decomposition has been measured, the utility of comparison with gamma radiation is restricted by lack of information of the higher excited states. It has been generally assumed that higher states in aromatic molecules undergo very rapid (10^{-13} sec.), efficient internal conversion.[56,57] Since the yield of the lowest excited singlet state of benzene has been established by scintillation measurement as only $G(^1B_{2u}) \lesssim 0.5$, we must then conclude that the yield of higher singlet states *in toto* is even smaller. If internal conversion is as efficient as claimed, then the rule-of-thumb that high energy radiation produces roughly equal primary yields of excited states and of ion pairs must be incorrect. There is, however, some recent evidence that radiationless transitions can intervene,[58] and one must therefore consider dissociative and energy transfer processes from high energy states which may compete with internal conversion. "This important process (of internal conversion) deserves more careful study from the theoretical and experimental point of view, instead of being taken for granted as is commonly done."[59]

In summary it may be said that, at this time, the significant primary indirect effects in gamma irradiated organic solutions are consistently interpretable in terms of ionic processes.

Acknowledgment.—The authors are indebted to Professor John L. Magee for many helpful discussions.

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(56) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

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[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, QUARTERMASTER RESEARCH AND ENGINEERING CENTER, U. S. ARMY, NATICK, MASSACHUSETTS]

A Flash Photolysis Study of 2-(2',4'-Dinitrobenzyl)-pyridine in Water

BY GUNNAR WETTERMARK[1]

RECEIVED FEBRUARY 17, 1962

The phototropism of 2-(2',4'-dinitrobenzyl)-pyridine in liquid water solution at 24 ± 0.5° has been studied by the flash photolysis method. The solution turns blue when exposed to light and is restored to the initial colorless form in the dark reaction. The fading reaction followed the kinetics of a first order reaction with a 10^5 fold variation in the rate constant over the pH range 2 to 12. The great change in reaction rate has been interpreted to be due to the existence of two dissociation stages of the compound in this pH range. At high pH values where the colored compound is largely in the form of a negative ion, the rate of the fading reaction is constant with a rate constant of 0.1 sec.^{-1}. At lower pH values where the equilibrium is shifted to a higher population in a zwitterion form the rate of the fading reaction is increased and shows the characteristics of a general acid catalyzed process.

Introduction

2-(2',4'-Dinitrobenzyl)-pyridine is known to show phototropism both in the crystalline state and in solution.[2] The pure compound is colorless when kept in the dark but turns blue when exposed to light. Hardwick, *et al.*, studied the fading reaction and found that the compound was restored to its original colorless form. By using a cryostat together with a Cary spectrophotometer, they were able to make measurements on the fading reaction in dilute liquid solutions with isopropyl alcohol as the solvent at −10° to −60°. Compounds with a structure similar to 2-(2',4'-dinitrobenzyl)-pyridine have been reported not to be phototropic and it has thus been thought that the behavior of the compound was specific.[2b] Exploratory work in this Laboratory has shown, however, that many derivatives of *o*-nitrotoluene also are phototropic.

Flash photolysis has provided an excellent tool for detecting and studying the above effects since the colored form produced by exposure to light is in many cases so short-lived as not to be detected by low intensity techniques. As part of an investigation of these reactions in depth, we have investigated the kinetics of the fading reaction of 2-(2',4'-dinitrobenzyl)-pyridine in considerable detail. Information has been obtained about the mechanism of the process in water under different conditions of pH where the compound is found to be largely in ionic or molecular form.

Experimental

Flash Apparatus.—A detailed description of the flash light source is to be published in the near future[3]; hence only some specific data are given here. The electrical energy discharged to produce the flash in four straight quartz tubes was 2400 joules at about 28 kilovolts. The flash duration was 5 μsec. ($1/e$ time). The lamp tubes were arranged symmetrically around a cylindrical quartz reaction vessel provided with optically flat end windows 20 cm. apart. A 0.5 cm. layer of aqueous filter liquid, containing 200 g. of $CuSO_4 \cdot 5H_2O$ per liter, surrounded the solution under investigation. The filter absorbed all light of wave lengths shorter than approximately 3100 Å. A fresh reaction solution was prepared for each experiment and flashed only once. All measurements were made at 24 ± 0.5°. A single beam absorption spectrophotometer recorded the light absorption changes in the system. The spectrophotometer consisted in part of a Bausch and Lomb grating monochromator and an E.M.I. 9552B photomultiplier tube. The signal from the tube was fed through a cathode follower to a Tektronix 535A oscilloscope. The light source for the spectrophotometer was a xenon arc; its light of wave lengths shorter than approximately 5200 Å. was cut off with Corning color filter 3486 in order to prevent the sample from being excited by the light of shorter wave length from this arc. The filter also served as a cut off for the secondary pass band of the grating.

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(1) National Academy of Sciences-National Research Council Visiting Scientists Research Associate and Guest of the Massachusetts Institute of Technology associated with Prof. L. J. Heidt of the Department of Chemistry.

(2) (a) A. E. Tschitschibabin, B. M. Kuindshi and S. W. Benewolenskaja, *Ber.*, **58**, 1580 (1925); (b) R. Hardwick, H. S. Mosher and P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960).

(3) L. Lindqvist, Institute of Physical Chemistry, Uppsala, Sweden.

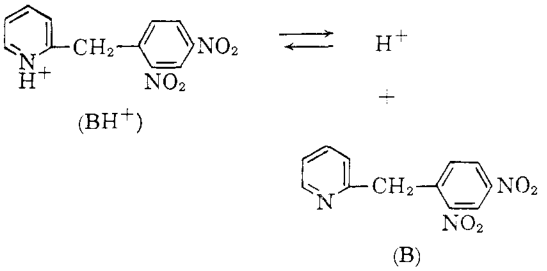
Solutions.—2-(2',4'-Dinitrobenzyl)-pyridine was prepared by others[4] of this Laboratory and was recrystallized seven times from absolute alcohol. An alcohol solution of the compound was finally passed in darkness through a 70 cm. long column of aluminum oxide and a sample of the compound obtained from a narrow middle fraction of the solution was used in these experiments. The same sample was also used in a low temperature study of the fading reaction.[4] The compound was brought into solution by dissolving it in absolute alcohol and then diluting the solution with distilled water. The final alcohol concentration was in all cases 1% (by weight). Air was not excluded since no change was found to occur in the kinetics of the reactions when carried out in an inert atmosphere of nitrogen.

Reagents used for the preparation of the buffer solutions were all standard A.R. chemicals. The pH values of the solutions were measured with a Beckman Zeromatic pH meter.

Results and Discussion

Proton Acceptor Property of the Uncolored Form.—The absorption spectrum of 2-(2',4'-dinitrobenzyl)-pyridine in water is similar to that observed in alcohol.[4] Absorption measurements at different acidities show that the unirradiated colorless compound exists in two different forms in water solution in the pH range 2–10. At low pH the absorption spectrum has a peak at 2650 Å. which is shifted to 2540 Å. at high pH. This shift is accompanied by a decreased over-all absorption. An equilibrium between the ionized form (BH^+) and the molecular form (B) of the pyridine ring would be expected to show this behavior.

Aqueous Colorless System



(1)

In order to evaluate the dissociation constant K_1 for BH^+ the absorption spectrum was measured as a function of pH using a total buffer concentration of 0.01 *M*. The extinction of the ionized form (ϵ_{BH^+}) and that of the molecular form (ϵ_B) were taken to be equal to ϵ at pH 2 and pH 9 respectively. Figure 1 shows a plot of log $[(\epsilon - \epsilon_{BH^+})/(\epsilon_B - \epsilon)]$ as a function of pH at the wave length 2600Å. (ϵ being the extinction of the system). The intersection with the pH axis gives $pK_1 = 4.1$.

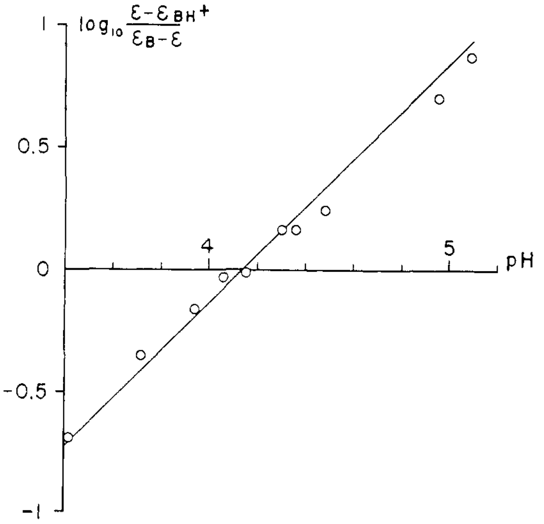
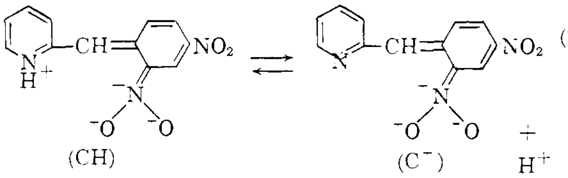


Fig. 1.—Determination of the p*K* value of the uncolored form of 2-(2',4'-dinitrobenzyl)-pyridine from extinction measurements at 2600 Å. The line is drawn with a slope of unity; its intercept with the pH axis gives a p*K* value of 4.1 for the equilibrium $BH^+ \rightleftharpoons H^+ + B$.

Properties of the Colored Form.—Possible mechanisms for the color change following exposure to light have been discussed by Hardwick, *et al.*[2b] Recent data from measurements on 2-(2',4'-dinitrobenzyl)-pyridine in the adsorbed state[5] support their mechanism of an intramolecular movement of a hydrogen atom from the $-CH_2-$ group to the *o*-nitro group. Furthermore, this mechanism is strongly supported by the fact that phototropism has been established in this Laboratory for 2,4-dinitrotoluene and similar compounds. A compound with a hydrogen atom attached to one of the oxygen atoms of the $=NO_2$ group is, however, likely to be a very strong acid and would probably be entirely dissociated in a water solution over the pH range 2–12. On the other hand it can be expected that the nitrogen of the pyridine ring will show proton acceptor properties in the colored state as well as in the colorless state. We should thus have in the colored state an equilibrium between a zwitterion and a negative ion.

Aqueous Colored System



(2)

It can be expected that the basicity of the pyridine ring is not the same in the colored and the colorless form, that is, the dissociation constant of CH is different from the dissociation constant of BH^+. By setting the monochromator at different wave lengths, it was established that the spectrum of the colored form is changed with pH in a way that is characteristic for a molecule in a dissociation equilibrium with a p*K* of 4 to 6. Due to the small difference in extinction of the colored solution below and above pH 4 and 6, respectively, it was not experimentally feasible to determine the dissociation constant accurately. It is likely that the value p*K* = 4 to 6, is the p*K* value of reaction 2, compared to $pK_1 = 4.1$ for reaction 1.

Kinetics of the Fading Reaction.—Using a total buffer concentration of 1, 0.1 and 0.01 *M* the fading reaction was followed at various pH values. It was found that the rate varied by a factor of 10^5 over the pH range 2 to 12. In each solution at

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[4] J. Sousa and J. Weinstein, to be published.

[5] G. Kortum, M. Kortum-Seiler and S. D. Bailey, Paper to be presented at the Symposium on Reversible Photochemical Processes, April 1962, University of North Carolina, Durham, N. C.

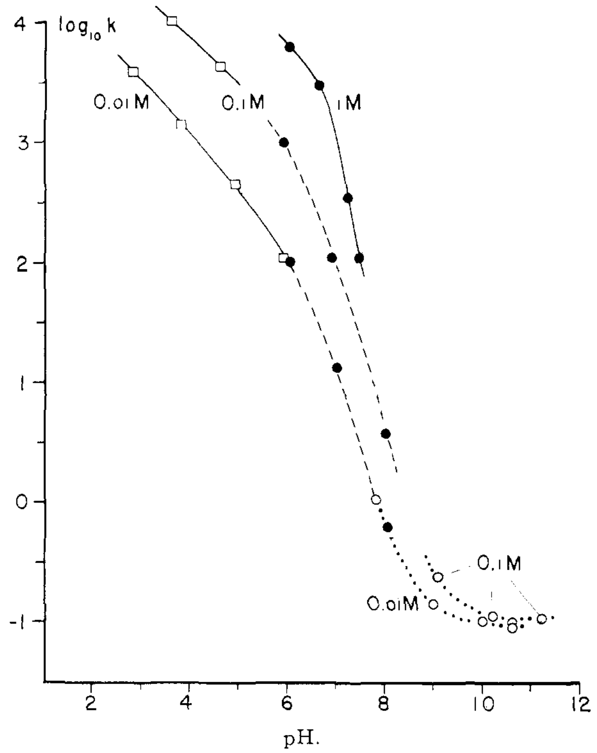

Fig. 2.—Evidence that the rate constant *k* of the fading reaction depends upon the pH and buffer concentration but is virtually independent of the nature of the buffer. The total concentration of buffer is indicated in the figure. The buffers were, ○ boric acid + sodium hydroxide, ● monosodium phosphate + disodium phosphate, □ citric acid + sodium citrate. The concentration of 2-(2′,4′-dinitrobenzyl)-pyridine was 10^{-4} *M*.

constant pH the reaction followed the kinetics of a first order reaction.

Figure 2 shows a plot of the logarithm of the rate constant for the first order bleaching as a function of pH. All points in the figure were obtained by following the reaction at 5600 Å. Other wave lengths of the absorption spectrum of the colored form also were employed and gave rate constants identical with those obtained at 5600 Å.

At high pH values the rate constant reached a limiting value independent of pH. At these pH values the colored and colorless forms C^- and B, respectively, are favored. The over-all fading reaction at high pH values can thus be described as

$$C^- + H^+ \xrightarrow{k_3} B \qquad (3)$$

The fact that at high pH values the rate constant reaches a limiting value independent of pH suggests that the primary step in reaction 3 is not the addition of a proton to C^- but a unimolecular decay of C^- to a negatively charged species having the structure of B but less a proton which is subsequently added. It should be noted that this limiting value of the rate constant, $k_3 = 0.1$ sec.$^{-1}$, is of the same magnitude as the author obtained in absolute alcohol, namely, 0.12 sec.$^{-1}$ at 22.6°.

Increasing the acidity of the solution was found to strongly increase the rate of the fading. This can be interpreted to mean that the colored state

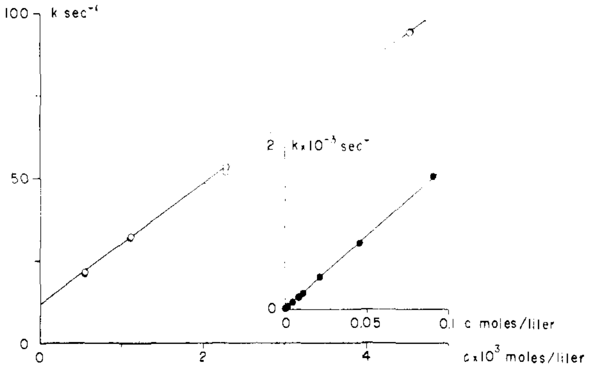

Fig. 3.—Plot of the rate constant for the fading reaction as a function of the total concentration of acetic acid plus sodium acetate in a molar ratio of 1.19:1. The concentration of 2-(2′,4′-dinitrobenzyl)-pyridine was 10^{-4} *M*. The slope of the line is 1.8×10^4 l. mole^{-1} sec.$^{-1}$; the intercept equals 12 sec.$^{-1}$.

decays much faster when it is in the form of the zwitterion, CH, reaction 4, than in the form of the negative ion, C^-, reaction 3. Thus a drastic change

$$CH \longrightarrow B \qquad (4)$$

in reaction rate was found to be brought about by small changes in pH values close to pK_2, 4 to 6, (the p*K* value of reaction 2), where the population in the colored state is shifted from C^- to CH.

The Fading as a General Acid Catalyzed Reaction.—The ionization reaction 2 may become important in the interpretation of the kinetics as it might determine the rate of the reaction. The rates of the ionization reactions depend upon the possibility of the proton exchange with the solvent and may be facilitated by the presence of a buffer. Lindqvist presented a discussion of the time needed to establish equilibrium in such systems[6] and found that a buffer concentration of 0.01 *M* was needed to obtain equilibrium within 10^{-5} sec., which corresponds to the time resolution of the present experiments. From Fig. 2, however, it is seen that the rate of the fading reaction is strongly dependent on the buffer concentration at molarities exceeding 0.01. As the fading reaction is catalyzed by the hydronium-ions and the buffer, it appears that the reaction can be classified as a general acid catalyzed reaction.[7,8] It should be noted that the curves for the three different buffer systems, at the same total buffer concentrations, overlap. This means that the catalytic effectivities of the buffer acids are such as to give virtually the same catalyzing effect for the same total buffer concentrations at the pH values where the curves overlap.

The rate constants are seen to increase with increasing concentrations of buffer at a constant pH, compare Fig. 2. Using acetate buffer with a fixed ratio between the concentration of acetic acid and sodium acetate (pH 4.3–4.6), the rate constant was plotted as a function of the total buffer

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[6] L. Lindqvist, *Arkiv Kemi*, **16**, 79 (1960).

[7] J. N. Brønsted and K. Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[8] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

concentration, Fig. 3. It is seen that over a wide concentration range the points fall on a straight line. The intercept at zero concentration gives the portion of the reaction which is catalyzed by the hydronium ions and the water (the uncatalyzed reaction).

A mechanism where the association reaction in equilibrium 2 becomes rate determining at lower pH values, agrees with the observed data of general acid catalysis. The fact that such a proton-transfer reaction is expected to occur in a much shorter time suggests that at lower pH values the rate of the fading reaction is determined by reaction 4 and that this latter reaction is being catalyzed by the buffer.

Acknowledgments.—The author wishes to express his sincere thanks to Dr. S. D. Bailey, Chief of this Laboratory, who helped make this work possible and to John Sousa and Dr. J. Weinstein who helped out on some of the experimental work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Addition of CF_3 Radicals to Aromatic Hydrocarbons. The Relative Selectivity of CF_3

BY A. P. STEFANI AND M. SZWARC

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The relative rate constants (k_2) of CF_3 addition to a series of unsubstituted aromatic hydrocarbons were determined. It was shown that a linear relation exists between log (k_2/n) and the atom localization energy of the most reactive center of the hydrocarbon, n being the number of such centers. This indicates the formation of an incipient C-CF_3 bond in the transition state, *i.e.*, in spite of the strongly electrophilic character of CF_3 such a transition state resembles a σ-complex and not a π-complex. The linear plot of $\log(k_2)_{CF_3}$ *versus* $\log(k_2)_{CH_3}$ has a slope 0.8 for the series of investigated hydrocarbons, *i.e.*, benzene, naphthalene, anthracene, etc. This slope is taken as a measure of the intrinsic selectivity of CF_3 radical; its value, lower than unity, shows that the intrinsic reactivity of CF_3 is larger than that of CH_3. The results obtained in this series of unsubstituted aromatic hydrocarbons are compared with those obtained in the series ethylene, propylene and isobutene. The latter reflect the high electrophilic nature of the CF_3 radical and must not be used in determining its intrinsic selectivity. The problem of π- and σ-complexes formed in the addition of a radical to a suitable substrate is discussed. It is suggested that a π-complex is a charge-transfer complex, and its formation does not require activation energy. The formation of σ-complex does require activation energy, this species being the classical adduct radical in which a new σ-bond is formed. Conditions favoring the stability of π-complexes are considered. The significance of such complexes is discussed with reference to the process of formation of σ-complexes.

A method allowing one to determine the relative rate constant of CF_3 radical addition to a series of suitable substrates was described in a preceding paper.[1] The radicals were generated by photolysis of hexafluoroazomethane in iso-octane, their reaction with solvent yielding CF_3H

$$CF_3 + \text{iso-octane} \longrightarrow CF_3H + \text{iso-octyl radical} \quad (1)$$

The addition of a suitable substrate to the solution leads to the reaction

$$CF_3 + \text{substrate} \longrightarrow CF_3.\text{substrate} \quad (2)$$

which competes with (1) for CF_3 radicals. The experimental conditions were such that *all* the CF_3 radicals which escaped "cage" recombination underwent reaction 1 or 2, and none interacted with the radicals formed in the system. Analysis of the products allows calculation of the ratio of the rate constants k_2/k_1, and since k_1 remains constant the data provide information about the relative reactivities of the substrates toward CF_3 radical addition. The results obtained for a series of non-substituted aromatic hydrocarbons are reported in this paper.

Experimental

The experimental technique developed for these studies was described fully in the preceding paper[1] to which the reader is referred for details. A high-pressure mercury lamp (General Electric, AH-6) was used for the irradiation, and since Pyrex glass was employed in the experiments, all light corresponding to $\lambda < 3600$ Å was cut off. The CF_3H/N_2 and C_2F_6/N_2 ratios were determined by gas-chromatography. All the experiments described in this paper were carried out at 65°, and at a constant temperature the C_2F_6/N_2 ratio remained constant. It was demonstrated[1] that "cage" recombination is responsible for the C_2F_6 formation.

The ratio of the rate constants k_2/k_1 was calculated from the equation

$$k_2/k_1 = (X_{HS}/X_A)\cdot\{(CF_3H)/N_{2\text{blank}} - (CF_3H)/N_2\}/\{(CF_3H)/N_2\}$$

where X_{HS} and X_A denote the mole fractions of the solvent and the substrate, $(CF_3H)/N_2$—the ratio of the respective products obtained in an experiment, and $(CF_3H)/N_{2\text{blank}}$ the corresponding ratio observed in the pure solvent, *i.e.*, in the absence of a substrate. The derivation of this equation and its experimental verification is given in reference 1.

The following unsubstituted aromatic hydrocarbons were investigated in the course of this study: benzene, biphenyl, naphthalene, phenanthrene, pyrene and anthracene. Analytically pure benzene was used, and the remaining hydrocarbons were of reagent grade. Each of these compounds was recrystallized several times from a suitable solvent and eventually sublimed in high vacuum. Phenanthrene was first freed from traces of anthracene, by heating its solution with maleic anhydride.[2] The purified compound was then thrice crystallized and vacuum sublimed. The "blue fluorescence" grade anthracene was three times crystallized and then vacuum sublimed.

Spectroscopically pure grade iso-octane was further purified by passing it through a silica-gel column to remove moisture and traces of olefins.

To avoid any photosensitization arising from the light absorption by an aromatic hydrocarbon,[3] a filter consisting of concentrated solution of the investigated hydrocarbon in iso-octane or toluene was introduced between the lamp and the irradiated samples. The calculation indicated that under such conditions more than 99.99% of the light absorbed by the investigated hydrocarbon was removed by the filter.

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[1] A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

[2] M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955).

[3] See *e.g.*, C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955).