

The Pulse Radiolytic Decomposition of *p*-Nitroperoxybenzoic Acid

J. Lillie,* E. Heckel, and R. C. Lamb

Contribution from the Hahn-Meitner-Institut für Kernforschung Berlin, GmbH, Bereich Strahlenchemie, 1 Berlin 39, Germany.

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Abstract: *p*-Nitroperoxybenzoic acid (I) is reduced by e_{aq}^- with $k_1 = 1.5 \times 10^{10} M^{-1} sec^{-1}$ and by 2-hydroxy-2-propyl radicals (derived from isopropyl alcohol) with $k_4 = 3.3 \times 10^9 M^{-1} sec^{-1}$. The resulting radical anion (II) eliminates an $\cdot OH$ radical with $k_3 = 2.1 \times 10^3 sec^{-1}$ and forms the *p*-nitrobenzoate anion. The pK_a of the conjugate acid of radical anion II is 2 or below and that of radical anion II itself is 8.25. When isopropyl alcohol is present, a chain reaction occurs which is apparently caused by 2-hydroxy-2-propyl free radicals which arise from the interaction of $\cdot OH$ with the alcohol.

Organic peroxides are of significant theoretical and practical interest, both to industrial and academic chemists.¹ Although they have a number of industrial uses, one usually thinks of their historic role as free radical initiators in polymerization reactions of vinyl monomers.² Most of the investigations of organic peroxides have been studies of their thermal decompositions, and although such studies are useful in defining the chemical behavior of the peroxides themselves, they are not easily adapted to the direct observation of the free radicals formed in their decompositions.

Pulse radiolysis is one of the useful techniques by which the direct observation of free radicals can be made. The pulse radiolysis method has been used to measure the rates of reaction of oxygen with free radicals formed in autoxidations of alcohols and ethers.³ Peroxy radicals have been considered to be important intermediates both in oxygen metabolism and in radiation damage in living cells.⁴

Pulse radiolysis is a useful method inasmuch as free radicals can be formed in a well-defined way, and their reactions can be observed by measuring the optical and electrical changes which occur immediately after each pulse. A minor shortcoming of the method lies in the fact that, at present, the primary radiolysis products are best defined for aqueous solutions. Although many polar organic compounds are sufficiently water soluble for such experiments (a concentration of $10^{-4} M$ is sufficient), our preliminary experiments with several bisaroyl peroxides indicated insufficient solubility. It was found, however, that *p*-nitroperoxybenzoic acid had sufficient solubility and sufficient resistance to hydrolysis (under the conditions used) to allow the pulse radiolytic study presented in this paper.

Experimental Section

p-Nitroperoxybenzoic acid, I, was prepared both by the method of Vilkas (which employs sodium peroxide and *p*-nitrobenzoyl chloride)⁵ and by the method of Silbert, Siegel, and Swern (which em-

plows 90% hydrogen peroxide and *p*-nitrobenzoic acid),⁶ mp 137° (lit.⁶ 138°). Iodometric titration indicated that a purer product was obtained by the latter method⁶ (99.5%) than by the former (98.0%).

The solubility of *p*-nitroperoxybenzoic acid is about $3 \times 10^{-4} M$ at 20°; however, in organic solvent-water mixtures, the solubility increases greatly, e.g., $4 \times 10^{-3} M$ in 30% methanol-water. The solution is slightly acidic; the pK_a of the *p*-nitroperoxybenzoic acid, as determined with a glass electrode, is 6.95.

The stability of the compound was checked by measuring the spectra of the solutions at various times after their preparation.⁷ No changes were observed in 2.5 hr in solutions with pH values in the range used in the experiments.

Pulse Radiolysis Experiments. All solutions were prepared with triply distilled water. The *tert*-amyl alcohol used was obtained from Schuchardt, Munich. The other chemicals were Merck analytical reagents.

The experiments were performed with a 1.6 MeV Van de Graaff generator. The reactions were observed by spectrophotometric measurements⁸ and by conductivity measurements with a 10 MHz ac conductivity bridge.⁹ Pulse durations were from 0.5 to 3.0 μsec with doses of 300 rads to 3 krad. The experiments were performed at room temperature (25°). The cell constant and absorbed dose were determined before and after each series of experiments using a $10^{-4} M$ tetranitromethane solution in water-5% isopropyl alcohol.¹⁰ The absorbed dose and the cell constant were calculated using $G = 6.0$ and $\epsilon = 1.4 \times 10^4 M^{-1} cm^{-1}$ for the yield and extinction coefficient, respectively, of the $C(NO_2)_3^-$ ion, and $\Lambda = 390 M^{-1} \Omega^{-1} cm^2$ for the sum of the equivalent conductivities of H^+ and $C(NO_2)_3^-$.

Results and Discussion

Solutions Containing *tert*-Amyl Alcohol. The primary radiolysis products formed in water are e_{aq}^- , an equivalent quantity of H^+ , along with $\cdot OH$ radicals and $H\cdot$ atoms. The G value (molecules per 100 eV of absorbed dose) is 2.7 for e_{aq}^- , for $\cdot OH$, and for $H\cdot$ (after neutralization of some additionally formed H^+ and OH^-) and that for $H\cdot$ is 0.6.¹¹ In order to study the reactions of e_{aq}^- alone, 0.5 M *tert*-amyl alcohol is added to the aqueous solution. Within less than 1 μsec , this alcohol undergoes hydrogen transfer from a β position to $\cdot OH$ ($k = 1.1 \times 10^9 M^{-1} sec^{-1}$) and to $H\cdot$ ($k = 2 \times 10^6 M^{-1}$

(1) "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970; Vol. 2, 1971; Vol. 3, 1972.

(2) Cf. K. F. O'Driscoll in ref 1, Vol. 1, Chapter XI, pp 609-632.

(3) (a) G. E. Adams and R. L. Willson, *Trans. Faraday Soc.*, **65**, 2981 (1969); (b) K. Stockhausen, A. Fojtik, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **74**, 34 (1970); (c) E. Hayon and M. Simic, *J. Amer. Chem. Soc.*, **95**, 6681 (1973).

(4) M. Simic and E. Hayon, *Biochem. Biophys. Res. Commun.*, **50**, 364 (1973).

(5) M. Vilkas, *Bull. Soc. Chim. Fr.*, 1401 (1959); cf. ref 1, Vol. 1, pp 491-492.

(6) L. S. Silbert, E. S. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962); Cf. *Org. Syn.*, **43**, 93 (1963), or ref 1, Vol. 1, p 492.

(7) Although their uv spectra are quite similar, *p*-nitroperoxybenzoic acid and *p*-nitrobenzoic acid have quite different extinction coefficients.

(8) A. Henglein, W. Schnabel, and J. Wendenburg, "Einführung in die Strahlenchemie," Verlag Chemie, Weinheim, 1969.

(9) J. Lillie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).

(10) B. Beck, *Int. J. Radiat. Phys. Chem.*, **1**, 361 (1969).

(11) Cf. E. J. Hart and M. Burton, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1973.

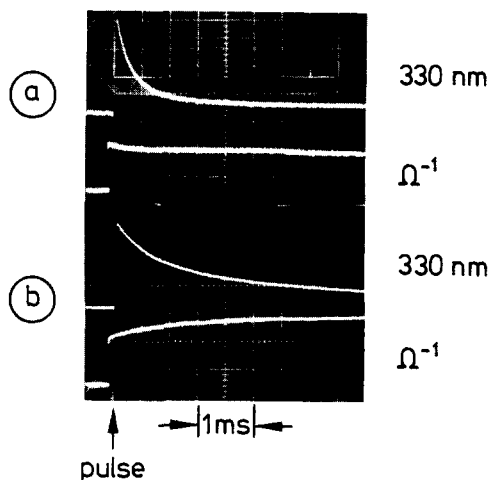


Figure 1. Absorbance (A) and conductivity (Δ) in a solution of $5 \times 10^{-5} M$ *p*-nitroperoxybenzoic acid, pH 5.0: (a) with $5 \times 10^{-1} M$ *tert*-amyl alcohol ($1 \text{ cm} \cong 0.88\% A$ and $\Delta\Delta = 90 \Omega^{-1} M^{-1} \text{ cm}^2$); (b) with $5 \times 10^{-1} M$ isopropyl alcohol ($1 \text{ cm} \cong 2.2\% A$ and $\Delta\Delta = 180 \Omega^{-1} M^{-1} \text{ cm}^2$) ($\Delta\Delta =$ equivalent conductivity, calculated for $G = 6$ for 1-cm signal height).

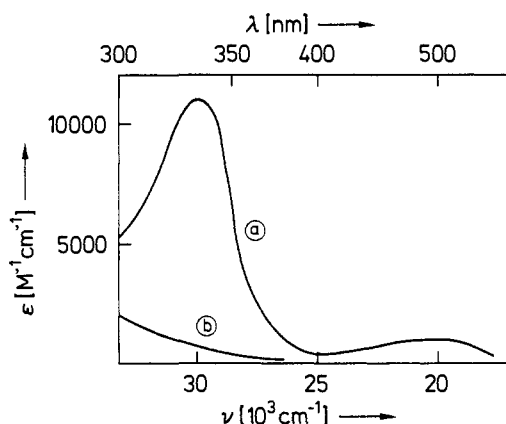


Figure 2. Spectrum in a solution of $5 \times 10^{-5} M$ *p*-nitroperoxybenzoic acid and $5 \times 10^{-1} M$ *tert*-amyl alcohol, pH 5.0: (a) immediately after the pulse, (b) 1 msec after the pulse.

sec^{-1}).^{12,13} The resulting radical (like that derived from *tert*-butyl alcohol) lacks the propensity of undergoing electron transfer reactions with reducible organic compounds, such as is exhibited by the 2-hydroxy-2-propyl radical (derived from 2-propanol).¹⁴

Figure 1a shows the time dependence of the absorbance at 330 nm and of the electrical conductivity in such a solution. The absorbance increases during the pulse and then slowly decays. The conductivity is also increased immediately after the pulse but then remains constant. Spectrophotometric measurements were made at various wavelengths shortly after the pulse in order to determine the uv-visible spectrum in the 300–550-nm range (Figure 2), which exhibits a strong maximum at 330–340 nm and a much weaker one near 500 nm. The spectrum shows similarities to that of the nitrobenzene radical anion (λ_{max} 300 nm)¹⁴ and that of the *p*-nitroacetophenone radical anion (λ_{max} 350 nm).¹⁵

(12) M. Simic and M. Hoffman, *J. Phys. Chem.*, **76**, 1398 (1972).

(13) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

(14) K. D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **70**, 862 (1966); (b) G. E. Adams and B. D. Michael, *Nature (London)*, **215**, 1248 (1967).

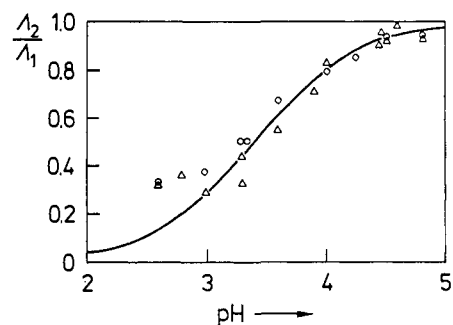
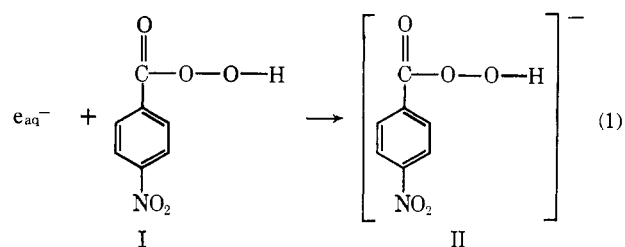


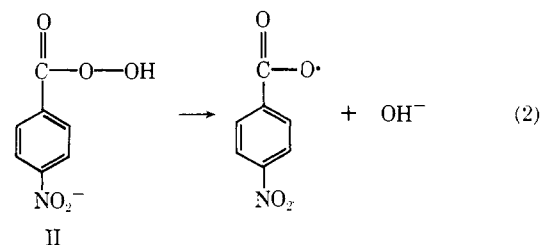
Figure 3. Ratio of the conductivities: (O) $\Delta_1 =$ initial value, $\Delta_2 =$ final value, *tert*-amyl alcohol as the OH scavenger; (Δ) $\Delta_1 =$ initial value at pH 6, $\Delta_2 =$ initial value of the actual pH, isopropyl alcohol as the OH scavenger.

Therefore, we attribute it to the radical anion (II) of *p*-nitroperoxybenzoic acid (I), which is formed by reaction of the latter with e_{aq}^- (reaction 1).



The rate of reaction ($k_1 = 1.5 \times 10^{10} M^{-1} \text{ sec}^{-1}$) was measured by following the decay of the absorption of e_{aq}^- . The conductivity change is due to H^+ ($\Lambda = 350 \text{ cm}^2 M^{-1} \Omega^{-1}$) formed by the pulse and to the radical anion II ($\Lambda = 40$). Inasmuch as the change in conductivity should be $\Delta\Lambda = 390$ and that observed is only $\Delta\Lambda = 310$, it is obvious that about 20% of the yield of e_{aq}^- is reacting in some other way. We attribute this difference to competition of H^+ .

The half-life of the 330-nm absorption ascribable to radical anion II is $t_{1/2} = 350 \mu\text{sec}$. It is independent of the dose, *i.e.*, independent of the "initial" concentration of radical anion II. Thus it is a first-order, and presumably a unimolecular, reaction. However, the conductivity remains constant while the 330-nm absorption decays; it does not change even at much longer times (the maximum time observed was 10 sec). This observation excludes the possibility of the elimination of a hydroxide ion according to eq 2. Other possibilities for



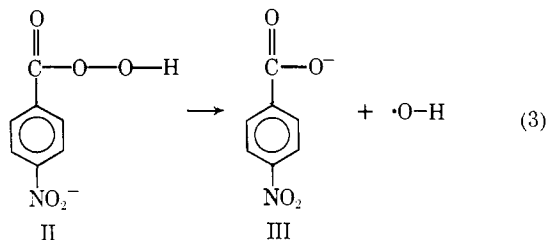
the first-order reaction are the elimination of either $\cdot\text{OH}$ or $\cdot\text{O}-\text{O}-\text{H}$, and an intramolecular rearrangement of II.

The conductivity remained constant only in the pH range 4.5–6.5. At lower pH values, the conductivity diminished somewhat as the absorbance at 330 nm decayed. Figure 3 is a graph of the ratio of final to

(15) G. E. Adams and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1*, 719 (1973).

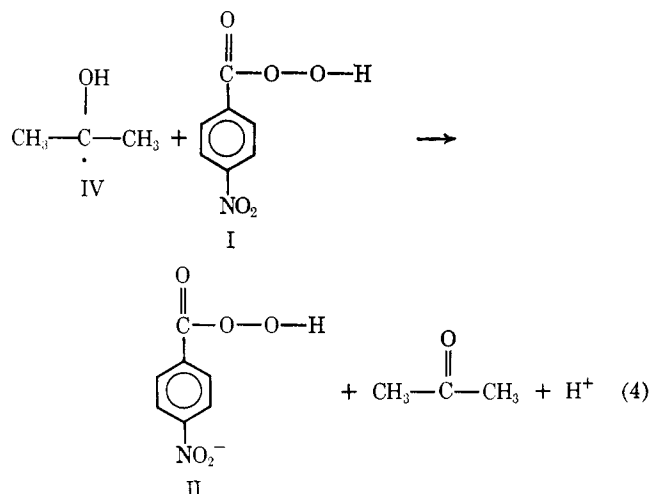
initial conductivities, Λ_2/Λ_1 , vs. pH. The curve (solid line in Figure 3) is the calculated degree of dissociation of *p*-nitrobenzoic acid ($pK_a = 3.4$). In the measurements at the low pH values, a serious complication arose which was caused by the reaction $H^+ + e_{aq}^- \rightarrow H\cdot$, and inasmuch as $H\cdot$ is scavenged by *tert*-amyl alcohol, the net effect of this reaction is to diminish the yield of II. At lower pH values, therefore, only small signals were obtained, but the Λ_1/Λ_2 ratios were measurable. Although the competing reaction causes rather serious deviations from the calculated dissociation curve at low pH values, there is a convincing correlation between Λ_2/Λ_1 and the calculated *p*-nitrobenzoic acid dissociation curve in the pH 3–5 range.

These results obviate the possibility of elimination of $\cdot O-O-H$ from II, inasmuch as the latter has a $pK_a = 4.8$,^{16a,b} which would yield a dissociation curve which would not correlate with the data nearly so well as does that for *p*-nitrobenzoic acid (Figure 3). Not only do conductivity measurements require the formation of *p*-nitrobenzoate, but the uv spectrum observed after cessation of optical decay (Figure 2b) corresponds to that of the *p*-nitrobenzoate anion, III, $\epsilon_{310nm} = 250 M^{-1} cm^{-1}$. These facts practically require $\cdot O-H$ elimination according to eq 3.



The rate constant for eq 3, determined from the rate of disappearance of anion II, is $k_3 = 2.1 \times 10^3 \text{ sec}^{-1}$. The $\cdot\text{OH}$ radicals formed in reaction 3 are scavenged by reaction with *tert*-amyl alcohol, yielding a nonconducting free radical (presumably the 2-methyl-2-hydroxy-3-butyl radical) which has no absorption above 300 nm.

Isopropyl Alcohol as $\cdot\text{OH}$ Scavenger. In an aqueous 0.1 *M* 2-propanol mixture saturated with nitrous oxide, all the electrons react with nitrous oxide to form $\cdot\text{OH}$ according to the equation $e_{aq}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{N}_2 + \cdot\text{OH} + \text{OH}^-$. The $\cdot\text{O}-\text{H}$ radicals subsequently react with 2-propanol to form the 2-hydroxy-2-propyl radical, IV. The observed spectrophotometric and electrical conductivity changes (Figure 1b) resemble those of the system water-*tert*-amyl alcohol (in the absence of nitrous oxide); however, the observed values are nearly twice as great. This indicates that the 2-hydroxy-2-propyl free radical (IV) is able to reduce I according to eq 4, which yields the same product as does eq 1 but does so with the *G* value twice as great. The reason for this is that in aqueous 2-propanol saturated with nitrous oxide both the $\cdot\text{O}-\text{H}$ formed in the primary step and that formed as a result of the reaction of e_{aq}^- with nitrous oxide are converted to radical IV which reduces I, whereas in the aqueous *tert*-amyl alcohol system only e_{aq}^- is effective at reducing I to II. Electron transfer reactions of IV with other nitroaromatic substrates have been reported previously.¹⁴ The rate of



reaction 4, measured by monitoring the absorbance of II at 330 nm, is $k_4 = 3.3 \times 10^9 M^{-1} \text{ sec}^{-1}$.

In water-2-propanol, the decay of the spectrophotometric signal (Figure 1) was of first order kinetically as in the water-*tert*-amyl alcohol experiments but was slower by a factor of 2. The conductivity, however, increased as the absorbance decreased. These observations can be explained by recognizing that, in the pulse radiolysis of I in water-2-propanol, a chain process (consisting of reaction 3, the formation of IV through the reaction of $\cdot\text{OH}$ with 2-propanol, and reaction 4) is occurring. Because of the relatively high concentration of 2-propanol, the $\cdot\text{OH}$ radicals formed in reaction 3 are scavenged immediately, and the resulting 2-hydroxy-2-propyl radicals cause the rapid formation of II again through reaction 4. If this chain process were efficient, the spectrophotometric signal (due to II) should not decay at all. However, since the overall effect of the chain process is to form *p*-nitrobenzoic acid, which is much more highly dissociated at pH 4.5 than either of its precursors (I or II), the conductivity should increase enormously.

However, the chain process is inefficient; the chain length is only about 2. The reason for this is that, at the high radical concentrations which are produced in pulse radiolysis, radical-radical termination reactions occur rapidly. The *G* values obtained by γ -radiolytic measurements of the decomposition of I are around 25 with 2-propanol as the OH scavenger and 200 with HCO_2^- as the OH scavenger.¹⁷

Figure 4 is a graph of the logarithm of the observed rate constant for the decomposition of anion II vs. pH. Since the most complete rate-pH profile was determined for the water-2-propanol system, we shall discuss that plot most completely. In the flat portion of the plot (*i.e.*, pH 4–7), the observed rate constant is approximately $1/2 k_3 \approx 1 \times 10^3 \text{ sec}^{-1}$, where the approximate factor of one-half is, as already explained, attributable to the inhibiting chain reaction. The basic portion of the plot, pH 8–10, is likewise understandable if the assumption is made that, in this pH region, a significant portion of anion II is converted to its conjugate base (a radical dianion), which does not itself decompose at a significant rate.¹⁸ If one assumes that only anion II

(17) Unpublished results of the authors of this paper.

(18) The word "decompose" used here refers to a homolytic decomposition similar to reaction 3, forming $\cdot\text{O}^-$. Difficulty was encountered at higher pH values because of the basic hydrolysis of *p*-nitroperoxybenzoic acid.

(16) (a) J. Rabani and S. O. Nielson, *J. Phys. Chem.*, **73**, 3736 (1969); (b) D. Behar, G. Czapski, L. M. Dorfman, J. Rabani, and M. A. Schwarz, *ibid.*, **74**, 3209 (1970).

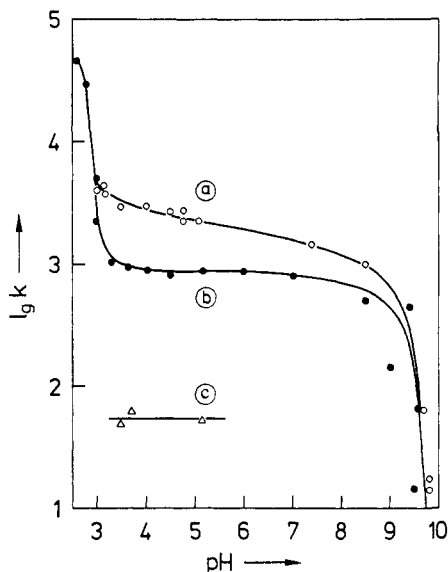


Figure 4. pH dependence of the logarithm of the first-order rate constant in a solution of $5 \times 10^{-5} M$ *p*-nitroperoxybenzoic acid in aqueous solutions containing: (a) $5 \times 10^{-1} M$ *tert*-amyl alcohol, (b) $5 \times 10^{-1} M$ isopropyl alcohol, (c) $5 \times 10^{-1} M$ methanol.

undergoes homolytic decomposition in the basic region, and if $pK_a = 8.25$ is assigned to anion II, one obtains the best fit to the $\log k_{\text{obsd}}$ vs. pH plot.

In the pH range 3.3–2.7, the interpretation of the rate behavior of anion II is not quite so unambiguous. It is sufficiently clear that anion II starts being protonated at pH values below 3.3 and that its conjugate acid, HAN_{II} (an acidic free radical), undergoes loss of the $\cdot\text{O-H}$ radical at a significantly faster rate than does An_{II}^- . If one assumes the steady state in HAN_{II} , the following "first-order" rate expression should apply in

$$-d[\text{An}_{\text{II}}^-]/dt = \left[\frac{1}{2}k_3 + \frac{k_{\text{H}^+}(k_{3\text{H}}/k_{-\text{H}^+})}{1 + (k_{3\text{H}}/k_{-\text{H}^+})} \right] [\text{H}^+] [\text{An}_{\text{II}}^-] \quad (5)$$

the low-pH region, in which k_{H^+} and $k_{-\text{H}^+}$ are the rate constants of protonation and deprotonation of An_{II}^- , respectively (i.e., $k_{-\text{H}^+}/k_{\text{H}^+} = K_a$ of HAN_{II}), and $k_{3\text{H}}$ is rate constant for the loss of the $\cdot\text{OH}$ radical from HAN_{II} .

There are two possible kinetic situations which could be obtained from eq 5: equilibrium control or kinetic control. If the reaction is equilibrium controlled, $k_{3\text{H}} \ll k_{-\text{H}^+}$ or $k_{3\text{H}}/k_{-\text{H}^+} \ll 1$. This circumstance leads to eq 6, while with kinetic control, $k_{3\text{H}}/k_{-\text{H}^+} \gg 1$ and eq 7 applies.

$$k_{\text{obsd}} = \frac{1}{2}k_3 + (k_{3\text{H}}/K_a)[\text{H}^+] \quad (6)$$

$$k_{\text{obsd}} = \frac{1}{2}k_3 + k_{\text{H}^+}[\text{H}^+] \quad (7)$$

The evidence indicates that eq 6 applies and that equilibrium control is obtained. Although it was not possible to measure K_a for HAN_{II} accurately, it can be estimated at $pK_a \leq 2$.¹⁹ Using this value, and the value $k_{\text{obsd}} = 6 \times 10^4 \text{ sec}^{-1}$ at the lowest pH (2.6), one ob-

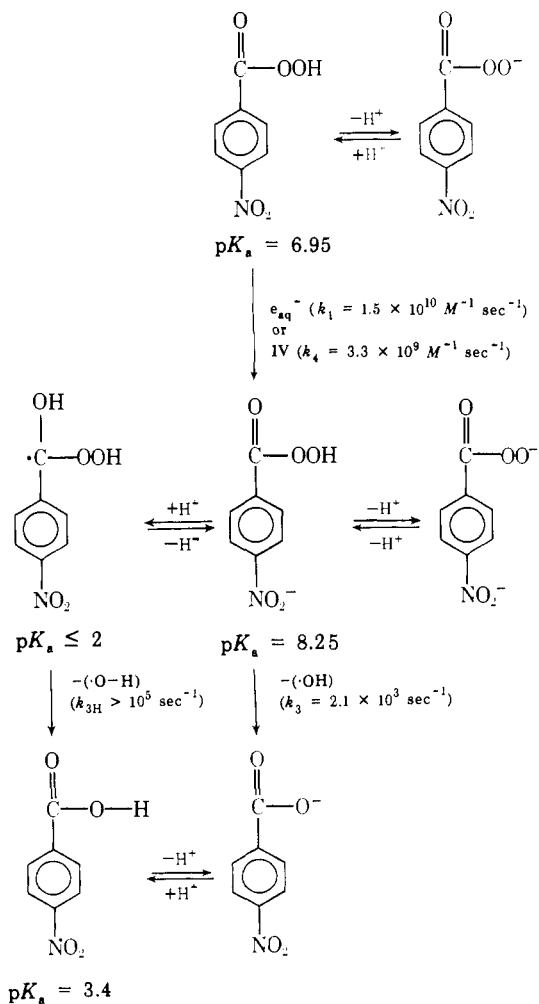
(19) This means that HAN_{II} is a significantly stronger acid than is the conjugate acid of the nitrobenzene radical anion ($pK_a = 3.2$), apparently because An_{II}^- , with a carbonyl group, has a more extended electron-poor π system than does the nitrobenzene radical anion.

tains the estimate $k_{3\text{H}} \approx 2 \times 10^5 \text{ sec}^{-1}$, and a higher estimate would result if the pK_a of HAN_{II} is less than 2. Thus the conjugate acid of An_{II}^- appears to lose hydroxyl radical at a rate that, at a minimum, is 100 times as great as is the rate of loss of $\cdot\text{OH}$ from An_{II}^- .

A difficulty was encountered in attempting to do experiments at low pH (the scavenging of e_{aq}^- through the reaction $e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}\cdot$). The effect of this reaction is more pronounced for the water-*tert*-amyl alcohol system because, when the $\text{H}\cdot$ atom reacts with *tert*-amyl alcohol, it produces a nonreducing free radical, and the two steps taken together have the effect of destroying e_{aq}^- , and therefore inhibiting the formation of An_{II}^- through reaction 1. On the other hand, when $\text{H}\cdot$ atoms are formed through capture of e_{aq}^- with H^+ in water-2-propanol, they remove the hydrogen atom from the central carbon, forming the 2-hydroxy-2-propyl free radical, IV, which then undergoes reaction 4 to produce An_{II}^- . At pH values below 2.6, the decay of An_{II}^- is faster than its formation by reaction 4, so measurements become impossible.

The reactions we have described are assembled into Scheme I. There is some ambiguity as to the structure

Scheme I

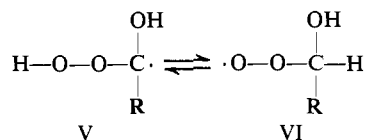


of the conjugate acid of An_{II}^- (HAN_{II}), because there are different types of oxygen atoms in An_{II}^- which could be protonated. We have arbitrarily chosen to represent HAN_{II} as that which the carbonyl oxygen has protonated; this tautomer can form hydroxyl radicals readily by homolysis of the peroxidic O–O bond.

Methanol as ·OH Scavengers. When methanol is used as an ·OH scavenger in a solution which is saturated with nitrous oxide, one observes a first-order growth of the 330-nm absorption. From the known concentration of I, one calculates the rate constant $k = 2 \times 10^8 M^{-1} \text{sec}^{-1}$ for the reaction of the hydroxymethyl radical with I. However, during the build-up of the absorbance, the conductivity increases only 20% as much as it does in the water-2-propanol solvent, which indicates that the reaction of the hydroxymethyl radical with *p*-nitroperoxybenzoic acid is not, exclusively, a reduction similar to reaction 4. Rather, it appears that I must undergo addition of ·CH₂-OH to yield an adduct which absorbs strongly but which is not as strong an acid as *p*-nitrobenzoic acid (formed by the chain decomposition of II in the water-2-propanol mixture). The data suggest that only 20% of the reaction of ·CH₂-OH with I proceeds by electron transfer.

Concluding Remarks

The question arises whether the OH elimination that has been observed for the peroxy acid radical V can take



place also with other peroxy radicals. The peroxy radical VI formed by the reaction of an alcohol radical with oxygen³ can be considered as a tautomeric form of V. When the equilibrium is laying on the left side, depending on the group R, and it is established fast enough (e.g., by H⁺ catalysis), the OH elimination could take place from the alcohol peroxy radicals. This would lead to the corresponding acid, as has been observed in the radiolysis of acidic oxygen containing solutions of alcohols.²⁰

Acknowledgment. Two of us (R. C. L. and E. H.) wish to express appreciation to Dr. A. Henglein and to the administration of the HMI for having sponsored us through Visiting Professorships at the HMI during the summer of 1973.

(20) M. T. Downes and H. C. Sutton, *J. Chem. Soc., Faraday Trans. 1*, 263 (1973).

Photodecarboxylation of Esters. Photolysis of α - and β -Naphthalenemethyl Derivatives¹⁻³

Richard S. Givens,* Bogdan Matuszewski,⁴ and Charles V. Neywick⁵

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66045. Received February 14, 1974

Abstract: The photochemistry of the three naphthalenemethyl esters, α - and β -naphthalenemethyl phenylacetates (1 and 5) and β -naphthalenemethyl β -naphthylacetate (10), and two benzyl esters, benzyl α - and β -naphthylacetate (8 and 9), was examined in detail. The photodecarboxylation was shown to proceed by way of the singlet state by sensitization and quenching experiments yielding benzyl or naphthalenemethyl (α or β) radicals which coupled or abstracted hydrogen from solvent. Measurements of quantum efficiencies for reaction and for fluorescence and determination of relative reaction rates established the order of reactivity of the five esters as $5 \sim 10 > 1 \gg 8 \sim 9$. Factors affecting the order of reactivity of the esters are also discussed.

Our studies on the photodecarboxylation of arylmethyl esters^{3,6-8} and other investigations of ester photochemistry⁹⁻¹² have shown that photodecarboxylation can be a competitive and often a major photolysis

(1) Mechanistic and Synthetic Studies in Organic Photochemistry. Part XII. For part XI, see R. S. Givens, L. Strekowski, and R. Devonshire, *J. Amer. Chem. Soc.*, **96**, 1631 (1974).

(2) This work was presented at the Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., on Nov 8-10, 1972, Abstract 318a.

(3) A preliminary account of this work has appeared: B. Matuszewski, R. S. Givens, and C. Neywick, *J. Amer. Chem. Soc.*, **95**, 595 (1973).

(4) On leave from A. Mickiewicz University, Poznan, Poland.

(5) NSF Summer Trainee, 1970; NDEA Title IV Fellow, 1971-1973.

(6) R. S. Givens and W. F. Oettle, *J. Org. Chem.*, **37**, 4325 (1972).

(7) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3301 (1971).

(8) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3961 (1971).

(9) (a) T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 1989 (1972), and references cited therein; (b) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Jap.*, **45**, 2571 (1972).

(10) I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969), and references cited therein.

(11) R. Simonaitis and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **91**, 108 (1969), and references cited therein.

(12) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967), and references cited therein.

pathway. We have directed our attention to the naphthyl analogs in an effort to gain more information about the scope and mechanism for the photodecarboxylation reaction. The naphthyl derivatives were selected for study because the naphthyl chromophore absorbs above 300 nm permitting quenching studies that are free of competitive absorption problems, the naphthyl residue has a triplet energy of 57-62 kcal/mol¹³ which does not vary appreciably with alkyl substitution and would be suitable for sensitization studies with available triplet sensitizers, and, finally, a comparison of effects of α - and β -naphthyl systems would be possible. Furthermore, photochemical studies of esters of α - and β -naphthalene carboxylic acids¹⁴ have been reported recently and provide a comparison with this study.

Results

A. Synthetic and Preparative Photochemical Studies. Synthesis of α - and β -naphthalenemethyl phenylace-

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(14) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971).