

REACTIONS OF PHOTOCHEMICALLY FORMED TRANSIENTS FROM 2-NITROTOLUENE

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Abstract—Kinetic data are reported for the thermal decay of colored transients formed by u.v. irradiation of aqueous solutions of 2-nitrotoluene. The transients display an acid-base equilibrium with a pK value of 3.7. The decay is catalyzed by acids and the following rate constants in liter sec⁻¹ mole⁻¹ were evaluated for the base form of the transient reacting with an acid at 30.0°C: 3.5×10^{-9} (H₂O), 2.6×10^8 (CH₃COOH), 4.7×10^4 (+NH₃CH₂COOH) and 4.2×10^6 (H⁺).

INTRODUCTION

PHENYL methanes having an *ortho*-nitro group produce, when they are exposed to ultraviolet light, short-lived species which absorb visible and near u.v. light.^(7,11-13) In particular an unexposed ethanol solution of the parent compound 2-nitrotoluene is slightly yellow and has an absorption peak at 257 mμ with continually decreasing absorption at longer wavelengths but on exposure to u.v. light there is produced an absorption band with a maximum near 380 mμ, which fades in the dark, following the kinetics of a first order reaction with a half-life in the millisecond region.⁽¹²⁾

A detailed study is presented here of the behavior of the parent compound 2-nitrotoluene in aqueous solutions of varying acidity.

EXPERIMENTAL

Flash photolysis

The conditions of the flash photolysis experiments have been described previously.^(6,14) The transient changes in light absorption were followed in the visible and in the near u.v. where they were not obscured by absorption due to the parent compound.

All solutions, unless otherwise stated, were prepared by dissolving the compound in ethanol and diluting with water solution of acid, base or buffer to give a final alcohol concentration of 1 per cent and a concentration of compound $\approx 10^{-4}$ M. Sodium perchlorate was sometimes employed to obtain constant ionic strength. pH measurements were made with a Beckman Zeromatic pH meter.

Deaeration was carried out by repeated freezing, melting and degassing until further treatment of this kind did not change the kinetics of the reaction. The data refer to such deaerated solutions unless otherwise specified.

All measurements were carried out at $30.0 \pm 0.2^\circ\text{C}$.

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A 0.5 cm layer of a copper sulfate filter was used to limit the wavelength range of the light flash reaching the reaction mixture. This solution consisted of 200 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter of water solution.

Materials

2-Nitrotoluene, Matheson Coleman and Bell, was purified through sublimation. 2,4-Dinitrotoluene, K and K Laboratories, was recrystallized from ethanol, M. P. 71°C. The fact that the measured characteristics of any test solution upon flashing were not affected by further purification indicated sufficient purity of samples.

Kinetic calculations

Rate constants, k_{exptl} , were obtained from plots of $-\log \log (I_\infty/I)$ as a function of time, the slope of the line being determined by the method of least squares. I denotes the intensity of the light transmitted through the solution at any time during the course of fading and I_∞ , the intensity transmitted after completion of the reaction. When error limits are given for a rate constant, the rate constant represents the arithmetic mean of at least four independent measurements and the limits, the maximum deviation of any value from the mean value.

RESULTS

Spectral characteristics

The absorption spectrum of an unirradiated solution of 2-nitrotoluene or 2,4-dinitrotoluene was found to remain essentially the same over the pH region 0–13. There is an absorption band which peaks in the u.v. and a weak absorption which extends into the visible.

The photoinduced short-lived species have strong absorption bands in the visible and near u.v. and exhibit different spectra in acid and in base.^{(13),(14)} In the case of 2-nitrotoluene in 1 *M* hydrochloric acid, the spectrum is essentially the same as in alcohol with maximum absorption near 370 $\text{m}\mu$. In 0.1 *M* sodium hydroxide, however, there is an entirely different spectrum having maximum absorption near 410 $\text{m}\mu$.⁽¹³⁾ The transient from 2,4-dinitrotoluene in strong acid displays minimum absorption at 400 $\text{m}\mu$ and peak absorption at 420 $\text{m}\mu$ but in strong base the minimum is at 450 $\text{m}\mu$ and the peak at 530 $\text{m}\mu$.⁽¹⁴⁾

By varying pH over the region 0–13, it was observed that the photoinduced transient produced from 2-nitrotoluene has the same spectrum between pH 4 and 13. The change discernable at lower pH is completed at about pH 3 where the spectrum is identical with that observed in strong acid. No change in the characteristics of the spectrum was noticeable for any solution during the course of fading. The same behavior is exhibited by the phototransients of 2,4-dinitrotoluene except that the transition from the acid spectrum to the base spectrum occurs at a pH near unity.⁽¹⁴⁾ The spectrum of the colored species at any pH was found to be unaffected by the presence of oxygen or the concentration of buffer. Similarly, the initial amount of the transient species produced by the light did not depend upon these two factors.

In addition to the transient absorption there is observed a residual, permanent increase in optical density and the solution turns yellow and then brown after repeated flashing or prolonged exposure to u.v. light. The irreversible photoproducts displayed increasing absorption towards shorter wavelengths over the range 380–600 $\text{m}\mu$, but the extent of coloration depended strongly on such factors as pH, buffer concentration and presence of oxygen.

Photolysis in strong base

The photo transients from both 2-nitrotoluene and 2,4-dinitrotoluene in 0.001 to 0.1 *M* sodium hydroxide decayed following first order fading with the rate constants independent of pH. In 0.001 *M* sodium hydroxide, which was also 1 *M* in sodium perchlorate, the rate constants for 2-nitrotoluene and 2,4-dinitrotoluene were $1.9 \pm 0.1 \text{ sec}^{-1}$ and 1.0 sec^{-1} respectively.

A small 'spike', initial fast fading, is noticed over the initial millisecond of the fading curves of the flash produced colored species. This 'spike' amounts to an optical density change of about 5 per cent of the total change.

Air-saturated solutions displayed the same kinetics for the fading as the deaerated system. The presence of dissolved oxygen, however, produced as noted above a major change in the irreversible photoproducts. The permanent increase in optical density after exposure to a flash never exceeded 10 per cent of the initial change at any wavelength between 380 and 600 $\text{m}\mu$. In all solutions there was a drop in initial response upon repeated flashing. For example, flashing of $2.4 \times 10^{-4} \text{ M}$ 2,4-dinitrotoluene in 0.1 *M* sodium hydroxide produced an initial change in optical density at 550 $\text{m}\mu$ of 0.158 and after the 27th flash, a change of only 0.097.

Photolysis in perchloric acid

At very low pH, where the acid form of the transient species predominates, the fading followed first order kinetics with no measurable difference between deaerated and air-saturated samples. This was the case at pH values below two for 2-nitrotoluene but for 2,4-dinitrotoluene a lower pH, between 0 and 1, must be attained.

Table 1 lists rate constants obtained from 2-nitrotoluene in perchloric acid solutions of various concentrations. The table shows that the addition of sodium perchlorate caused a fairly small change in the value of the rate constant. It is also seen from Table 1 that the kinetics of the reaction was not affected by the presence of the alcohol at 1 per cent. Moreover, the absence or presence of sodium perchlorate or ethanol produced no observable difference in the degree of conversion to the colored species by flashing.

TABLE 1.

| [HClO ₄] (mole liter ⁻¹) | k _{exptl} (sec ⁻¹) | |
|--|---|------------------------|
| | Deaerated Solution | Air-Saturated Solution |
| 1.8 ¹ | 70 ± 5 | 68 ± 7 |
| 0.91 ¹ | 55 ± 5 | 52 ± 3 |
| 0.55 ¹ | 48 ± 4 | 50 ± 1 |
| 0.30 ¹ | 51 ± 1 | 49 ± 1 |
| 0.10 ¹ | 48 ± 2 | 49 ± 2 |
| 0.10 ² | 60 ± 2 | 58 ± 2 |
| 0.10 ³ | 60 ± 3 | 59 ± 2 |

First order rate constants, k_{exptl}, for the thermal fading of the transient species from 2-nitrotoluene in aqueous perchloric acid at the stated concentrations.

1. Solution contained also 1 *M* sodium perchlorate and 1% ethanol.
2. Solution contained 1 per cent ethanol but no sodium perchlorate.
3. Solution contained neither sodium perchlorate nor ethanol.

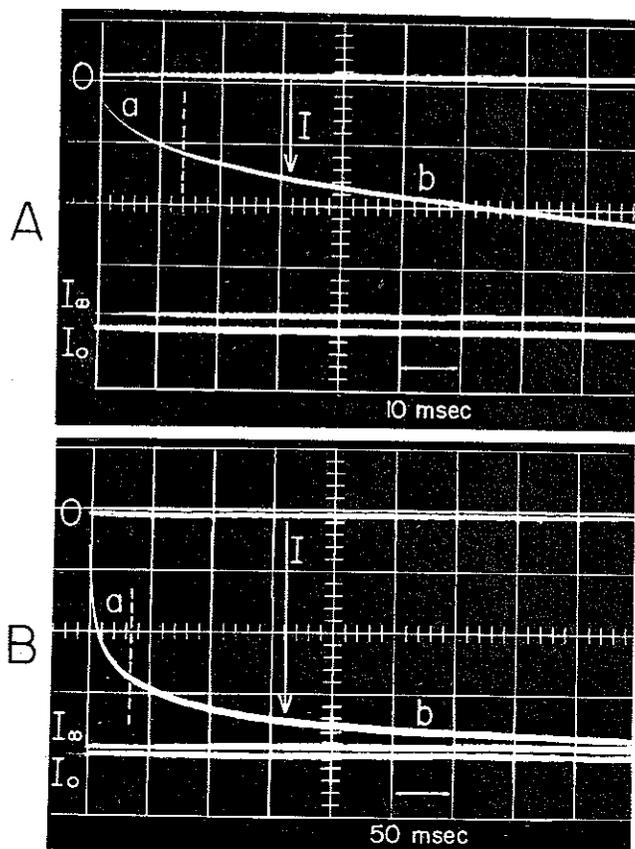


FIG. 1. Oscillograms showing fading curves for the colored species at 400 $m\mu$ from 2-nitrotoluene in acetic acid — sodium acetate buffer with a molarity ratio of 1:10.

A: 0.001 M acetic acid.

B: 0.0002 M acetic acid.

The solutions also contained 1 M sodium perchlorate.

The four sweeps in each picture refer to:

O: dark current, no light reaching photomultiplier tube.

I_0 : light intensity transmitted through solution before flashing.

I: light intensity transmitted through solution during fading of the short-lived species (sweep triggered simultaneously with flash).

I_∞ : light intensity transmitted after completion of reaction.

In the case of 2-nitrotoluene in 0.01 M to 0.001 M perchloric acid the kinetics of the fading reaction proved to be approximately second order in the initial stages of the reaction. The optical density decreased to one-half its initial value in about 5 msec. Repeated flashing of a solution perturbed the fading kinetics. Oxygen caused a dramatic change in the fading process. Air-saturated solutions gave essentially first order kinetics with rate constants of the order of 10^2 sec^{-1} .

For 2,4-dinitrotoluene identical rate constants were obtained for a deaerated and an air-saturated solution at any perchloric acid concentration between 0.3 and 4.7 M . At concentrations close to 0.1 M some oxygen sensitivity appeared but in more dilute perchloric acid there was again no effect of oxygen.

Photolysis in acetic acid-sodium acetate buffer

In the case of 2-nitrotoluene in acetic acid-acetate buffer the absorption spectrum of the transient species is similar to that in strong base.

Fig. 1 presents typical fading curves in dilute buffer with acetic acid concentration below 0.05 *M*. The formation of some nonreversible photo-product is shown by the difference in the values of I_0 and I_∞ . The fading curves could be divided into two branches, an initial fast fading, *a*, followed by a much slower fading, *b*. Branch *a* is only very slightly affected by the buffer concentration and shows kinetics which approached second order in the initial stages and gradually become of lower order. Branch *b* yields linear first order

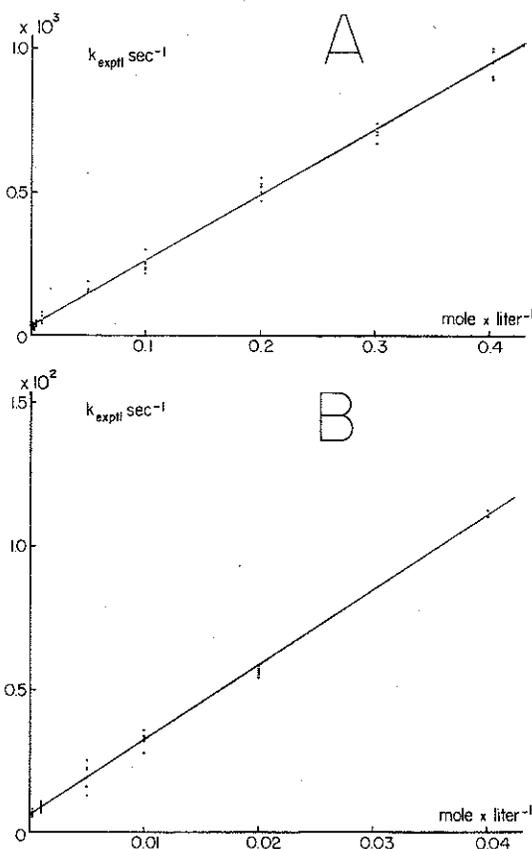


FIG. 2(A). First order rate constant versus acetic acid concentration for solutions of 2-nitrotoluene in acetic acid - sodium acetate, molarity ratio 1:1. At an acetic acid concentration of 0.05 *M* and below, the values refer to curve branch *b* of curves of the type shown in Fig. 1 obtained from deaerated solutions. At 0.1 *M* and above, i.e. where the curves were continuous, the data obtained from the entire fading curves of both deaerated and air-saturated solutions. All solutions contained 1 *M* sodium perchlorate. Intercept: 30 sec⁻¹. Slope: 2.3×10^8 liter sec⁻¹ mole⁻¹.

FIG. 2(B). First order rate constant versus acetic acid concentration for solutions of 2-nitrotoluene in acetic acid - sodium acetate, molarity ratio 1:10. The values refer to curve branch *b* of curves of the type shown in Fig. 1 obtained from deaerated solutions. All solutions contained 1 *M* sodium perchlorate. Intercept: 6.2 sec⁻¹. Slope: 2.6×10^8 liter sec⁻¹ mole⁻¹.

plots with rate constants proportional to buffer concentrations. Plots of the latter as a function of acetic acid concentration for two different buffer ratios are presented in Fig. 2.

At an acetic acid concentration between 0.05 and 0.1 *M* the rate of *b* becomes equal to the rate of *a* and above this concentration the entire fading curve follows first order kinetics, with rate constants dependent on the buffer concentration, i.e. catalysis by the buffer, only apparent in branch *b* at low acetic acid concentration, 0.05 *M* and below, is present as a catalysis of the entire fading process at acid concentration above this level, Fig. 2. The plots show that acetic acid, and not acetate ion, is the catalyzing agent, as essentially the same slopes are obtained at the two buffer ratios.

The effect of oxygen on the fading of the photoinduced transient species from 2-nitrotoluene in acetic acid-acetate buffer depends also upon whether the acetic acid concentration is higher or lower than about 0.1 *M*. In the lower concentration region the introduction of small amounts of oxygen to the solution caused an increase in the relative contribution of the *a* branch and a concomitant decrease in the *b* branch which further addition of oxygen ultimately caused to disappear. In addition, oxygen markedly influences the rate associated with the *a* branch and changes the order of the reaction without drastically affecting the time frame. The *b* branch, when present, continues to follow linear first order kinetics independent of the relative magnitude of the two curve branches with essentially the same rate constant as obtained from the completely deaerated solution. In the region of higher buffer concentration no effect of oxygen was detectable.

Photolysis in glycine buffer

In glycine buffers with the ratios of four to one and one to one between acid and base concentration, the colored species from 2-nitrotoluene produced the spectrum of the acid form.⁽¹³⁾ At buffer acid concentrations above 0.02 *M* the fading followed first order kinetics, apparently with a linear dependence of the rate constant on the buffer concentration, Fig. 3. The presence of oxygen in the system had no observable influence in this concentration region. The catalysis of the buffer acid, as estimated by the slopes of the straight lines in Fig. 3, is considerably lower for the higher than for the lower buffer ratio, namely, 2.3×10^2 versus 1.19×10^3 liter sec⁻¹ mole⁻¹.

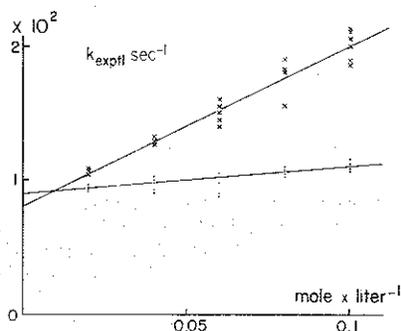


FIG. 3. First order rate constant versus acid concentration for solutions prepared by mixing perchloric acid and glycine in a constant molarity ratio of 4:1 (○) and 1:1 (×). All solutions contained 1 *M* sodium perchlorate. The slopes of the two lines are 2.3×10^2 and 1.19×10^3 liter sec⁻¹ mole⁻¹. Intercepts: 88 and 81 sec⁻¹.

Summary of results

A brief summary of the findings is presented in Table 2.

TABLE 2. CHARACTERISTICS OF THE FADING OF THE PHOTOCHEMICALLY PRODUCED COLORED TRANSIENTS FROM 2-NITROTOLUENE

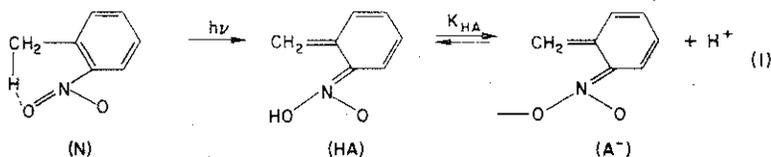
| Solution | Deaerated | Air-saturated |
|--|--|--|
| Sodium hydroxide 0.1 – 0.001 M | Initial fast fading in millisecond region ('spike'). Major fading first order: $k_{\text{exptl}} = 1.9 \text{ sec}^{-1}$ | Same as deaerated. |
| Perchloric acid 0.1 – 1.8 M | Continuous fading curve, first order: $k_{\text{exptl}} 50 - 70 \text{ sec}^{-1}$. | Same as deaerated. |
| Perchloric acid 0.01 – 0.001 M | Continuous fading curve, essentially second order, about 5 msec for optical density to decrease to one-half of original value. | Continuous fading curve, first order $k_{\text{exptl}} \approx 10^2 \text{ sec}^{-1}$. |
| Acetate buffer (buffer ratio 1:1 and 1:10) Acetic acid < 0.05 M | Two branches of fading curve, <i>a</i> and <i>b</i> <i>a</i> essentially second order <i>b</i> first order, k_{exptl} proportional to acetic acid concentration, Fig. 2. | Continuous fading curve, essentially first order $k_{\text{exptl}} \approx 10^2 \text{ sec}^{-1}$. |
| Acetate buffer (buffer ratio 1:1 and 1:10) Acetic acid > 0.1 M | Continuous fading curve, first order, k_{exptl} proportional to acetic acid concentration with same proportionality constant as for branch <i>b</i> above. Fig. 2. | Same as deaerated. |
| Glycine buffer (buffer ratio 4:1 and 1:1) Glycinium ion > 0.02 M | Continuous fading curve, first order, k_{exptl} proportional to glycinium ion concentration with different proportionality constants for the two ratios. Fig. 3. | Same as deaerated. |

DISCUSSION

Identity of the transient species

The transients observed in the photolysis of 2-nitrotoluene behave as if they formed an acid-base pair with a pK of 3–4. The data also indicate that such an equilibrium between an acid form and a conjugate base is established prior to the fading.

It is believed that the photoinduced color formation observed with 2-nitrophenyl methane derivatives is due to nitro — aci-nitro tautomerism.^(7,11–13) For the photolysis of 2-nitrotoluene and 2,4-dinitrotoluene it has been proposed that the aci-nitro structure, HA, represents the acid form of the colored species obtained in water solutions at low pH and that the conjugate anion, A[−], constitutes the base form of the colored species observed at high pH,^(13,14) cf. (1). With some related structures it is found that addition of strong base causes their solutions to turn deeply colored with absorption spectra quite similar to the spectra obtained from neutral or less basic photocolored solutions^(1,5,7). As the color formed on addition of base is likely due to the formation of anion, this supports the assumption that the anion is one of the observed photochemically produced colored species.



Formation of the transient species

The photochemical reaction responsible for the formation of the colored transient species appears to involve a hydrogen abstraction by the nitro group. Due to the proximity of the methyl group—probably hydrogen-bonded to an oxygen of the nitro group—this abstraction proceeds intramolecularly leading to the formation of the aci-nitro isomer.

The formation of the colored species may be quite analogous to what has been observed with a number of aromatic ketones. Such ketones, when photo-excited, are known to abstract hydrogen in an intermolecular reaction with a great variety of hydrogen containing organic compounds; particularly efficient is the reaction with isopropyl alcohol leading to the formation of pinacol.^(3,8) In 2-benzylbenzophenone a photoinduced hydrogen deuterium exchange involving the aliphatic hydrogens is known⁽¹⁷⁾ to take place and similar experiments⁽¹⁶⁾ with 2,4-dimethylacetophenone and 2,5-dimethylacetophenone support the view that hydrogen atoms on a carbon atom *ortho* to the keto group can be photo-forcibly exchanged. This exchange is interpreted to be caused by the formation of the enol tautomer and this enol tautomer is probably responsible for a phototropism of such compounds in solutions at low temperature.^(7,16) The presence of an *ortho* methyl group is known to inhibit the pinacol reaction⁽⁹⁾ and it may be generally true that an intramolecular hydrogen abstraction replaces the intermolecular reaction when the structure of the compound is such as to place a hydrogen atom in the immediate vicinity of the carbonyl group, for instance when an *ortho* methyl hydrogen is present.

Other similar photoinduced hydrogen transfer reactions over a six-membered ring are known, i.e. with aromatic Schiff bases having a hydroxyl group *ortho* to the C = N bond.^(2,4,15)

The aci-nitro isomer, HA, and the nitro isomer, N, have the common conjugate base, the nitro anion, A⁻, cf. (1). However, as the aci-nitro structure, HA, is a much stronger acid than the nitro form, N, $pK_{HA} \ll pK_N$, the nitro isomer is the predominating species under equilibrium conditions in the dark at $pH < pK_N$. A photochemical production of the aci-nitro molecule from the nitro structure may, however, cause the appearance of the anion in an equilibrium between aci-nitro form and anion,



if $pH > pK_{HA}$ and equilibrium (2) is established faster than the fading of the colored HA and A⁻.

Rate Determining Steps in the Acid Catalyzed Fading Process

In the case of 2,4-dinitrotoluene it has been demonstrated⁽¹⁴⁾ that the fading process can be described as a reaction of the anion with different acids. Primarily because decomposition was slight, it was assumed that this reaction constituted the neutralization of the anion to reform the nitro isomer. Also in the case of 2-nitrotoluene such a reaction involving the different acids of the system appears as an important fading process.



HB_i represents the different acids present, including protons, buffer acid and the solvent, water. k_{HB_i} represents the rate constant and P some product. (At $pH > pK_{HA}$, when A⁻ predominates in relation to HA, reaction (3) is responsible for the general acid catalyzed

fading. At $\text{pH} < \text{pK}_{\text{HA}}$, with a strongly dissociated acid to maintain a pH, the fading becomes independent of acid concentration since the catalyzing acid, HB_1 , cf. reaction (3), in this case predominantly the proton, is proportional to acid concentration, but the concentration of A^- , governed by equilibrium (2), is inversely proportional to the acid concentration. In base when the only catalyzing acid is the solvent, H_2O , the acid-catalyzed process also becomes independent of pH.) Both for 2-nitrotoluene and for 2,4-dinitrotoluene there is no conclusive evidence to prove that P equals $\text{N} + \text{B}_1^-$ although present data may lend support to such a conclusion.

Competing fading reactions

For both 2-nitrotoluene and 2,4-dinitrotoluene there is a pH interval where the major fading reaction cannot be described by reaction (3), and where the kinetics of fading becomes more complex compared to the kinetics at either higher or lower pH. This interval coincides with the region where transition between the acid form and the base form of the colored species occurs, $\text{pH} \approx \text{pK}_{\text{HA}}$, and constitutes for 2-nitrotoluene a fairly wide interval of about five pH units around $\text{pH} = 4$ but only a narrow interval of about one unit around a $\text{pH} = 1$ for the 2,4-dinitro compound. In this region the kinetics is dependent on the presence of oxygen in the solution and for 2-nitrotoluene the fading process does not follow simple first order kinetics.

In the case of 2-nitrotoluene it is evident that at least two competing fading processes are involved at a pH close to pK_{HA} , the acid-catalyzed reaction (3) and a process which is essentially independent of acid concentration. Only reaction (3) appears, both for degassed and air-saturated solutions, if (3) is made sufficiently fast by using high concentration of catalyzing acid, HB_1 . Also at low acetic acid concentrations, it is possible to observe (3) but only as a portion of the fading curve (branch *b*) and only in degassed solutions. Other processes were responsible for the *a* branch and dominated in such air-saturated solutions. In dilute perchloric acid solution, these other processes appeared responsible for the entire fading curve both in degassed and air-saturated systems.

The oxygen sensitivity at $\text{pH} \approx \text{pK}_{\text{HA}}$ indicates that oxygen enters directly into a reaction with the colored species in this pH region. An explanation for the reactivity of the colored species at $\text{pH} \approx \text{pK}_{\text{HA}}$ may be that an electron transfer occurs between ionized and unionized compound, i.e. A^- and HA , to form radical species. Such a reaction has been postulated to explain the formation of radical anions observed in electron spin resonance measurements on alkaline solutions of some aromatic nitro compounds.⁽¹⁰⁾

There is no evidence of any spectral change in the visible region during the course of fading of any of these solutions which indicates that the absorbing molecules constitute either a single species or several species in equilibrium. It should be noticed, however, that a small spectral change would pass undetected as the spectra were determined by a scanning technique^(13,15) which did not permit a very accurate determination of the spectrum.

A possible explanation for the occurrence of the *a* branch is that light produces—besides the tautomeric change—other species, i.e. free radicals which a lifetime in the millisecond region and which during the course of their decay attack HA and A^- , or some radical species in equilibrium with HA and A^- , cf. above. The rate of decay of these other species may be principally determined by other reactions. Furthermore, the species may have no absorption or very weak absorption in the visible region but absorb only in the ultraviolet, which makes it impossible to observe directly their decay as the parent compound absorbs in this region and the degree of conversion is low.

Another possibility is that branch *a* is actually associated with the formation of an equilibrium—in addition to (2)—possibly to form radical species. It appears, however, somewhat unlikely that any such species would not absorb strongly in the visible and cause major change in absorption spectrum during the course of fading. Furthermore, the catalysis coefficient for acetic acid is the same for branch *b* as for the entire fading when (3) is made faster than the competing reactions, Fig. 2.

It appears likely that the processes associated with branch *a* are also responsible for the fading in dilute perchloric acid and for the 'spike' in strong base.

Evaluation of rate constants and equilibrium constants for the acid catalyzed fading

Considering reaction (2), between the aci-nitro isomer and the anion, fading reaction (3) leads to the following expression for the experimentally observed rate constant:

$$k_{\text{exptl}} = (1 + [\text{H}^+]/K_{\text{HA}})^{-1} \sum k_{\text{HB}_i} [\text{HB}_i] \quad (4)$$

When $\text{pH} \gg \text{p}K_{\text{HA}}$ the anion predominates equation (4) can be approximated by

$$k_{\text{exptl}} = \sum_i k_{\text{HB}_i} [\text{HB}_i] \quad (5)$$

In alkaline solutions the solvent molecules are the only important acid species and equation (5) becomes $k_{\text{exptl}} = k_{\text{H}_2\text{O}} [\text{H}_2\text{O}]$. In acid solutions with pH still much larger than $\text{p}K_{\text{HA}}$ the term $k_{\text{H}^+} [\text{H}^+]$ becomes important and when buffer acid is present, acetic acid, the term $k_{\text{CH}_3\text{COOH}} [\text{CH}_3\text{COOH}]$ is also added. In the case of 2-nitrotoluene the experimental data presented above allow these quantities to be estimated. The rate constant $k_{\text{H}_2\text{O}}$ is obtained from the experiments in strong base as 3.5×10^{-2} liter sec^{-1} mole $^{-1}$. The intercepts in Fig. 2 represent $k_{\text{H}^+} [\text{H}^+] + k_{\text{H}_2\text{O}} [\text{H}_2\text{O}]$ and using the values of pH which were recorded with the glass electrode 4.1 and 5.0, respectively, the values 3.5×10^5 and 4.2×10^5 liter sec^{-1} mole $^{-1}$ are calculated for k_{H^+} . The slopes of the lines in Fig. 2 are identified with $k_{\text{CH}_3\text{COOH}}$, 2.3×10^3 liter sec^{-1} mole $^{-1}$ and 2.6×10^3 , respectively. It should be noted that the buffer ratio 1:1, between acetic acid and sodium acetate, yields a pH close to $\text{p}K_{\text{HA}}$, estimated from the spectral change. At the pH of this buffer, 4.1, a notable portion of the colored species may be present in the aci-nitro form, thus the condition, $\text{pH} \gg \text{p}K$, for equation (5) to be valid may not be fulfilled. It is, therefore, assumed that the values of k_{H^+} and $k_{\text{CH}_3\text{COOH}}$ obtained from the solutions with a lower buffer ratio, $\text{pH} = 5.0$, represent more nearly correct values.

In a strong acid, which is essentially completely dissociated, and at low pH, $\text{pH} \ll \text{p}K_{\text{HA}}$, H^+ becomes the predominating acid species and equation (4) is reduced to

$$k_{\text{exptl}} = K_{\text{HA}} k_{\text{H}^+} \quad (6)$$

Table 1 shows that k_{exptl} in perchloric acid is essentially constant at very low pH. Using the mean value of k_{H^+} as calculated above, and k_{exptl} from a 0.1 *M* perchloric acid solution, Table 1, a value of 3.9 is estimated for $\text{p}K_{\text{HA}}$ of 2-nitrotoluene.

At low pH, $\text{pH} \ll \text{p}K_{\text{HA}}$ and buffer acid present, which was the case in the experiments with 2-nitrotoluene in glycine buffer, equation (4) approaches

$$k_{\text{exptl}} = K_{\text{HA}} (k_{\text{H}^+} + k_{+\text{NH}_3\text{CH}_2\text{COOH}} [^+\text{NH}_3\text{CH}_2\text{COOH}]/[\text{H}^+]) \quad (7)$$

In agreement with the experimental findings equation (7) shows that the catalyzing effect of the acid is reduced at lower pH. According to equation (7) the intercepts of Fig. 3 equal $K_{\text{HA}} k_{\text{H}^+}$. With the value 4.2×10^5 liter sec^{-1} mole $^{-1}$ for k_{H^+} this leads to a value of 3.7 for

pK_{HA} . It is believed that this value of pK_{HA} is the better value as it is based on measurements at a pH close to the pH for the determination of k_{H^+} . The slopes of Fig. 3 give values of 2.3×10^2 and 1.19×10^3 liter sec^{-1} mole^{-1} for $K_{HA}k_{+NH_3CH_2COOH}/[H^+]$. Using the recorded pH of 1.5 for the 4:1 ratio and pH = 2.1 for the 1:1 ratio between buffer acid and base, $k_{+NH_3CH_2COOH}$ becomes 3.5×10^4 and 5.9×10^4 liter sec^{-1} mole^{-1} .

Mean values of the quantities estimated above are collected in Table 3. For comparison the corresponding quantities for 2,4-dinitrotoluene taken from reference (14) are also included in the table.

TABLE 3. VALUES OF pK_{HA} FOR EQUILIBRIUM (2) AND k_{HBI} IN REACTION (3)

| | 2-Nitrotoluene | 2,4-Dinitrotoluene |
|---------------------|----------------------|--|
| pK_{HA} | 3.7 | 1.1 |
| P_{H_2O} | 3.5×10^{-2} | 1.8×10^{-2} (liter sec^{-1} mole^{-1}) |
| k_{H^+} | 4.2×10^5 | 7.4×10^4 " " " |
| K_{CH_2COOH} | 2.6×10^8 | 4.8×10^8 " " " |
| $k_{+NH_3CH_2COOH}$ | 4.7×10^4 | 2.4×10^4 " " " |

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