

Radiation Chemical Studies of the Oxidation of Aniline in Aqueous Solution*

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Dedicated to Professor D. Schulte-Frohlinde on the occasion of his 60th anniversary

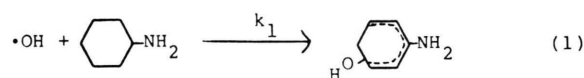
Oxidation of aniline in aqueous solution by $\cdot\text{OH}$ radicals proceeds predominantly via addition to the ring followed by elimination of OH^- on the microsecond time scale to form the aniline radical cation. Direct oxidation by electron transfer accounts for less than 4% of the $\cdot\text{OH}$ reactions. The different hydroxycyclohexadienyl isomers produced by $\cdot\text{OH}$ addition decay at different rates with this decay catalyzed both by protons and phosphate. In basic solution the resultant radical cation deprotonates to form the anilino radical. The pK_a for the equilibrium between the acidic and basic forms of this radical is 7.05 ± 0.05 . Secondary radicals such as $\text{Br}_2\cdot^-$ or $\text{N}_3\cdot$ oxidize aniline directly by electron transfer and allow rapid preparation of the radical cation even in basic solution, as is conclusively demonstrated by observation of the Raman spectrum of the radical cation on the nanosecond time scale at pH 10.4. The deprotonation process can be followed directly by time resolved absorption spectrophotometry in the pH range of 9–11 and is shown to occur via reaction of the radical cation with OH^- at a rate constant of $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Reaction of anilino radical with water is relatively slow ($k \sim 2 \times 10^3 \text{ s}^{-1}$). Time resolved Raman methods show that benzidine radical cation is an important tertiary transient, indicating that second order reaction between radical cations results to an appreciable extent from coupling at ring positions.

The oxidation of aniline in aqueous solution by $\cdot\text{OH}$ radicals has been examined several times by optical pulse radiolysis methods [1, 2] and it has been shown that the predominant intermediate present in acidic solutions, after decay of the initial intermediate, is the aniline radical cation ($\text{C}_6\text{H}_5\text{NH}_2^{\cdot+}$). In basic solution the anilino radical ($\text{C}_6\text{H}_5\text{NH}\cdot$) is formed, as is confirmed by in-situ radiolysis-ESR studies [3]. Interpretable ESR spectra of the intermediates in acidic solution have not as yet been obtained, apparently because of line broadening very likely associated with exchange of the amino protons. However, recent time resolved resonance Raman studies clearly show that at pH 5

the radical cation is present at microsecond times and it has been possible to obtain sufficiently strong Raman signals to assign frequencies to its symmetrical vibrations [4]. The Raman spectrum shows that this radical is structurally very similar to phenoxyl. In basic solution only relatively weak Raman signals attributable to anilino radical, which absorbs less strongly than does the radical cation, are observed [5]. In order to obtain a more complete mechanistic picture of this oxidation process for optimizing the Raman and ESR experiments we have carried out pulse radiolytic studies on a somewhat shorter time scale than used in the previous studies. Many details and complications not previously evident become apparent. In agreement with the previous investigations [1, 2] our studies show that oxidation by $\cdot\text{OH}$ radical occurs predominantly via its addition to the aromatic ring to form amino substituted hydroxycyclohexadienyl radicals

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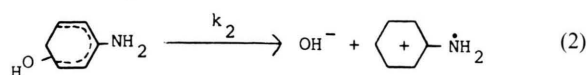
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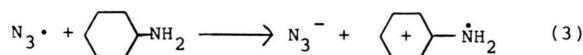
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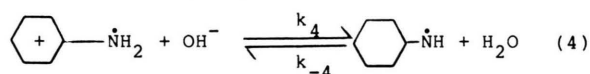
followed by elimination of OH^- from the adduct



to produce the radical cation. Above pH 4 OH^- elimination occurs mainly on the microsecond time scale in contrast to the $\cdot\text{OH}$ oxidation of phenol where formation of phenoxyl radical from the adduct is strongly catalyzed by both acids and bases [6]. We have found it possible to bypass this slow step by using secondary oxidants such as Br_2^- or $\text{N}_3\cdot$ to oxidize aniline directly and rapidly to the cation by electron transfer [7], e.g.



and as a result have been able to follow its deprotonation in basic solution.



We report here our various observations which give a rather detailed picture of the overall oxidation and equilibration processes.

Experimental

Pulse radiolysis methods using optical absorption detection, as employed in this study, have been previously described [8–10]. A 5 ns pulse from the Radiation Laboratory's 8 MeV LINAC produced $\cdot\text{OH}$ radicals at an initial of concentration in N_2O saturated solutions of $\sim 3 \times 10^{-6}$ M. The signals of the transients were recorded digitally and processed locally during the experiments with an LSI 11/2 micro-processor. The resultant data were then transferred to a VAX 11/780 computer for examination of details of both the time and spectral response of the system [10]. Signal averaging methods were used extensively to develop available details. Dosimetry was via a secondary emission monitor calibrated by reference to the thiocyanate dosimeter (10 mM SCN^- ; N_2O saturated) [11].

Time resolved resonance Raman experiments were also carried out, using pulse radiolytic approaches previously described [12], in order to confirm the formation of the radical cation in basic

solution and to examine the second order processes. Raman signals were observed on the microsecond time scale after pulse irradiating 10 mM aniline solutions with 2 MeV electrons. Initial radical concentrations in these cases were $\sim 10^{-4}$ M.

Aniline was vacuum distilled and made up by weight to a known concentration in 18 Megohm water prepared by a Millipore Milli-Q system. Perchloric acid or potassium hydroxide was normally used to adjust the pH of the system. In the pH range of 5–9 appropriate concentrations of monobasic and dibasic sodium phosphates (Baker analyzed) were usually used to buffer the system. An Orion 811 pH meter calibrated with Orion reference buffers was used to determine the pH of these solutions. pH measurements are generally accurate to ± 0.02 units or better. In a number of studies Fluka sodium azide or Baker potassium bromide was used to prepare $\text{N}_3\cdot$ or Br_2^- as a secondary oxidant. Solutions were purged of air and saturated with N_2O to convert e_{aq}^- to $\cdot\text{OH}$ with a flow system being used to replenish the sample between pulses. $\text{C}_6\text{D}_5\text{NH}_2$ obtained from Merck, Sharpe and Dohme was used to examine effects of ring deuteration on the absorption spectra. Experiments were carried out in D_2O to examine effects of amino deuteration.

Results and Discussion

Spectra of the radicals

For reference purposes absorption spectra attributable to the aniline radical cation and the anilino radical observed in studies using azide radical as the oxidant are given in Figure 1. These spectra, which, as commented on below, appear to be without complications from other contributions, were observed $\sim 2 \mu\text{s}$ after pulse irradiating acidic or basic 10^{-3} M solutions of aniline containing 0.1 M sodium azide and saturated with N_2O to convert e_{aq}^- to $\cdot\text{OH}$. The extinction coefficients reported in Fig. 1 are based on a radical yield of 5.5 radicals/100 eV, as is pertinent to reactions with millimolar solutes in N_2O saturated solutions [13, 14]. In these solutions $\cdot\text{OH}$ radical reacts very rapidly with N_3^- ($k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [7], so that $\text{N}_3\cdot$ radical is produced in $\sim 10^{-9}$ s. The $\text{N}_3\cdot$ then serves as a secondary oxidant to oxidize the aniline directly via

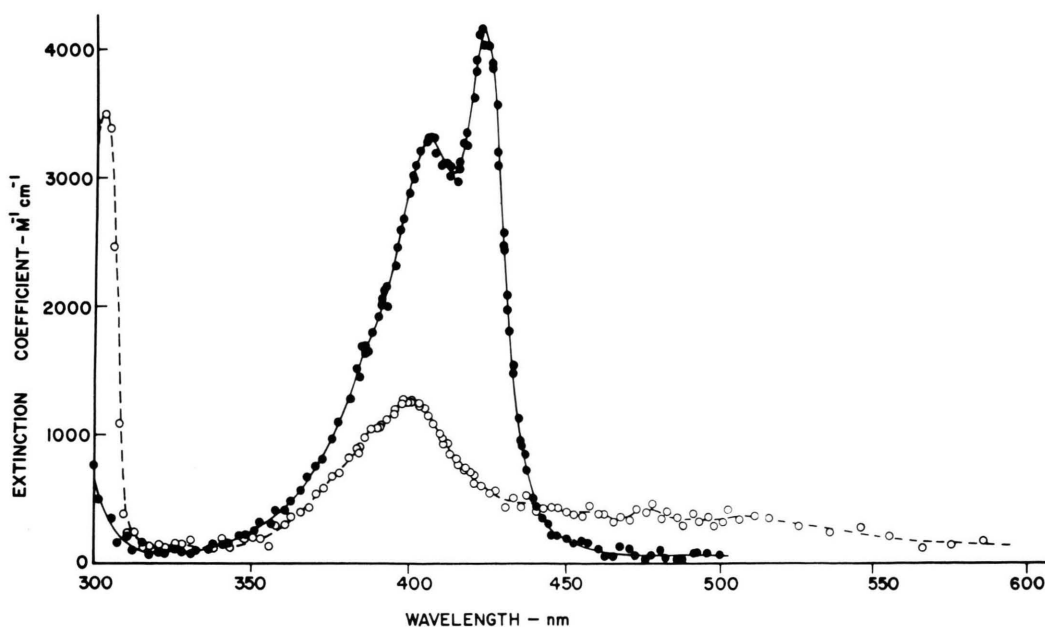


Fig. 1. Absorption spectra of the aniline radical cation (●) and anilino radical (○) observed 2 μ s after pulse irradiating a N_2O saturated solution containing 0.1 M NaN_3 and 0.001 M aniline at, respectively, pH 5.2 and 10.5.

electron transfer (reaction 3) and thus avoid the adduct formed in reaction 1 [7].

The spectrum obtained in acidic solution in Fig. 1 has a moderately intense absorption in the 390–430 nm region with well defined maxima at 406 and 423 nm and very little absorption above 440 nm. In Raman experiments with excitation in the 423 nm band one finds very pronounced resonance enhanced signals which clearly show that this band is attributable to the aniline radical cation [4]. In early flash photolysis studies of aniline solutions at pH 4.6 Land and Porter [15] also found an absorption band in the 380–430 nm region with a maximum at 423 nm which they attributed to the radical cation. The spectrum of Fig. 1 represents a more well resolved version of their reported spectrum. In pulse radiolysis studies both Wigger *et al.* [1] and Christensen [2] have reported that reaction of $\cdot OH$ with aniline initially results in an intermediate absorbing at ~ 350 nm (presumably the $\cdot OH$ adduct) which in acidic solutions decays on the microsecond time scale to give the aniline radical cation with a broad absorption at ~ 420 nm. In basic solution they attributed a weak absorption at 400 nm to the anilino radical. Our studies of the $\cdot OH$ oxidation

process (see below) show spectra at long times which are qualitatively similar to these previous results but somewhat complicated by the presence of contributions from other transients. The spectra of Fig. 1 are by far the simplest we have observed among the various oxidants and in particular exhibit only a low absorption in the region of 350 nm where Christensen [2] has shown that the cyclohexadienyl radicals produced by H atom addition absorb significantly. We conclude that the H atoms produced in the radiolysis of N_2O saturated solutions at a yield of 0.52 [13, 16] are effectively removed by reaction with the azide.

From Fig. 1 the extinction coefficients of the aniline radical cation at its 406 and 423 nm maxima are, respectively, 3310 and 4110 $M^{-1} cm^{-1}$. The latter value is approximately twice that estimated by Land and Porter [15], but should be accurate to $\pm 200 M^{-1} cm^{-1}$ [14]. The extinction coefficient of anilino radical at its 401 nm maximum is $1250 \pm 50 M^{-1} cm^{-1}$.

The structure in the spectrum of the radical cation exhibited in Fig. 1 very closely resembles that of phenoxyl radical [12, 17], with which it is isoelectronic, suggesting that the band at 423 nm

corresponds to a transition between the lowest vibrational levels of the ground and excited states. The frequency difference ($\sim 1050\text{ cm}^{-1}$), though slightly less than in the case of phenoxyl, indicates that the band at 406 nm involves a relatively high frequency vibration in the excited state. Although the anilino radical and its radical cation are also isoelectronic, both their optical absorption and Raman spectrum [5] are quite different indicating a large change in the electronic structure on deprotonation.

Deuterium substitution has only a minor effect on the absorption spectrum of the radical cation. As with phenoxyl radical complete deuteration of the ring shifts the principal absorption to shorter wavelengths by less than 1 nm with very little change in intensity. The change in the appearance of the $1 \leftarrow 0$ transition found for phenoxyl [12] is not observed in the present case. Deuteration of the amino group has a modestly greater effect, shifting the absorption to shorter wavelengths by $\sim 1.5\text{ nm}$ with about a 5% increase in intensity.

The acid-base equilibrium

The pK_a for acidic dissociation of aniline radical cation has been estimated by Land and Porter to be ~ 7.0 [15]. As is shown below the dissociation equilibrium is, in fact, controlled by the reaction of the cation with base (reaction 4). We have examined the pH dependence of the contribution of the radical cation as manifested by the relative absorbance at 423 nm following $\cdot\text{OH}$ oxidation. Measurements made over the interval 20–30 μs after the pulse in 10^{-2} M phosphate buffer, when decay of the OH adduct and equilibration are complete, fit a simple titration curve extremely well (Figure 2). The inflection point corresponds to a pK_a of 7.05 ± 0.05 , with the stated error limits determined from the standard deviation between the data and the sigmoidal titration curve between pH 6.5 and 7.5. The slope of the latter at its inflection point, calculated from the difference between the acidic and basic forms of the radical [18], agrees with the observed dependence, giving assurance that artifacts do not contribute significantly to the equilibrium processes in the region of pH 7.

Oxidation by $\cdot\text{OH}$

During the present study the rate constants for reaction of $\cdot\text{OH}$ with aniline were determined from

the product buildup kinetics for a solution $2 \times 10^{-4}\text{ M}$ in aniline in both acidic and basic solutions. In order to avoid complications from reaction 2 measurements were made at isosbestic points between the $\cdot\text{OH}$ adducts and the aniline radicals (375 nm in acidic solution; 395 nm in basic solution; see below). The measured rate constants are $8.9 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ at pH 5.0 and $7.3 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ at pH 11.1. Correcting the latter for the presence of 14% O_2^- , which reacts at a lower rate (see below), we obtain a rate constant of $8.2 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ for reaction of $\cdot\text{OH}$ at pH 11.1. Since the rate constant should be independent of pH over this range the small difference appears to result largely from uncertainties in interpretation of the growth curves. From the combined results the rate constant for reaction 1 is $8.6 \pm 0.4 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$. This value is similar to determinations

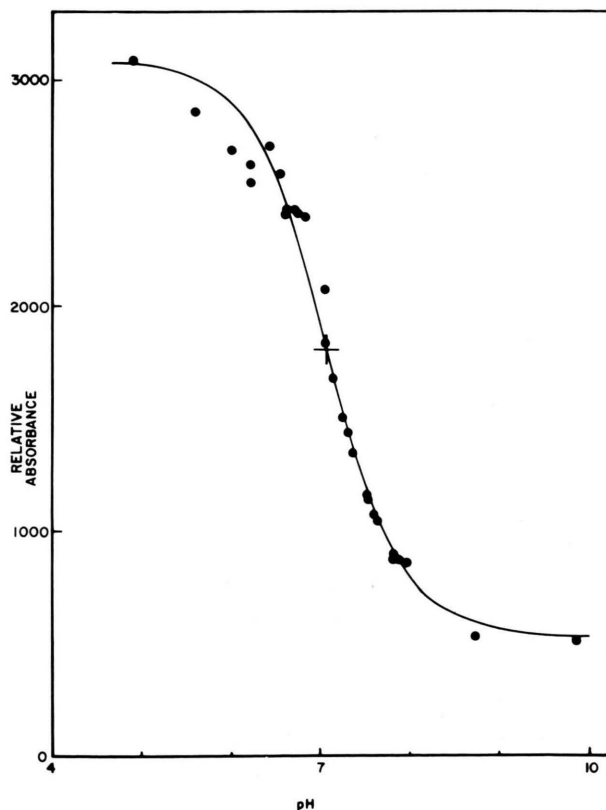


Fig. 2. pH dependence of the relative absorbance observed 20–30 μs after pulse irradiating a N_2O saturated solution 0.001 M in aniline also containing 0.01 M phosphate. The sigmoidal curve corresponds to simple equilibrium with $pK_a = 7.05$.

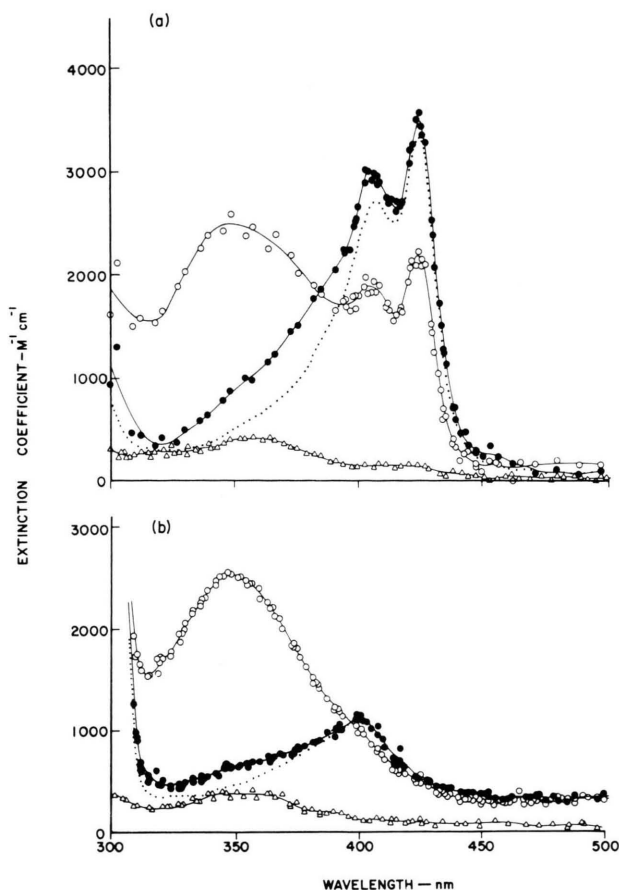


Fig. 3. Absorption spectra observed at (○) 2 and at (●) 24 μ s and (△) for solutions also containing 0.2 M tert-butyl alcohol after pulse irradiating a N_2O saturated 0.001 M aniline solutions (a) at pH 5.2 and (b) at pH 9.0. The sum of the contributions expected from Fig. 1 and the H atoms adducts is given by the dotted spectra.

made by competitive methods (Matthews and Sangster ($7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [19] and Anbar, Meyerstein and Neta ($8.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [20]), but considerably lower than the value of $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ given by the previous pulse radiolysis studies of Christensen [2]. We note here that when growth is followed by rapid decay one tends to underestimate the initial reaction period and as a result overestimate the rate constant. This problem is avoided in the present study by working at the isosbestic points.

In a 1 mM aniline solution reaction of $\cdot\text{OH}$ will, from the above rate constant, be essentially complete in less than 1 μ s. As indicated by the dotted curves in Fig. 3 and also as reported by the previous

investigators [1, 2] the spectra observed immediately after pulse irradiating a N_2O saturated 1 mM aniline solution are dominated by a broad absorption band at 350 nm which can be attributed to the mixture of hydroxycyclohexadienyl radicals resulting from $\cdot\text{OH}$ addition. This absorption largely decays on the microsecond time scale so that the spectra observed 24 μ s after the pulse, given by the solid curves in Fig. 3, have features similar to those found with azide oxidation. It is seen, however, that these latter spectra exhibit appreciable absorption at ~ 350 nm whereas very little is found in the case of azide oxidation. Experiments with tert-butyl alcohol added to selectively remove $\cdot\text{OH}$ radicals show that the observed difference can be largely attributed to the H atom adducts. In the experiment at pH 5 at 24 μ s there is, however, additional absorption of $\sim 350 \text{ M}^{-1} \text{ cm}^{-1}$ which indicates that $\sim 10\%$ of the radicals are still of a hydroxycyclohexadienyl type even though decay, from the apparent period of 3.5 μ s, should be virtually complete. We will comment on this point below. Since about 10% of the radicals will have been consumed in second order processes the concentration of the radical cation at 24 μ s will be only $\sim 80\%$ of the $\cdot\text{OH}$ radicals initially produced. If we correct for this factor the contribution attributable to the radical cation at 423 nm in Fig. 3a ($3300 \text{ M}^{-1} \text{ cm}^{-1}$) corresponds to an extinction coefficient of $4125 \text{ M}^{-1} \text{ cm}^{-1}$, corroborating the determination using azide oxidation. It is noted that if the observed spectrum is only corrected for the contribution from H atom addition the spectrum attributed to the radical cation will be distorted toward shorter wavelengths and the extinction coefficient of the peak at 423 nm underestimated. At pH 9.0 the absorption at 350 nm is slightly in excess of the sum of the signals expected from anilino radical and the H atom adduct, after corrected for decay. The observed difference indicates that $\sim 5\%$ of the OH adducts still contribute at the observation time in basic solution.

The time dependence of the absorbance at 423 nm (Fig. 4), taken in the absence of phosphate, shows that the initial absorbance is very low. Extrapolation to zero time gives an initial value of $330 \text{ M}^{-1} \text{ cm}^{-1}$, which places an upper limit of 9% on the fraction of $\cdot\text{OH}$ radicals which oxidize aniline directly to the radical cation by electron transfer. However, from the spectrum observed at 0.1 μ s (Fig. 5a) we estimate that more than half of this

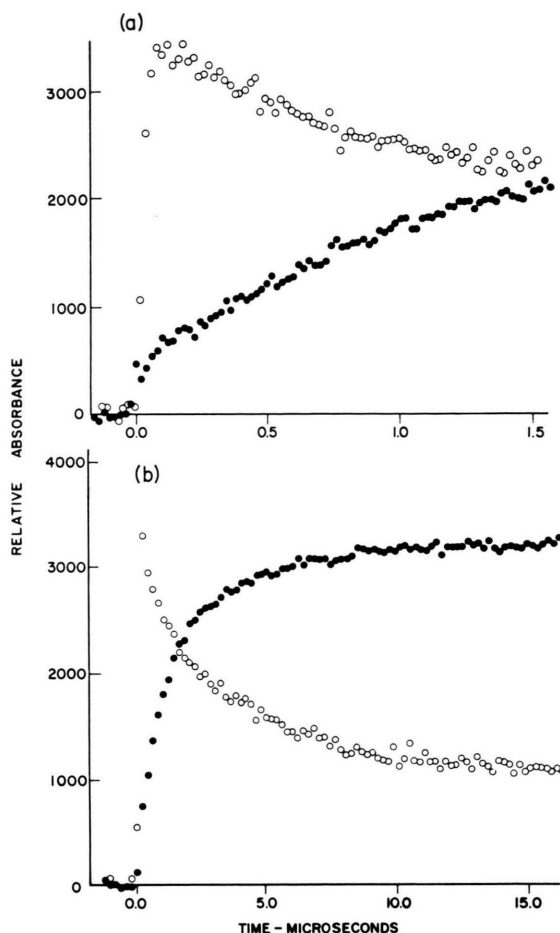


Fig. 4. Time dependence of the relative absorbance observed at 423 nm (●) and at 350 nm (○) for a solution containing 0.01 M aniline at pH 5.2 in the absence of buffer at (a) 20 ns/pulse, (b) 200 ns/pulse.

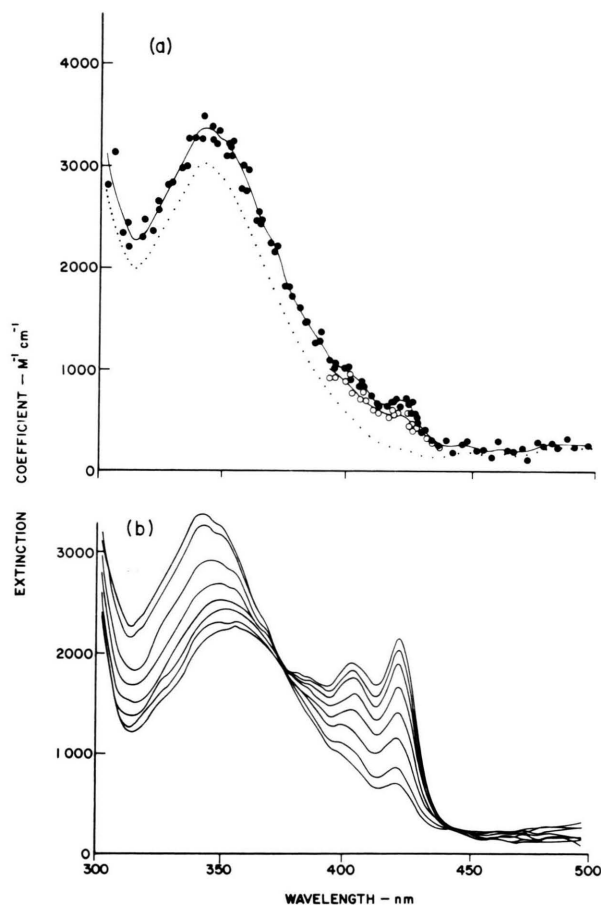


Fig. 5. (A) Absorption spectra observed (○) 0.05 microsecond and (●) 0.1 microseconds after pulse irradiating a 10 mM aniline solution (N_2O saturated) at pH 5.2. (B): Absorption spectra observed 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 microseconds after the pulse. Absorption monotonically decreases with time at 350 nm and increases at 423 nm.

absorbance is attributable to H atom and OH radical adducts. OH radicals clearly react mainly by addition with direct oxidation by electron transfer from aniline accounting for less than 4% of the reaction path.

Decay of the $\cdot OH$ adducts

In the previous studies decay of the hydroxycyclohexadienyl radicals was treated on the assumption that the observed time dependence could be characterized by a simple exponential. That this is

not so is readily seen in Fig. 4 where in the absence of phosphate both the decrease in absorbance observed at 350 nm and the increase found at 423 nm manifest a rapidly decaying component having a period $\sim 0.5 \mu s$ and additional components with periods ~ 2 and $10 \mu s$. A longer lived component must also be present since the absorbance at $15 \mu s$ is still rising and is only 80% of that expected from the other studies. These measurements were made at pH 5.2 in a 10^{-2} M aniline solution where addition of $\cdot OH$ is complete in $\sim 0.1 \mu s$. Because four isomeric hydroxycyclohexadienyl radicals are ex-

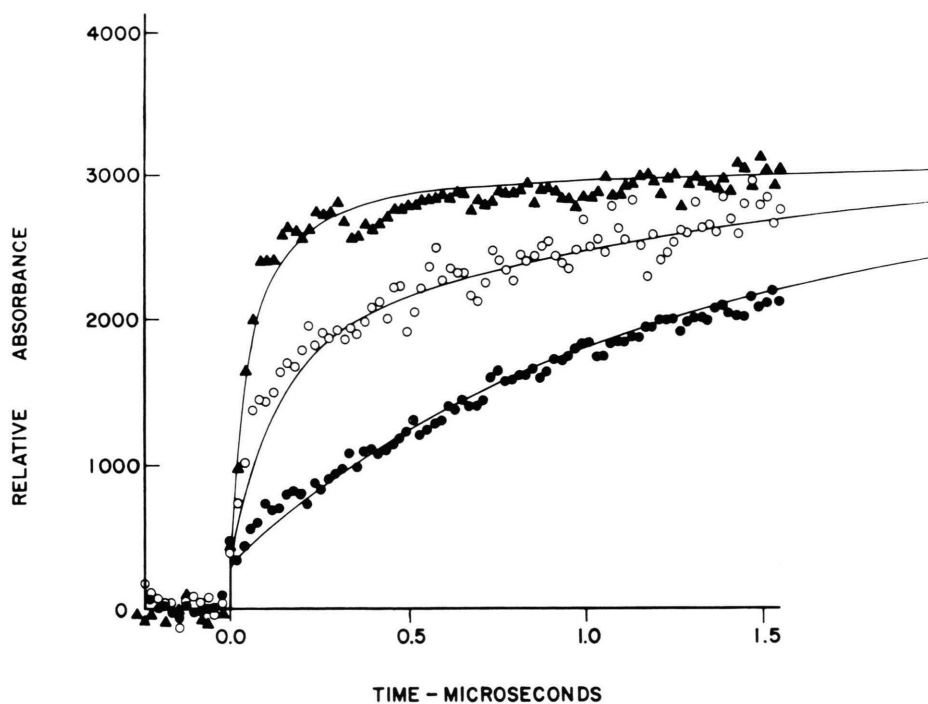


Fig. 6. Growth of the radical cation as observed at 423 nm for solutions containing (●) 0, (Δ) 1.3, (○) 6.8, and (▲) 23 mM NaH_2PO_4 at pH ~ 5.2 .

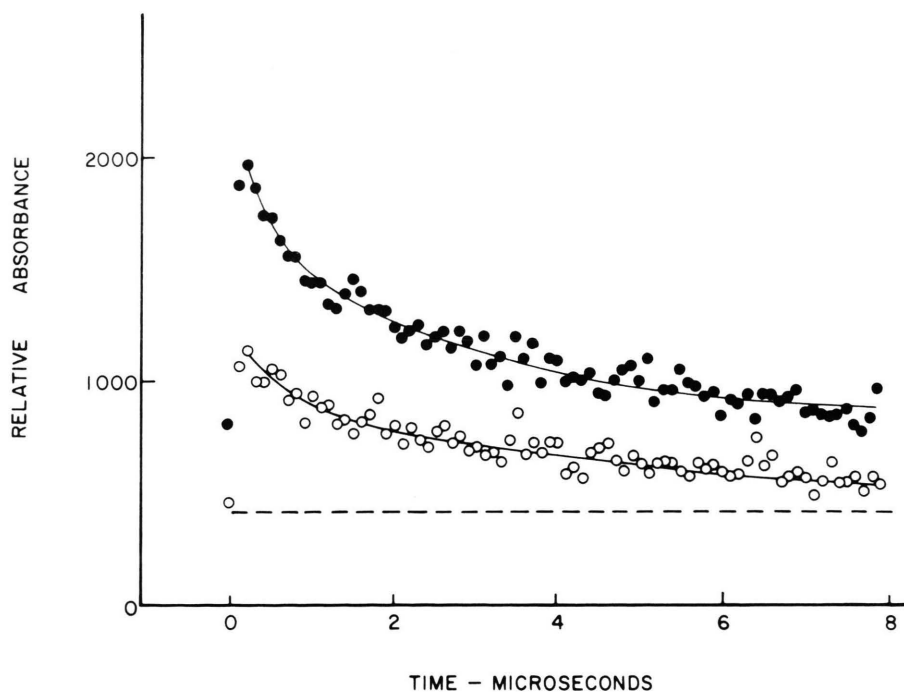


Fig. 7. Decay of aminohydroxycyclohexadienyl radicals as observed at 350 nm (●) at pH 12. (—) and (○) at pH 13.4.

pected to be produced in reaction 1, it is not surprising that the decay pattern is complex, as was previously suggested in the case of $\cdot\text{OH}$ oxidation of phenol [6]. The curves given in Fig. 4 are calculated on the assumption that there are four different contributions with half periods of 0.6, 1.4, 7.0 and 30.0 μs , also taking into account second order decay of the radicals with the rate constant as described below. From the growth of the radical cation signal these different components have approximate fractional contributions of 0.40, 0.35, 0.15 and 0.10, suggesting that addition may be near to statistical. However, in the present case, because their lifetimes do not differ greatly, it is difficult to resolve the different contributions accurately.

One notes in Fig. 5b that with time there is a significant shift of the absorption maximum of the OH adducts (from 344 nm at 0.1 μs to 355 nm at 1.5 μs). This shift demonstrates quite conclusively that there must be several contributions, with the species absorbing at the shorter wavelength decaying more rapidly than that absorbing at the longer wavelength. The shorter lived component absorbs more nearly like the unsubstituted hydroxycyclohexadienyl radical than the others, indicating that the amino group has a minimum interaction with the radical's π electronic system and is, therefore, at a position of low spin density. This aspect suggests it is the 2 amino hydroxycyclohexadienyl radicals produced by $\cdot\text{OH}$ addition at the meta position. While it is also possible that it represents $\cdot\text{OH}$ addition to the nitrogen, as suggested by Wigger *et al.* [1] one would expect such a radical to transfer an electron rapidly and thus be very short lived.

In one early experiment 10 mM phosphate was used in solutions near neutral to control the pH and catalyze equilibration. As the experiments progressed it became obvious that the phosphate also catalyzed decay of the hydroxycyclohexadienyl radicals appreciably. This aspect is illustrated very well in Fig. 6 where it is seen that 70% of the radical cation is produced in 0.5 μs in the presence of 23 mM phosphate but only 25% in its absence. The rapid initial growth of the cation signal seen in Fig. 6 is also reflected by a similarly rapid decay of the adduct signal. Dihydrogen phosphate clearly acts as a proton donor, catalyzing the loss of OH^- . From the data of Fig. 6 we estimate that at phosphate concentrations ~ 10 mM the decay rates are increased by about an order of magnitude. This

increase corresponds to catalytic coefficients in the range $10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$, depending on the isomer. As a result the more stable isomers decay on the microsecond time scale so that decay is about 90% complete at $\sim 20 \mu\text{s}$. The previous reports of a decay with a period of 2–5 μs [1, 2] appear to be largely the result of apparatus constraints that limited observations to the microsecond time frame. Even in the presence of 23 mM phosphate there is a small component of decay of the adduct on the 10 μs time scale so it is, in retrospect, not surprising that a contribution to the absorption spectrum remains at this time in Figure 3.

Oxidation by O^-

The pK_a of $\cdot\text{OH}$ radical is 11.9 [21] so that at high pH it is converted to O^- . This latter radical does not add to aromatic systems rapidly and reacts with aniline somewhat more slowly than does $\cdot\text{OH}$ [22–24]. The rate constant measured at pH 13.6 is, after correction for the 2% $\cdot\text{OH}$ remaining, $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value compares favorably with rate constants, of 1.6×10^9 and $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ given previously [2, 23].

Even at pH 13.5 a moderately strong absorbance is observed at 350 nm. It is seen in Fig. 7 that this absorbance decays appreciably on the microsecond time scale. The transient component is attributable to hydroxycyclohexadienyl type radicals. The initial magnitude of this component ($\sim 700 \text{ M}^{-1} \text{ cm}^{-1}$ at pH 13.5) is somewhat in excess of the contribution expected from $\cdot\text{OH}$ addition ($\sim 300 \text{ M}^{-1} \text{ cm}^{-1}$). We estimate from this that $\sim 10\%$ of O^- reacts by addition to the ring, i.e., that the partial rate constant for O^- addition is $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This value is, however, somewhat higher than expected from the rate constants found for addition of O^- to other aromatic systems [23, 24] so it needs confirmation by more extensive studies. At longer times the signal at 350 nm decays to a relative absorbance of $\sim 400 \text{ M}^{-1} \text{ cm}^{-1}$, as expected from the sum of contributions from the anilino radical and the H atom adducts. Of particular importance is the decay noted in Fig. 7, which exhibits contributions of ~ 1 and $\sim 6 \mu\text{s}$ even at very high pH, showing that complete loss of OH^- from the adducts is surprisingly slow in strong base. Decay appears to be complete at $\sim 20 \mu\text{s}$ and the resultant spectrum is essentially the sum of the expected contributions from the anilino radical and the H atom adducts.

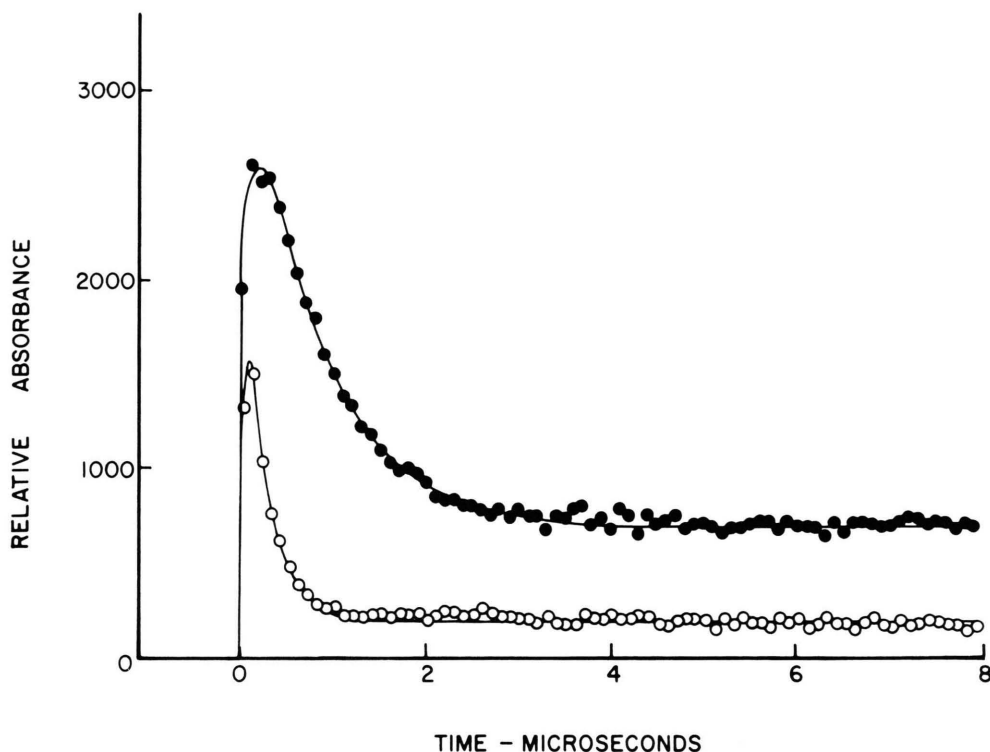


Fig. 8. Time dependence of optical absorbance (○) at 360 nm and (●) at 423 nm for a N_2O saturated solution containing 0.1 M Br_2^- and 0.01 M aniline at pH 9.7. The signal at 360 nm represents the decay of Br_2^- . A transient signal having a decay half period of 0.53 μs is observed at 423 nm after decay of the Br_2^- is complete. This latter signal is attributable to the radical cation initially found in the oxidation by Br_2^- .

Oxidation by Br_2^-

The rate constant for oxidation of aniline by Br_2^- , as determined from the decay of the absorbance of the latter at 360 nm in 0.1 M Br_2^- solutions, is $2.1 \pm 0.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and independent of pH from 5.9 to 11.3. The spectrum observed at 2 μs for a solution 0.01 M in aniline and 0.2 M in KBr at pH 5.9 is, after correction for the H atom adduct and the trace of Br_2^- remaining, as given for the radical cation in Figure 1. There is no indication of any addition of bromine. In this case oxidation appears to occur entirely by electron transfer to the Br_2^- .

At pH 9.7, for a solution 10^{-2} M in aniline, one observes a signal at 423 nm which decays with a half period of 0.53 μs after the Br_2^- has completely decayed (Figure 8). This transient is attributed to the radical cation produced by electron transfer to Br_2^- with the decay manifesting its deprotonation

by reaction with base. We estimate that the rate constant for reaction 4 is approximately $2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The Br_2^- absorption, however, interferes in measurements at shorter times and effectively precludes detailed studies of this intermediate at significantly higher pH values.

Oxidation by azide

Azide radical is a considerably better secondary oxidant than Br_2^- in that it does not absorb significantly at wavelengths longer than 300 nm and allows the initial buildup of the radical products to be followed readily. The rate constant for reaction 3, as determined from the growth of the anilino signal in 10^{-4} M aniline solution, is $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 12. Under these conditions equilibration is more rapid than oxidation (see below) so that the growth period should accurately reflect the rate for reac-

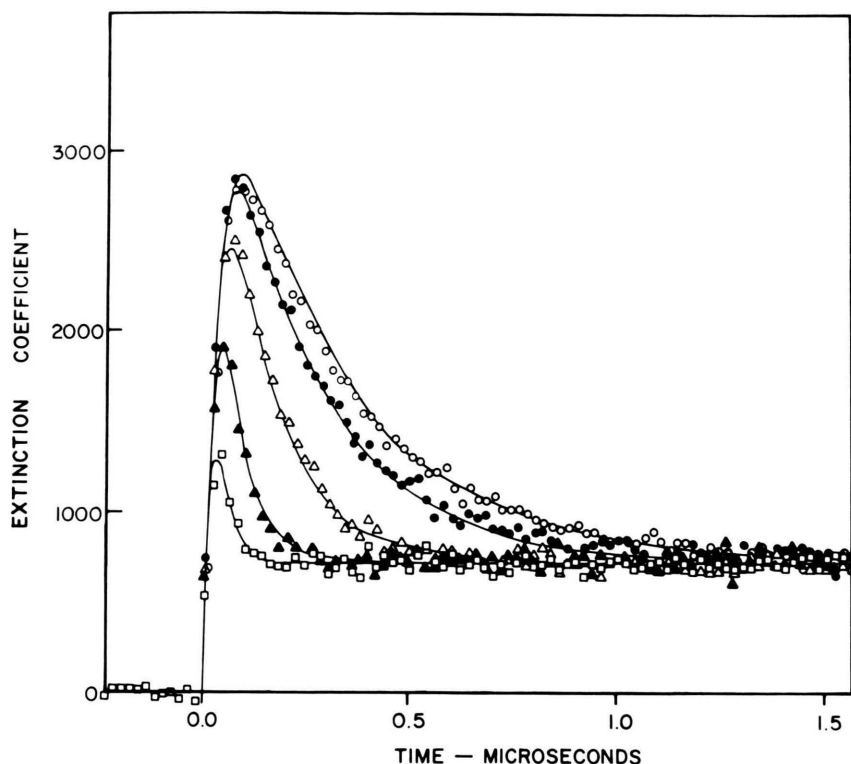


Fig. 9. Time dependence of the absorption at 423 nm at pH (○) 10.05, (●) 10.26, (△) 10.50, (▲) 11.00, (□) 11.43 for a N_2O saturated solution 0.1 M in sodium azide and 10^{-2} M in aniline. Curves are calculated assuring that reactions 3 and 4 occur consecutively with k_3 taken as $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and k_4 ($\sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) optimized for best fit of the data.

tion 3. This value is in very good agreement with the previous measurement of $4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [7].

Because the pK_a for protonation of aniline is low (4.6) one does not expect the rate for its oxidation by $\text{N}_3\cdot$ to be strongly dependent on acidity above pH 5. Examination of the time dependence of the radical cation signal in a 10^{-4} M aniline solution at pH 5.4 showed the growth to be exponential with a period corresponding to a rate constant of $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is in agreement with the previous determination [7] but 10% lower than found in basic solution. This slight difference very likely reflects a low rate for oxidation of anilinium ion by $\text{N}_3\cdot$.

At concentrations above 10^{-3} M the time dependence in acidic solutions is no longer exponential but rather exhibits two components, as found in the case of $\text{N}_3\cdot$ oxidation of p-methoxyphenol [7]. For a solution 10^{-2} M in aniline the signal at 423 nm initially increases on the nanosecond time scale at the rate expected from the rate constant reported above. However, after oxidation is $\sim 75\%$ complete additional oxidation occurs on the microsecond

time scale with the rate being proportional to the acid concentration. Similar spectra were observed at both short and long times so that two oxidation paths, both of which produce the radical cation, are implicated. The explanation previously given in the case of p-methoxyphenol cannot apply here since the nature of the substrate is not affected by pH. Rather the nature of the oxidizing species in acidic solution must be brought into question. At this point it seems likely that $\cdot\text{OH}$ oxidation of azide yields, in part, an intermediate which decomposes to $\text{N}_3\cdot$ only on the microsecond time scale in an acid catalyzed process. Such a two step process would be expected to affect the secondary oxidation only when carried out at very high substrate concentrations. Aspects of this problem are currently being examined in more detail.

Deprotonation of the radical cation by OH^-

In basic solution it is clear from the strong absorption initially observed at 423 nm (Fig. 9) that with azide radical, as with Br_2^- , oxidation takes

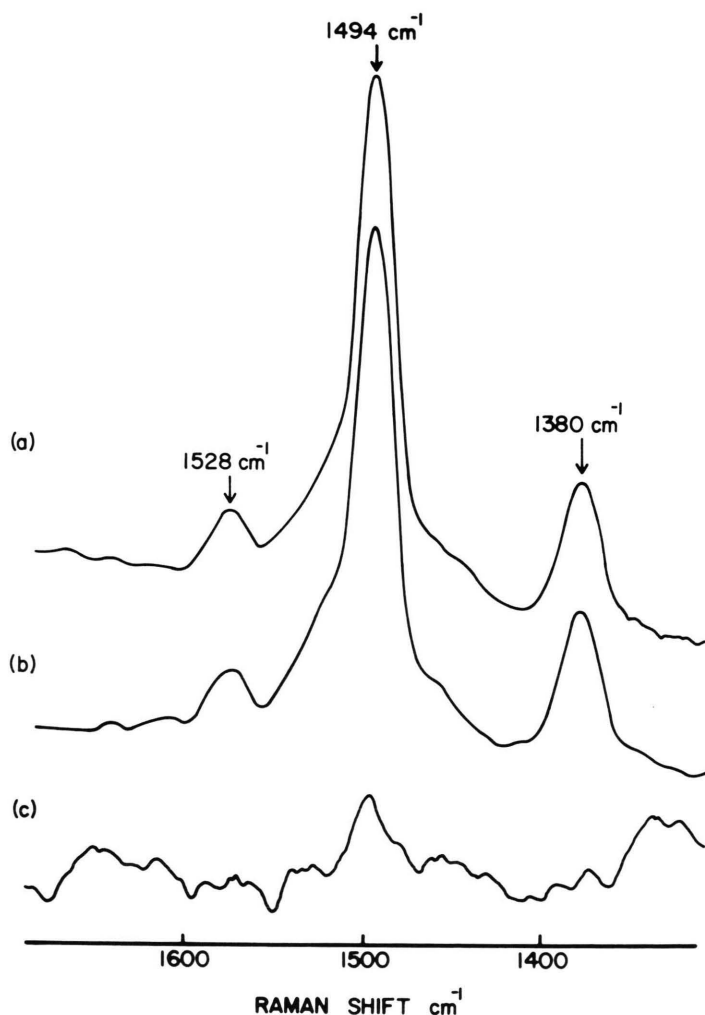


Fig. 10. Raman emission characteristic of the aniline radical cation observed 0.1 μ s after pulse irradiating a N_2O saturated 0.1 M sodium azide solution containing 10^{-2} M aniline at (a) pH 6.23 (scaled by a factor of 0.13) and (b) at pH 10.4. Excitation was in the absorption band of the radical cation at 423 nm. The 1494 cm^{-1} signal decays by a factor of 6 at 0.3 μ s, as indicated in (c) and is absent at 0.5 μ s. Spectra a and b represent averages of 15,000 experiments. Spectrum c is noisier because only 1000 experiments were averaged.

place via electron transfer followed by deprotonation of the resultant radical cation. Reaction is primarily via this path since the maximum intensity of the 423 nm signal is, within errors of interpretation, as expected from the measurements in acidic solution after appropriately taking into account the growth and decay kinetics. It is especially interesting to note in Fig. 9 that initial production of the radical cation is manifest by its absorption even up to pH 11.5, 4.5 units above the equilibrium point.

That the radical cation is initially produced in basic solution is conclusively demonstrated by the Raman spectrum observed 0.1 μ s after pulse irradiating a solution 10^{-2} M in aniline and 10^{-1} M in sodium azide at pH 10.4. One sees in Fig. 10 strong Raman emission at 1494 cm^{-1} characteristic of the

aniline radical cation [4]. This signal decays by a factor of 6 at 0.3 μ s and is not observably present at 0.5 μ s. We estimate a decay half period of 0.08 μ s from the Raman studies, in good agreement with the period expected at this pH from the absorption measurements. Quantitative studies of deprotonation at lower pH values by Raman methods are, at the moment, effectively precluded by the necessarily high required doses which result in the radiolytic production of $\sim 10^{-4}$ M OH^- . The sensitivity is insufficient for studies at significantly higher pH values.

The pseudo first order rate constant for deprotonation, determined by fitting the absorption data to curves calculated assuming that reactions 3 and 4 occur consecutively, are given in Figure 11. The

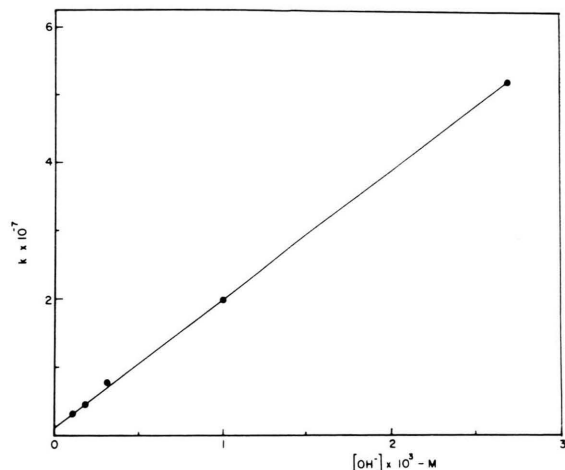


Fig. 11. Hydroxide ion dependence of the pseudo first order rate constant determined from the field of the data of Fig. 9. From the slope of the linear dependence the rate constant for deprotonation of the radical cation by reaction with base is determined to be $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

linear dependence on base concentration shown in that figure corresponds to $k_4 = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In a similar study deprotonation of the N-methylaniline radical cation by OH^- was found to be $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [7]. Schmidt, Bromberg and Meisel [21] have recently reported that the diphenylamino radical cation produced by flash photolysis of the $\cdot\text{OH}$ adduct also reacts with OH^- at a rate constant of $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. It is clear that in basic solution the rate of deprotonation of these radicals is essentially controlled by diffusion of OH^- . From the equilibrium constant ($K_4 = 1.12 \times 10^7$) the pseudo first order rate constant for reaction of anilino radical with water (k_{-4}) is $2.0 \times 10^3 \text{ s}^{-1}$ which implies that in neutral solution the half period for equilibration should be $\sim 175 \mu\text{s}$. The data of Fig. 11, however, show a considerably greater intercept ($4 \times 10^5 \text{ s}^{-1}$) than expected from the above so we must assume that deprotonation is catalyzed by the presence of azide which appears to act as a weak base in the present instance. Acidic dissociation of the radical cation cannot play a significant role here, as it does in the case of the diphenylamino radical cation where the pK_a is much lower (4.25) [21], since such would imply an unreasonably high rate constant for reaction of the anilino radical with hydrogen ion in order for the limiting deprotonation

rate to be as high as is indicated by the intercept of Figure 11.

Second order reactions

It is difficult to determine the second order rate constant for reaction between the aniline radicals accurately by optical absorption techniques because the products absorb appreciably in the same region as the radicals. One finds, for example, that in acidic solutions the absorption at 423 nm changes very little over the first several hundred microseconds after the pulse even though there is an appreciable increase at longer wavelengths. It is clear from this latter observation that the radical cations, in fact, combine on the hundred microsecond time scale. Since the radical concentration is only micromolar the second order rate constant must be of the magnitude of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ but lack of optical resolution between the individual components makes more detailed interpretation questionable. Raman spectroscopy provides the selectivity required to examine the individual components. Time resolved resonance Raman studies of the decay of the radical cation produced from 10 mM aniline by azide oxidation at pH 5 give the results of Figure 12. The decay

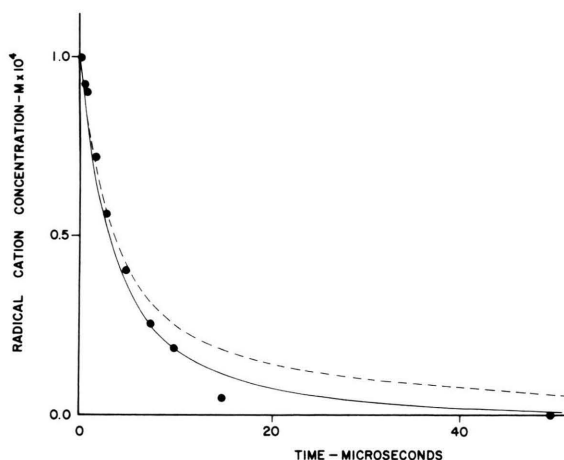


Fig. 12. Decay of the aniline radical cation (●) as determined from the time dependence of the Raman signals at 1494 cm^{-1} and 1614 cm^{-1} , respectively. Excitation was at 423 nm. Dashed curve represents the expected decay of the aniline radical cation taking $2k_5$ as $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Solid curve approximately takes into account reaction electron transfer to the radical cation from benzidine and other radicals and products that buildup as the reaction progresses using numerical integration methods. The rate constant for reaction 7 and similar reactions is taken as $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

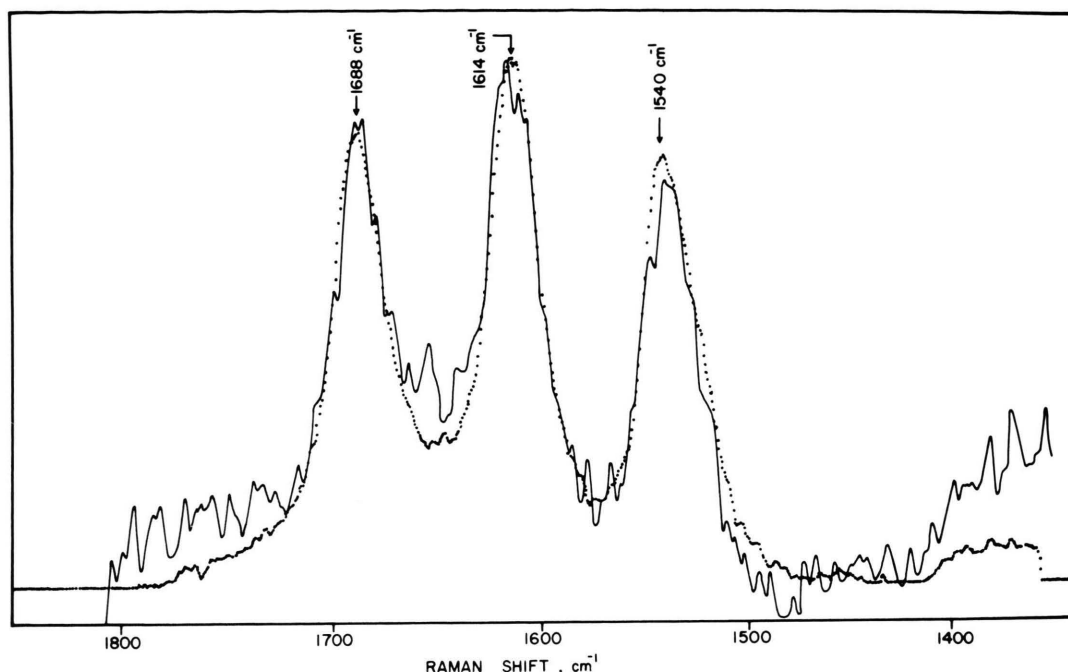
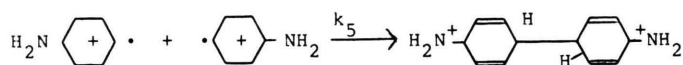


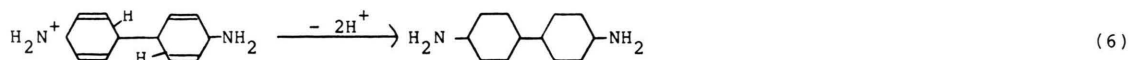
Fig. 13. Raman signals observed 50 μs after oxidation of aniline (solid spectrum) and benzidine (dotted spectrum); at a relative sensitivity of 0.15 by $\text{N}_3\cdot$. Excitation is in the 450 nm absorption band of the benzidine radical cation.

pattern is similar to that previously noted for phenoxyl. Initially the radical decays at a rate corresponding to a second order rate constant for reaction between like radicals ($2k$) of $\sim 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. However, as product builds up decay is more rapid than expected solely from second order processes because of a superimposed reaction of the radical cations with the products. During the course of this study it was, in fact, noted that as the Raman signals of the aniline radical cation at 1494 cm^{-1} decreased, three rather intense lines appeared at

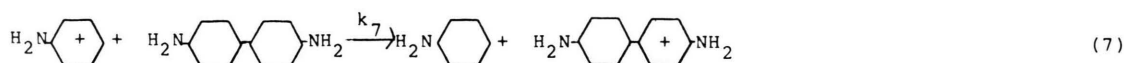
1688 , 1614 and 1540 cm^{-1} . These latter frequencies are those of the benzidine radical cation as reported by Hester [26]. Raman signals observed 100 μs after oxidizing aniline with $\text{N}_3\cdot$, with excitation at 450 nm where the benzidine radical cation has an extinction coefficient of $\sim 25,000 \text{ M}^{-1} \text{ cm}^{-1}$, are reported in Figure 13. It is seen in this figure that the features are identical to that of the radical produced directly from benzidine. It is clear from this result that coupling of the radical cations at the para positions



represents a major fate of the radicals. Presumably reaction 5 is followed by deprotonation



to give benzidine which is subsequently oxidized by electron transfer to the aniline radical cation still remaining in the system.



Because the product concentration is $\sim 10^{-4}$ M in these Raman studies processes such as the latter, which should have a rate constant $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$, explain the rapid decay of the aniline radical cation on the microsecond time scale. Since production of the benzidine radical via this mechanism requires three radicals we estimate from the relative intensities in Fig. 13 that more than 30% of the second order processes involve coupling at the 4 positions of the two radicals. One, of course, expects that isomers of the benzidine radical will also be produced but these are not apparent under the conditions of our experiment. In any event the present observations show that, as with phenoxyl [12], coupling of these radicals at ring positions is very important in the oxidation and a direct result of delocalization of the unpaired spin density to the 2, 4 and 6 positions of the ring.

We find that when aniline is oxidized directly with OH that the signals of the benzidine radical cation are very weak. It is noted that production of

this radical cation requires rapid deprotonation of the product of the coupling via reaction 6 so that electron transfer will occur only if benzidine is formed before the initial radicals have completely decayed. Apparently azide acts as a base in deprotonating the initial product formed in reaction 5. Deprotonation appears to be sufficiently slow in the case of direct oxidation by $\cdot\text{OH}$ that the initial radicals will have largely decayed before the benzidine appears.

In general we must conclude that for systems such as this, pulse experiments will give qualitatively different reaction products than found in steady state experiments since in the latter case the initial radicals will be rapidly removed by tertiary processes. As a result the course of the overall reaction will be altered appreciably. If one wishes to examine products of second order processes studies must largely be carried out using appropriate pulse methods.

- [1] A. Wigger, W. Grunbein, A. Henglein, and E. J. Land, *Z. Naturforsch.* **24b**, 1262 (1969).
- [2] H. Christensen, *Int. J. Radiat. Phys. Chem.* **4**, 311 (1972).
- [3] P. Neta and R. W. Fessenden, *J. Chem. Phys.* **78**, 523 (1974).
- [4] G. N. R. Tripathi and R. H. Schuler, *Chem. Phys. Letters* **110**, 542 (1984).
- [5] G. N. R. Tripathi and R. H. Schuler, *Proceedings of the Ninth International Conference on Raman Spectroscopy*, The Chemical Society of Japan, Tokyo, Japan, 1984, page 326.
- [6] E. J. Land and M. Ebert, *Trans. Faraday Soc.* **63**, 1181 (1967).
- [7] Z. Alfassi and R. H. Schuler, *J. Phys. Chem.*, in press.
- [8] L. K. Patterson and J. Lilie, *Int. J. Radiat. Phys. Chem.* **6**, 129 (1974).
- [9] E. Janata and R. H. Schuler, *J. Phys. Chem.* **68**, 1078 (1982).
- [10] R. H. Schuler, *Chemistry Education*, in press. Available from the author as report NDRL-2687.
- [11] R. H. Schuler, L. K. Patterson, and E. Janata, *J. Phys. Chem.* **84**, 2088 (1980).
- [12] G. N. R. Tripathi and R. H. Schuler, *J. Chem. Phys.* **81**, 113 (1984).
- [13] R. H. Schuler, A. L. Hartzell, and B. Behar, *J. Phys. Chem.* **85**, 192 (1981).
- [14] While the initial yield of azide radicals for 0.1 M N_3^- sodium azide solution is expected to be much higher (see [13]) examination of the concentration dependence of the azide signals shows that the yield available for oxidation at microsecond times is not appreciably dependent on azide concentration. As with $\cdot\text{OH}$ radicals, azide radicals produced within the radiation track appear to be lost to subsequent track processes and do not contribute to the secondary oxidations. While it is likely that the yield of 5.5 used here is accurate to better than 5% final resolution of this point awaits the results of investigations currently in progress.
- [15] E. J. Land and G. Porter, *Trans. Faraday Soc.* **59**, 2027 (1963).
- [16] The H atom yield in N_2O saturated solutions is 0.52, significantly lower than the usually assumed yield of 0.65. — H. A. Schwarz, private correspondence. See also [13].
- [17] R. H. Schuler and G. Buzzard, *Int. J. Radiat. Phys. Chem.* **8**, 563 (1976).
- [18] H. Tanaguchi and R. H. Schuler, *J. Phys. Chem.*, in press.
- [19] R. W. Matthews and D. F. Sangster, *J. Phys. Chem.* **69**, 1938 (1965).
- [20] M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.* **70**, 2660 (1966).
- [21] J. Rabani and M. S. Matheson, *J. Phys. Chem.* **70**, 761 (1966); J. L. Weeks and J. Rabani, *ibid.* **70**, 2100 (1966).
- [22] P. Neta, M. Z. Hoffman, and M. Simic, *J. Phys. Chem.* **76**, 847 (1972).
- [23] P. Neta and R. H. Schuler, *Radiation Res.* **64**, 233 (1975); *J. Amer. Chem. Soc.* **97**, 912 (1975).
- [24] P. Neta and R. H. Schuler, *J. Phys. Chem.* **79**, 1 (1975).
- [25] K. H. Schmidt, A. Bromberg, and D. Meisel, *J. Phys. Chem.*, in press.
- [26] R. E. Hester and K. P. J. Williams, *J. Chem. Soc. Faraday Trans. 2*, **77**, 541 (1981).