 10-mm path lengths. Special care was taken to dry the 3-methylpentane to avoid the presence of any hydrogen-bonding contaminants and to prevent any turbidity in the glass. Irradiation was accomplished by a 1-kw xenon lamp with filters used to select the wavelength of irradiation. In most cases light in the range 220–400 mμ was used, except in those cases in which a narrow-band pass filter was required to irradiate into a particular band.

The emission apparatus consisted of a 1-kw xenon exciting lamp, a Bausch and Lomb grating exciting monochromator, an Aminco grating monochromator, and an EMI 9558B photomultiplier. In most cases the emission recorded was that from the front surface of the sample cell. The excitation spectra in the 400–500-mμ region were recorded utilizing a 150-w tungsten source with a built-in parabolic reflector which gives the equivalent of approximately 500 w. This was necessary in order to prevent spectral distortion caused by line emission from the usual excitation sources. The excitation curves have not been corrected for change in the intensity of the source or efficiency of the exciting monochromator as a function of wavelength. Thus, for example, in Figure 3 the excitation curve falls off more rapidly in the 400–450-mμ region than it should. Emission spectra have not been corrected for photomultiplier tube response as a function of wavelength.

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[2] Taken from a dissertation to be submitted in partial fulfillment of the requirements for the Ph.D. degree, NASA predoctoral trainee, 1966–1967.

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

[4] M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *J. Chem. Soc.*, 2051, 2060 (1964).

[5] Y. I. Koslov, D. N. Shigorin, R. N. Nurmuknametov, and V. A. Puchkov, *Russ. J. Phys. Chem.*, 37, 1315 (1963).

[6] G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, 88, 2407 (1966).

[7] J. W. Ledbetter, Jr., *J. Phys. Chem.*, 70, 2245 (1966).

[8] D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, 87, 1433 (1965).

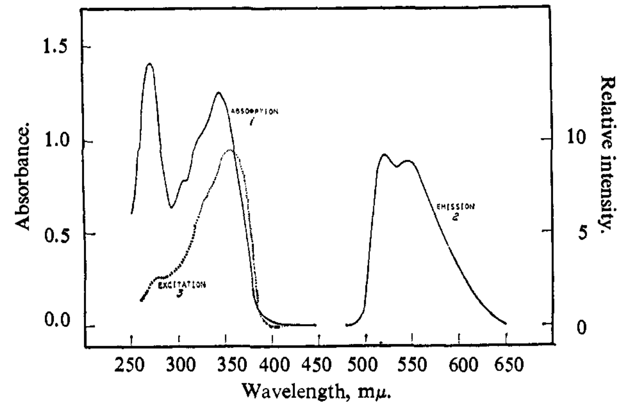

Figure 1. Absorption (1), emission (2), and excitation (3) spectra of the enol species of salicylidene-*o*-toluidene in 3-methylpentane at 77°K.

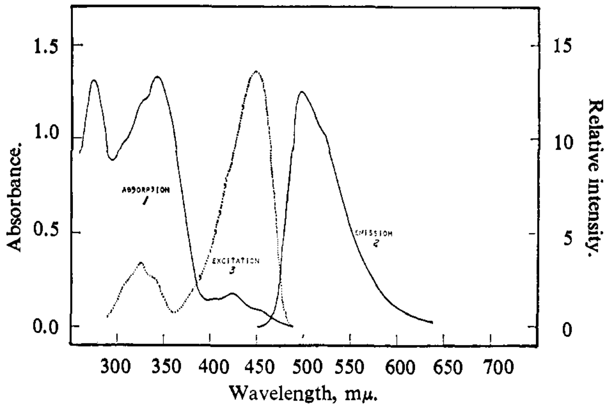

Figure 2. Absorption (1), emission (2), and excitation (3) spectra of the *cis*-keto species of salicylidene-*o*-toluidene formed at 77°K in 3-methylpentane plus 1 drop of propionic acid per 25 ml.

Results and Discussion

We shall discuss individual cases first and afterwards make comparisons and general conclusions.

Salicylidene-*o*-toluidene. In a nonhydrogen-bonding solvent such as 3-methylpentane, this anil exists almost exclusively in the enol form at 77°K. The absorption spectrum (see Figure 1) shows an onset near 400 mμ with intensity maxima near 345, 325, 307, and 273 mμ. The emission of the anil, although offset from the absorption onset (by about 90 mμ in this case), has been previously designated as fluorescence.[3,5] In addition, we observed that it would not pass through a phosphoroscope. The onset of emission is near 490 mμ with intensity maxima near 525 and 550 mμ (see Figure 1). We assign the large difference in energy between absorption and emission to be the result of intramolecular proton transfer in the enol excited state and emission from a species which resembles the *cis*-keto form. This species will be designated "enol." This is substantiated by the similarity in energy and band shape of the *cis*-keto emission (Figures 2 and 4) and the "enol" emission. This also provides further verification of the fact that the emission from the "enol" form is fluorescence. Finally, the excitation spectrum closely resembles the absorption spectrum except that the maximum occurs at slightly longer wavelength than that in absorption. The weakness of the 274-mμ band in the excitation spectrum is due to a diminution of lamp intensity between 350 and 275 mμ of about 60% and a decrease in the efficiency of the grating monochromator.

It was discovered that the addition of small amounts of organic acids to the 3-methylpentane solution resulted in the formation of new absorption bands (390–500 mμ) at 77°K quite similar to those observed in strongly hydrogen-bonding solvents at room temperature (Figure 2). Solvent studies by us, as well as investigations by others,[6–8] show that this band is the result of the formation of some *cis*-keto anil. In our solvent system, the band is structured with intensity maxima near 450, 424, and 400 mμ. Excitation into this band results in an emission with onset near 460 mμ and intensity maxima near 497 and 525 mμ (Figure 2). We assign this emission to be fluorescence on the basis of its overlap with the long-wavelength absorption band. The excitation spectrum obtained by monitoring this emission resembles the absorption of the low-temperature, *cis*-keto band in the 390–500-mμ region.

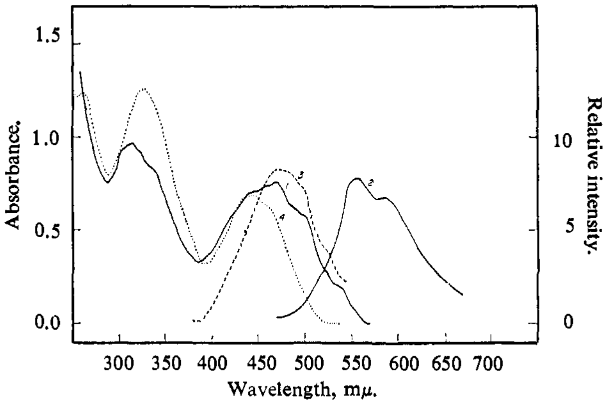

Figure 3. Absorption (1), emission (2), and excitation (3) of the *trans*-keto species of salicylidene-*o*-toluidene formed by irradiation in 3-methylpentane at 77°K. Absorption (4) of *cis*-keto species formed by warming and recooling a solution irradiated at 77°K.

Irradiation of the colorless 3-methylpentane solution at 77°K (rigid) causes it to acquire a dark orange color which is the result of the formation of a structured absorption band (~400–570 mμ) with a long-wavelength onset near 570 mμ and maximum intensity near 470 mμ (see Figure 3). In the ultraviolet portion of the absorption spectrum, the maximum intensity occurs near 316 mμ. In comparison to the absorption spectrum of the enol, the species present before irradiation, there is a large decrease in intensity around 350 mμ and a disappearance of the sharp peak at 273 mμ. We propose that this molecular species formed upon irradiation is the *trans*-keto anil. Further evidence supporting this idea follows.

The onset of emission of the *trans*-keto species occurs near 490 mμ with intensity maxima near 560, 588, and 630 mμ. The nature of the emission does not change with excitation wavelength throughout the entire region of absorption of approximately 400–570 mμ. Further, no emission of the *cis*-keto form is observed. It was observed that upon warming the irradiated solution to near the softening point of the 3-methylpentane glass, the color changed from orange to yellow. As the warming continued to room temperature, the solution gradually became colorless as it was before irradiation.

In order to investigate and identify the species responsible for the yellow color, the solution was allowed to

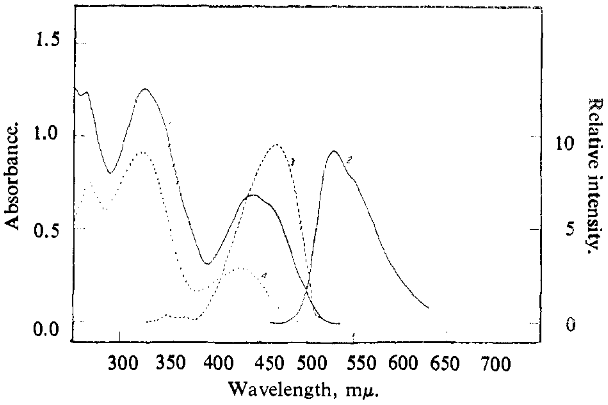

Figure 4. Absorption (1), emission (2), and excitation (3) of *cis*-keto species formed by warming and recooling (77°K) a previously irradiated 3-methylpentane solution of salicylidene-*o*-toluidene. Room-temperature absorption (4) of *cis*-keto species in 2,2,2 trifluoroethanol.

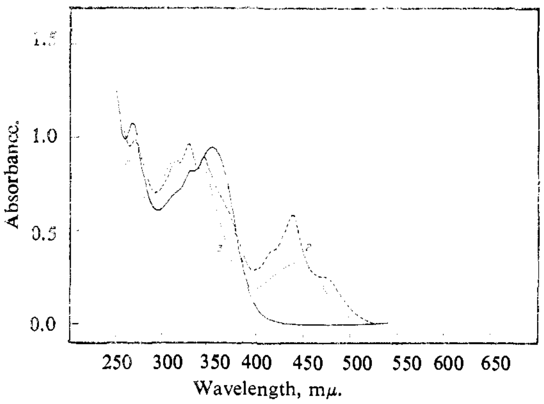

Figure 5. Absorption spectra of 5-bromosalicylidene-*o*-toluidene in 3-methylpentane plus acid at room temperature (1), at 77°K (2), and in 2,2,2-trifluoroethanol at room temperature (3).

warm to the softening point, then was rapidly recooled to 77°K. So long as this temperature was maintained no fading of the yellow color was observed. The absorption spectrum (see Figure 4) of this solution showed a long-wavelength onset near 520 mμ with intensity maxima in the visible near 442 and 460 mμ, and intensity maxima in the ultraviolet near 325 and 262 mμ. A comparison of this absorption with that of this anil in 2,2,2-trifluoroethanol, a solvent in which the anil would exist primarily as the *cis*-keto species, shows that the spectra are essentially identical except for the position of the long-wavelength maximum which is blue shifted in the strongly hydrogen-bonding trifluoroethanol.

The emission of this yellow solution has an onset near 475 mμ and intensity maxima near 528 and 550 mμ. A comparison with the emission of the *cis*-keto anil present in the 3-methylpentane solution containing small amounts of acids (see Figure 2) shows a great similarity in shape, although the intensity maxima are blue shifted in the latter solvent system as would be expected from its more polar nature. Similarly, the excitation spectra are of the same shape although again that of the 3-methylpentane plus acid solution is blue shifted. Finally, irradiation throughout the entire region of absorption gives only the emission noted above (no emission from the photoproduct).

Of equal importance to the close resemblance of the absorption, emission, and excitation spectra of the *cis*-keto anil and the species produced on warming is the great difference between the absorption and emission of this species and that produced by irradiation. Figure 3 shows a comparison of these absorption spectra.

Thus, it seems evident that no cis-keto anil is produced upon cooling a 3-methylpentane solution to 77°K and that only the trans-keto species is formed upon irradiation with light. This is validated by the emission obtained from the photocolored species. Excitation in the region in which the *cis*-keto anil absorbs produced the same and only the emission as excitation into that region where only the photocolored species (the *trans*-keto form) absorbs. Also, the absorption and excitation spectra provide further evidence for the assignment of the photoproduced species as the *trans*-keto form. However, the *cis*-keto species is formed as the irradiated solution is warmed. This is validated by the absorption, emission, and excitation spectra. Continued warming of the solution causes disappearance of the *cis*-keto form and formation of the original enol form. This is validated by absorption, emission, and excitation spectral results. The totality of the evidence thus provides strong evidence that the molecular species formed upon irradiation is the *trans*-keto anil, which in the reverse, thermal reaction isomerizes to the *cis*-keto anil which then undergoes proton transfer to produce the enol.

5-Bromosalicylidene-*o*-toluidene. The observations recorded for this anil almost duplicate those of salicylidene-*o*-toluidene. The principal differences result from the increase in acidity of the phenolic proton with the substitution of bromine on the salicylaldehyde ring. Thus, in comparison to salicylidene-*o*-toluidene, a great deal more of the enol is converted to the *cis*-keto form when the temperature is lowered to 77°K in a 3-methylpentane solution containing a small quantity of organic acid (see Figure 5).

As in the case of salicylidene-*o*-toluidene, the room-temperature absorption spectrum of this anil in the above solution is apparently due solely to the enol with no or little of the *cis*-keto species present. Upon lowering the temperature to 77°K, a new *cis*-keto absorption appears with maximum intensity near 439 mμ and shoulders near 420 and 475 mμ. The ultraviolet portion of the spectrum also undergoes some change in that there is a loss of intensity in the 345–355-mμ region as compared to the room-temperature enol absorption (see Figure 5). The spectral location and very strong resemblance of the low-temperature absorption spectrum to that of this anil in 2,2,2-trifluoroethanol at room temperature is assurance that the low-temperature species is indeed the *cis*-keto anil. This assignment is further substantiated by both emission and excitation spectra.

By means of a narrow-band pass filter we were able to irradiate exclusively into the long-wavelength *cis*-keto absorption band. It was found that 45 min of irradiation with a 1-kw xenon lamp resulted in no change in the characteristics of this band and no additional formation of a photocolored species (see Figure 6). *Thus, it is not possible to photochemically convert the cis-keto form into the trans-keto form.* It is also very probable that it is not possible to photochemically convert the *cis*-keto form into the enol form since there was no change in the intensity of absorption of the *cis*-keto band over the irradiation period.

Irradiation into the absorption bands at shorter wavelengths did cause photocoloration at 77°K. In a 3-methylpentane solution, the *trans*-keto absorption band resulting from this irradiation had a long-wavelength onset near 575 mμ and a maximum intensity near 473 mμ (see Figure 6). In the case of a 3-methylpentane–acid solution, the absorption band of the *trans*-keto species was superimposed upon the low-temperature *cis*-keto band.

As in the case of salicylidene-*o*-toluidene the photocolored solution changed from orange to yellow as the solution was warmed from 77°K. As before, comparison was made of (1) the absorption, emission, and excitation spectra of the *trans*-keto anil formed upon irradiation in a 3-methylpentane solution at 77°K, (2) the *cis*-keto anil formed in a 3-methylpentane–acid solution at 77°K, (3) the enol in 3-methylpentane at 77°K, and (4) the yellow species formed upon warming. These observations also verified the fact that the yellow species produced in the thermal back-reaction was the *cis*-keto anil.

Salicylideneaniline. The results obtained for salicylideneaniline, the unsubstituted parent anil, are quite consistent with those for the two preceding anils and further validate the conclusions drawn previously. Again the principal differences arise from the acidity of the phenolic proton, which in this case is less than that of either of the two preceding anils.

3-Nitrosalicylideneaniline, 5-Nitrosalicylideneaniline, and 5-Nitrosalicylidene-2,4-dimethylaniline. In these three compounds a nitro group is substituted on the salicylaldehyde ring. The nature and positions of this substitution make the phenolic proton much more acidic in the ground state, compared to the previously discussed anils. This increased acidity results in the formation of some *cis*-keto form at 77°K even in a 3-methylpentane solution containing no acid. By assuming the extinction coefficient for the *cis*-keto form of the 3-nitrosalicylideneaniline is the same as that for the parent,[6] the percentage conversion of the enol to the *cis*-keto form is calculated to be approximately 100%. However, the emission spectra indicate the presence not only of the *cis*-keto species but also of the "enol" species.

By recalling that irradiation into the *cis*-keto absorption band of the other anils resulted in no photocoloration, we expected that irradiation of the 3-nitrosalicylideneaniline solution at 77°K (into the *cis*-keto absorption band) would result in a similar lack of photocoloration. This was indeed the case. Furthermore, irradiation with a 1-kw xenon lamp over the entire region of absorption (2300–4800 A) for 30 min resulted in no change in the low-temperature absorption spectrum. If a similar procedure is followed for the other two nitro anils, the per cent conversion of enol to *cis*-keto is calculated to be approximately 25%. From this consideration, it might be expected that irradiation over the entire region would cause photocoloration since presumably some enol form would still be present. However, no photocoloration occurs when such irradiation is carried out. One reason for this apparent ambiguity could be that the calculated per cent conversion is incorrect because of the assumptions concerning the extinction coefficients.

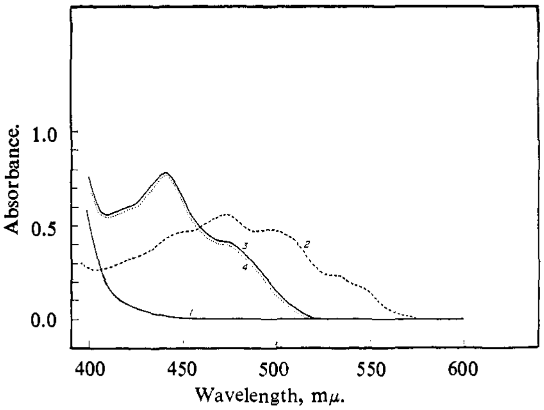

Figure 6. Absorption spectra of 5-bromosalicylidene-*o*-toluidene at room temperature (1) and of the *trans*-keto species at 77°K (2) obtained by irradiation of a 3-methylpentane solution at 77°K. Absorption spectra of *cis*-keto species at 77°K in 3-methylpentane plus acid solution (3) and the same after 45 min of irradiation into the absorption band from 405 to 530 mμ (4).

It would appear that in the nitro cases there are at least two possible explanations for the lack of photocoloration. The nitro group has increased the acidity of the phenolic group to such an extent that the anil exists completely or nearly completely in the *cis*-keto form. Secondly, the acidity has been increased to such an extent that the proton is nearly equidistant between the oxygen and nitrogen atoms and excitation essentially causes no significant difference in its location. A corollary to this would be the consideration that this situation results in a barrier too high to be crossed by light absorption, and thus no *trans*-keto form is produced.

We shall first consider a general summary of our results before considering that of other investigations. (1) In nonpolar, nonhydrogen-bonding solvents such as 3-methylpentane at 77°K, most anils of salicylaldehyde exist in the enol form. However, the addition of a small quantity of an organic acid results in the conversion of some enol to *cis*-keto anil as the temperature of the solution is lowered to 77°K. The nitrosalicylidene anils show formation of the *cis*-keto species on cooling to 77°K without the addition of organic acid. (2) Irradiation of most enol forms causes photocoloration which is the result of the formation of *trans-keto anil.* No photocoloration or erasure results from irradiation of the *cis*-keto anil; thus, it is *not* possible to have the reaction

$$\textit{cis}\text{-keto} \underset{\Delta}{\overset{h\nu}{\longrightarrow}} \textit{trans}\text{-keto or } \textit{cis}\text{-keto} \underset{\Delta}{\overset{h\nu}{\longrightarrow}} \text{enol}$$

For these reasons we postulate that the *trans*-keto form is photolytically produced from the enol by means of a concerted reaction which involves an intramolecular proton transfer with extensive electron redistribution accompanied by rotation about the ring carbon–imine carbon bond finally resulting in the *trans*-keto anil. (3) The nitrosalicylidene anils show no photocoloration even when irradiated throughout the entire region of absorption. This is most likely the result of increased acidity and a resulting strongly intramolecularly bonded molecule. (4) The *cis*-keto form is produced in the thermal back-reaction from the *trans*-keto form as

$$trans\text{-keto} \xrightarrow{\Delta} cis\text{-keto} \xrightarrow{\Delta} \text{enol}$$

(5) The emission spectrum of the enol is actually that of a species closely resembling the *cis*-keto form which is designated "enol."

Several investigators[3–5,8] have postulated the formation of a quinoid (keto) isomer by irradiation of various anils in both solution and crystal. However, in solution the geometric isomer involved was not defined,[8] possibly incorrectly defined,[5] or not definitively considered.[3,4] In the crystal, both a *cis*- and *trans*-keto form were postulated and were associated separately with thermochromic or photochromic behavior.[3,9] In the case of the Russian work,[5] the emission spectra indicate the possibility of the presence of the *trans*-keto form; however, some of the bands existing for the colored species are residual from those of the uncolored species, making interpretation difficult. Emission from the *cis*-keto form is considerably more intense than that from the *trans*-keto form. If any hydrogen-bonding solvents were initially present, the *cis*-keto emission would be present before and after irradiation of the anil. In any event, the colored species was indicated to be the *cis*-keto rather than the *trans*-keto form.

The most extensive investigations have been those of Cohen, *et al.*[3,4,9] In a general sense, the results of this investigation and those of Cohen, *et al.*, are compatible. The one notable exception is that nitrosalicylidene anils are not photochromic, which is contradictory to the generality they give. With the knowledge of the present investigation, it is possible to interpret some of their results. The weak absorption they note in the 424–500-mμ region for some anils in a strongly hydrogen-bonding solvent or at low temperature can now be associated with the formation of the *cis*-keto form. Further, the broader absorption in the 425–580-mμ region resulting from irradiation of the anils can be assigned as arising from the photochemically produced *trans*-keto form. Also, the fact that only partial photoerasure occurs in some cases[4] can be explained on the basis of the presence of both *cis*- and *trans*-keto forms and the inability to photoconvert the *cis*-keto form to the enol form.

Further investigation of the hydroxynaphthaldehyde and -salicylaldehyde anils is in progress.

(9) M. D. Cohen, G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 2041 (1964).

Photosensitized Chain Reactions in Alkaline Solutions of Nitrous Oxide in 2-Propanol

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Abstract: Solutions of di-*t*-butyl peroxide (DTBP) in 2-propanol have been photolyzed under anaerobic conditions with a high-pressure mercury lamp. In the absence of any other solute, DTBP was consumed and acetone formed at identical rates. The addition of potassium hydroxide considerably increased both rates, and a base-catalyzed chain reaction is indicated. Large yields of nitrogen, methane, acetone, and potassium acetate were produced in the photolysis of alkaline solutions containing both DTBP and nitrous oxide. The magnitude of the product yields suggests a chain reaction involving nitrous oxide. The reaction was retarded and inhibited by small concentrations of nitrobenzene, benzophenone, and carbon tetrachloride, but relatively unaffected by benzene and acetone. In all experiments the ratio of yields of nitrogen:methane remained constant (14 ± 2). The dependence of the yields on the concentrations of potassium hydroxide and nitrous oxide closely resembled that found in the γ radiolysis of alkaline solutions of nitrous oxide in 2-propanol in the absence of DTBP. It is concluded that DTBP acts both as a photosensitizer and a chain terminator in the light-induced reaction, and apart from the modes of initiation and termination the reaction mechanisms are identical. Nitrogen was also formed in the photolysis of alkaline solutions containing benzophenone and nitrous oxide, but in yields which were lower than observed in the DTBP-sensitized reaction. Methane was produced in addition to nitrogen only in the presence of low initial concentrations of benzophenone.

It has been shown that the cobalt-60 radiolytic decomposition of nitrous oxide in alkaline 2-propanol solutions involves a chain reaction.[2] In a more detailed study[3] it is suggested that the propagation steps for the formation of nitrogen involve the transfer of an electron from the ketyl radical anion I to nitrous oxide.

$$\underset{\text{I}}{(CH_3)_2\dot{C}O^-} + N_2O \longrightarrow (CH_3)_2CO + N_2O^- \qquad (1)$$

$$N_2O^- \longrightarrow N_2 + O^- \qquad (2)$$

$$O^- (\text{or } N_2O^-) + (CH_3)_2CHOH \longrightarrow OH^- (\text{or } N_2 + OH^-) + \underset{\text{II}}{(CH_3)_2\dot{C}OH} \qquad (3)$$

$$\text{II} + (CH_3)_2CHO^- \longrightarrow \text{I} + (CH_3)_2CHOH \qquad (4)$$

If the above mechanism is in fact correct, it should be possible to initiate the same chain reaction in the ab-

(1) The Radiation Laboratory, University of Notre Dame, Notre Dame, Ind.

(2) W. V. Sherman, *Chem. Commun.*, 250 (1966).

(3) W. V. Sherman, *J. Phys. Chem.*, in press.