# Reaction of Azide Radicals with Aromatic Compounds. Azide as a Selective Oxidant

# Zeev B. Alfassi and Robert H. Schuler\*

Radiation Laboratory<sup>1</sup> and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Nuclear Engineering, Ben Gurion University of the Negev, 84121 Beer Sheva, Israel (Received: December 20, 1984)

In basic aqueous solution the N<sub>3</sub>, radical is found to oxidize aromatic systems such as aniline and phenoxide ions and their derivatives at rate constants of  $(3-5) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. In contrast to the reactions of OH radicals, where addition to the ring dominates, oxidation appears to be directly by electron transfer. Compounds such as benzene, toluene, and anisole are not observably oxidized by N<sub>3</sub>. Phenol, in its neutral form in acidic solution, is oxidized several orders of magnitude more slowly than is the phenoxide anion. The rate of oxidation of phenols is strongly dependent on substitution, with activating groups increasing the rate in the order para > ortho > meta. N<sub>3</sub>, can be readily prepared radiolytically by OH oxidation of azide. Being a neutral radical which does not absorb significantly above 300 nm it is very promising as a selective oxidant for pulse radiolysis studies.

#### Introduction

Many radicals and radical ions prepared by radiolysis and photolysis can be used as oxidants to study the chemical and spectral properties of organic radicals and radical ions. Secondary oxidants commonly used are  $Cl_2^{-1}$ ,  $(CNS)_2^{-1}$ ,  $SO_4^{-1}$ ,  $Br_2^{-1}$ , and Ag<sup>2+</sup>. Several investigators in recent years have used the  $N_{3}$ . radical as an oxidant in radiation chemical research of interest to inorganic<sup>2,3</sup> and radiobiological systems.<sup>4-9</sup> The N<sub>3</sub> radical is readily formed either by flash photolysis<sup>10</sup> or pulse radiolysis<sup>11</sup> of aqueous sodium azide solutions and has a very narrow absorption band at  $\sim$  274 nm and little absorption above 300 nm. This low absorption provides an important advantage in optical pulse radiolysis studies since it readily allows measurements on many transients in a spectral region where radicals such as  $Br_2^{-}$ ,  $(SCN)_2$ , and  $Cl_2$  mask observations at short times. As a result one can directly examine the production of the oxidized product and study details of the oxidation process even while the initial radical is present. Another advantage of N<sub>3</sub> is its nonionic character, whereas most of the more commonly used secondary oxidants are ionic. Effects of charge and dependence on ionic strength are, thus, not involved. While the hydroxyl radical is also neutral, it frequently reacts simultaneously via several competing pathways, e.g., abstraction of an H atom, addition to a double bond or to an aromatic ring, or by electron transfer, so that a number of intermediates may be initially present. In contrast N3. radicals appear to react primarily via electron transfer thus simplifying the secondary chemistry. This latter point has been found to be particularly important in a recent study of the oxidation of aniline<sup>12</sup> where the cyclohexadienyl radicals initially produced in the case of •OH addition have a relatively long lifetime. Because  $N_3$  reacts primarily by electron transfer it is also expected to be much more selective in its reactions than is •OH. We report here studies of the oxidation of aromatic systems chosen to illustrate the use of  $N_3$  as a selective secondary oxidant.

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2661 from the Notre Dame Radiation Laboratory.

- (2) Buxton, G. V.; Janovsky, I. J. Chem. Soc., Faraday Trans. 1, 1976, 72, 1884.
- (3) Eriksen, T. E.; Lind, J.; Merenyi, G. Radiochem. Radioanal. Lett. 1981, 48, 405.
  - (4) Land, E. J.; Prutz, W. A. Int. J. Radiat. Biol. 1977, 32, 203.
  - (5) Land, E. J.; Prutz, W. A. Int. J. Radiat. Biol. 1979, 36, 75.
- (6) Chauvet, J. P.; Viovy, R.; Santus, R.; Land, E. J. J. Phys. Chem. 1981, 85, 3449.
- (7) Singh, A.; Koroll, G. W.; Cundall, R. C. Radiat. Phys. Chem. 1982, 1., 137.
- (8) Land, E. J.; Sloper, R. W.; Truscott, T. G. Radiat. Res. 1983, 96, 450.
   (9) Butler, J.; Land, E. J.; Swallow, A. J.; Prutz, W. Radiat. Phys. Chem. 1984, 23, 265.

- (11) Hayon, E.; Simic, M. J. Am. Chem. Soc. 1970, 92, 7486.
   (12) Qin, L.; Tripathi, G. N. R.; Schuler, R. H. Z. Naturforsch., in press.

TABLE I: Rate Constants for Oxidation of N<sub>3</sub><sup>-</sup> by •OH

pH	$10^{-10}k_{obsd}$	foн <sup>a</sup>	$10^{-10}k_3^{b}$	
7.89	1.25	1.00	1.25	
10.66	1.19	0.95	1.26	
11.00	1.05	0.89	1:18	
11.36	0.84	0.78	1.08	
12.2	0.34	0.33		
13.1	0.076	0.06		
14.1	0.033°	0.006		
			$1.19 \pm 0.05$	

<sup>a</sup> Fraction of •OH radical remaining, assuming  $pK_a = 11.9$ . <sup>b</sup>  $k_{obsd}$ /  $f_{OH}$ . Slow oxidation in 1 M KOH appears to be attributable to reaction of O<sup>-</sup>, with a rate constant  $\sim 2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>.

#### Experimental Section

The N<sub>3</sub> radicals were produced by pulse radiolysis of aqueous solutions of  $NaN_3$ , purged of oxygen, and saturated with  $N_2O$ to convert hydrated electrons to hydroxyl radicals. For measurement of the rate of formation of  $N_3$  the buildup of the radical was monitored directly at 274 nm. The rate of reaction of  $N_3$ . with the various reactants was measured by following the kinetics of the formation of the transient of interest in the latter's principal absorption band. All the organic chemicals used were from Aldrich, except *p*-methoxyphenol which was from Eastman, and were of the highest purity available. Sodium azide was from Alfa Products. The pH of the solutions was adjusted by using reagent grade HClO<sub>4</sub> or KOH. Solutions were prepared with water from a Millipore Milli-Q system.

The solutions were irradiated with 5-ns electron pulses from an ARCO LP-7 linear accelerator. The computer-controlled pulse radiolysis apparatus previously described<sup>13</sup> allowed averaging of traces taken consecutively while the solution flowed through the irradiation cell. Digitization of the transient signal was usually with a Biomation 8100. A Biomation 6500 was used for experiments below 1- $\mu$ s full scale. Dosimetry was with a secondary emission monitor calibrated with N2O-saturated 0.01 M SCNsolution, taking the yield of  $(SCN)_2$  as 6.14 and its extinction coefficient at 472 nm as 7580  $M^{-1}$  cm<sup>-1</sup>.<sup>14</sup> Most experiments were carried out at an initial radical concentration of  $\sim 3 \times 10^{-6}$  M.

### **Results and Discussion**

Production and Decay of  $N_3$ . In the pH range of 4-13 the  $N_3$  radical can be readily prepared by  $\cdot OH$  oxidation of azide anion

$$\cdot OH + N_3^- \xrightarrow{k_1} OH^- + N_3^-$$
(1)

<sup>(10)</sup> Treinin, A.; Hayon, E. J. Chem. Phys. 1969, 50, 538.

<sup>(13)</sup> Modified form of apparatus described by Patterson, L. K.; Lilie, J.

Int. J. Radiat. Phys. Chem. 1974, 6, 129. (14) Schuler, R. H.; Patterson, L. K.; Janata, E. J. Phys. Chem. 1980, 84, 2088.



Figure 1. Absorption spectrum of  $N_3$  as determined 1  $\mu$ s after pulse irradiating a  $N_2O$ -saturated 0.00077 M NaN<sub>3</sub> solution at pH 11. Extinction coefficients are based on SCN<sup>-</sup> dosimetry (ref 14) with the  $N_3$ -yield taken as 5.5. Absorption maximum is at 274 ± 1 nm where the extinction coefficient is 2025 ± 50 M<sup>-1</sup> cm<sup>-1</sup>.

The production of  $N_3$ , by reaction 1 is demonstrated very nicely by the ESR spin-trapping experiments of Behar and Fessenden.<sup>15</sup> Its absorption spectrum, obtained  $\sim 1 \ \mu s$  after pulse irradiating a N<sub>2</sub>O-saturated 0.0008 M NaN<sub>3</sub> solution at pH 11.3, is given in Figure 1. The extinction coefficient at 274 nm, based on a  $N_3$  radiation chemical yield of 5.5 pertinent to the  $N_3^-$  concentration of this experiment, <sup>16</sup> is  $2025 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ . Though more detailed, this spectrum agrees with that previously reported from flash photolysis<sup>10</sup> and pulse radiolysis experiments<sup>7,11</sup> although the extinction coefficient is at considerable variance with the values of 1400<sup>2</sup>, 2300,<sup>11</sup> and 1300  $M^{-1}$  cm<sup>-15</sup> reported by other investigators at  $\sim$ 274 nm. Rate constants observed for N<sub>3</sub> formation are given in Table I. After correction for the low rate of oxidation by  $O^{-}$ , as is noted below, these values give an average of (1.19)  $\pm$  0.05)  $\times$  10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> for reaction 1, in complete accord with the rate constant of  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  reported by Hayon and Simic<sup>11</sup> from competition studies.

Measurements in the pH region of 12–13 show that for the most part the observed rate constant represents the contribution from reaction 1, with very little contribution from oxidation of  $N_3^-$  by  $O^-$ .

$$O^{-} \cdot + N_3^{-} \xrightarrow{k_2} O^{2-} + N_3^{-}$$
 (2)

A rate constant of  $3 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> was observed at pH 14 showing that  $k_2$  is at least two orders of magnitude lower than  $k_1$ . After the small contribution from reaction 1 was corrected for, this measurement suggests that O<sup>-</sup> does, in fact, oxidize N<sub>3</sub><sup>-</sup> at a rate constant  $\sim 2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. However, pending a more-detailed study at very high pH this value should be regarded only as an upper limit for  $k_2$ . This low rate constant must, of course, be taken into account in designing experiments in strongly basic solutions.

In highly acidic solution, reactions are complicated by the relatively high  $pK_a$  of hydrazoic acid  $(4.74)^{17}$  which is oxidized considerably more slowly by  $\cdot$ OH than is the azide anion. While a spectrum similar to that of Figure 1, but slightly less intense, was observed at pH 4 the N<sub>3</sub> production period corresponds to a rate constant of only  $1.9 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Since hydrazoic acid is 15% ionized at this lower pH, this value essentially represents reaction of  $\cdot$ OH with the residual N<sub>3</sub><sup>-</sup>. The rate constant for  $\cdot$ OH oxidation of hydrazoic acid is considerably less than  $10^9$  M<sup>-1</sup> s<sup>-1</sup> and as a result N<sub>3</sub> is not a practical oxidant much below pH 4. Absorption of HN<sub>3</sub> in the near-ultraviolet interferes with direct



Figure 2. Decay of N<sub>3</sub>, as measured at 274 nm for solutions initially (O)  $5 \times 10^6$ , ( $\times$ )  $3 \times 10^6$ , and ( $\Delta$ )  $1 \times 10^{-6}$  M in N<sub>3</sub>. Data represent averages of 100 experiments. The latter two sets of data are displayed, as described in the text, with delays of 15 and 110  $\mu$ s indicated by the arrows to take into account the lower initial radical concentration. The solid curve corresponds to second-order decay with a rate constant ( $2k_3$ ) of  $8.8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>.

measurements of •OH attack in more acidic media where relatively high HN<sub>3</sub> concentrations are required.

In the absence of other solutes  $N_{3^{\circ}}$  decays considerably more rapidly than many radicals so that the mechanism for this decay is of some interest. The decay, as observed in a  $1.3 \times 10^{-4}$  M azide solution at initial radical concentrations of  $0.9 \times 10^{-6}$ ,  $2.9 \times 10^{-6}$ , and  $4.7 \times 10^{-6}$  M, is illustrated in Figure 2. In these cases, in order to assure reliability at long times, the analyzing lamp was not pulsed and as a result the signal-to-noise ratio was relatively poor (<3 in the individual experiments). However, as in seen in the figure, it was possible to obtain reasonable kinetic data by averaging information from 100 pulses. Comparative experiments at 290 nm show very little absorption at long times, assuring that the tail in the absorption observed at 274 nm can be attributed to N<sub>3</sub>. In Figure 2 the data at the lower doses (D') are displaced on the time coordinate by times expected for second-order decay

$$N_{3} + N_{3} \xrightarrow{k_{3}} 3N_{2}$$
 (3)

at the respective initial concentrations, i.e.,  $t_0 = t_m(D/D'-1)$  where D' is the dose and  $t_m$  the median lifetime at the reference dose D. Within experimental error the initial decay rates are proportional to the initial radical concentrations. Overall the three sets of data of Figure 2 are fitted very well by a rate constant  $(2k_3)$ of 8.8  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> with the probable error being estimated to be  $\pm 0.5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. As is usual in this type of measurement the principal uncertainty is in the absolute determination of the initial radical concentration. In view of the inherent difficulties in measuring second-order rate constants there is surprising consistency between this measurement and the previously reported values of  $(8.0 \pm 0.7) \times 10^{9,2} 9.2 \times 10^{9,10} (9 \pm 1) \times 10^{9,11}$  and  $6 \times 10^9$  M<sup>-1</sup> s<sup>-1.3,5</sup> There is no evidence in Figure 2 of any significant first-order component even at N<sub>3</sub> concentrations as low as  $5 \times 10^{-7}$  M. Reaction of N<sub>3</sub> with impurities or with azide anion

$$N_{3} + N_{3} \rightarrow N_{6} \rightarrow (4)$$

as has previously been suggested,<sup>7,9,18</sup> is unimportant at the low azide ion concentration percent. Butler et al.<sup>9</sup> attribute an absorption at 650 nm observed at molar  $N_3^-$  concentrations to  $N_6^-$  and report an equilibrium constant of 0.3  $M^{-1}$  for reaction 4.

Comparison of the decay at long times in 0.4 and 150 mM azide solutions shows very similar decay profiles, i.e., there is no observable effect of azide concentration on the intensity of the signal or the second-order decay rate. At the higher concentration we find, in agreement with Hayon and Simic,<sup>11</sup> no manifestation of any first-order contribution that can be attributed to reaction 4.

<sup>(15)</sup> D. Behar, R. W. Fessenden, J. Phys. Chem. 1972, 76, 1710.
(16) Schuler, R. H.; Hartzell, A. L.; Behar, B. J. Phys. Chem. 1981, 85, 192.

<sup>(17)</sup> Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley-Interscience: New York, 1966; 2nd ed, p 339.

<sup>(18)</sup> Kraljic, I. Proc. Tihany Symp. Radiat. Chem., 3rd 1972, 1405.

TABLE II: Rate Constants for the Reactions of N<sub>3</sub> in Aqueous Solution at pH 11.2-12.2

reactant	$10^{-9}k, M^{-1} s^{-1}$
phenoxide	4.3
hydroquinone <sup>a</sup>	4.5
<i>p</i> -methoxyphenoxide	4.2
<i>p</i> -fluorophenoxide	4.6
o-cyanophenoxide	4.7
<i>m</i> -cyanophenoxide	4.6
p-cyanophenoxide	3.8
<i>p</i> -hydroxybenzoic acid	4.0
aniline	4.5
N-methylaniline	5.8
N,N-dimethylaniline	3.7
<i>m</i> -dimethoxybenzene	$<7.2 \times 10^{6}$
<i>p</i> -dimethoxybenzene	$<2 \times 10^{7}$
benzene	$<3 \times 10^{6}$
toluene	$<3 \times 10^{6}$
anisole	$<3 \times 10^{6}$
benzoic acid	$<3 \times 10^{6}$
pyridine	$<3 \times 10^{5}$

<sup>a</sup> Present as the dianion.

The spectrum observed at the higher azide concentration is also identical in shape and magnitude with that reported in Figure 1. These observations are in agreement with the low equilibrium constant reported by Butler et al.9 which indicates that, at azide concentrations below 0.1 M >95% the radical will be present as  $N_3$ . The study of Butler et al.<sup>9</sup> also indicates that the intrinsic lifetime of  $N_6^-$  is less than  $10^{-7}$  s so that decay of  $N_3^-$  should be dominated by reaction 3 under the conditions of these studies.

The rate constant for reaction 3 is very high, indicating both that N<sub>3</sub> diffuses very rapidly in water and that all radical encounters result in reaction, i.e., that there is little or no spin selectivity in reaction 2. If this is the case, spin relaxation must occur within the lifetime of the encounter pair. Such would be expected for a linear radical.

*Reactions in Basic Solution.* The reaction of  $N_3$  with various simple aromatic systems in basic solution was monitored by following product buildup. The rate constants observed are reported in Table II. At the concentration of azide used (>0.1 M) •OH radical was converted to  $N_3$ • on the nanosecond time scale and did not interfere with the secondary kinetics. Reactive solutes were mostly examined at  $\sim 10^{-3}$  M where >99% of the  $\cdot$ OH reacted with azide and yet the N<sub>3</sub> reaction period was  $<1 \mu s$  so that second-order decay did not interfere. For the phenols and anilines, spectra recorded on the microsecond time scale were similar to those obtained with other oxidants such as  $Br_2$ . In these cases reation appears to be simple, straightforward, and presumably quantitative.

For the less reactive solutes, where oxidation products were not observed, measurable pseudo-first-order rate constants are limited to those >10<sup>4</sup> s<sup>-1</sup> by the rapid second-order N<sub>3</sub> decay. In cases where the measurable rates were limited by solubility, values are given as upper limits in Table II. For m- and p-dimethoxybenzene slow (i.e., 100  $\mu$ s) formation of transients with absorptions in the visible range was observed. The spectra, however, do not correspond with those of the radical cations<sup>18</sup> prepared with stronger oxidants so it is likely that they represent products from impurities. The rates of formation of these transients are taken as upper limits for the rate of reaction of  $N_3$  with dimethoxybenzenes. For benzene, toluene, benzoic acid, and pyridine no absorbing transients were observed. Somewhat surprisingly with 1 mM anisole no products with any significant absorption in the 330-500-nm region were observed for either acidic or basic solutions even at millisecond times. O'Neill et al.<sup>19</sup> found that anisole and dimethoxybenzenes are oxidized quite rapidly by  $Tl^{2+}$ ,  $SO_4^{-}$ , and Ag<sup>2+</sup>, where rate constants for formation of the radical cation are typically  $\sim 5 \times 10^8$ ,  $7 \times 10^9$ , and  $5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>, respectively. The N<sub>3</sub> radical is clearly a considerably milder oxidant than these

TABLE III: Rate Constants for the Reaction of N<sub>3</sub>· in Aqueous Solution at pH ~5.8

reactant	pKa <sup>a</sup>	$10^{-9}k, M^{-1} s^{-1}$
aniline	4.6	4.2
N-methylaniline	4.9	4.7
N,N-dimethylaniline	5.2	3.8
phenol	9.9	0.05
catechol	9.5, 12.8	3.8
resorcinol	9.2, 11.3	1.0
hydroquinone	9.8, 11.4	4.2
o-methoxyphenol	9.9	2.4
<i>m</i> -methoxyphenol	9.6	0.48
p-methoxyphenol	10.1	4.0
o-cresol	10.2	0.44
<i>m</i> -cresol	10.0	0.18
p-cresol	10.2	1.5
<i>p</i> -hydroxybenzoic acid	9.3	0.02
m-cyanophenol	8.6	0.02
p-cyanophenol	7.9	0.04

<sup>a</sup>Acid dissociation constants for the phenols, protonation constants for the anilines.

other intermediates, apparently unable to attack the oxygen of the methoxy substituents at any appreciable rate even though it reacts rapidly when a formal charge is present on the oxygen. This situation with methoxy derivatives contrasts with analogous nitrogen-containing compounds where, for example, reaction is rapid with N,N-dimethylaniline.

Table II shows that all the phenol derivatives react with rate constants  $\sim 4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Substituents that usually accelerate electron transfer such as hydroxy and methoxy do not increase the rate, which is not too surprising since the rates are essentially controlled by diffusion. However, the rate constants are high even with substituents such as  $CO_2^-$  or CN, where electron transfer might be expected to be deactivated.<sup>20</sup> Functionality, dominated by readily oxidized lone electron pairs, clearly is more important than substituent effects.

Reactions in Acidic Solutions. Because of the buffering action of azide  $(pK_a = 4.7)$  it is relatively easy to study reactions of N<sub>3</sub>. in the pH region of 5-6. Rate constants measured at pH 5.8 are given in Table III. As expected, rates for reaction of N<sub>3</sub> with the anilines, which protonate only in more acidic media, are essentially the same as at higher pH. The rates constant for reaction with phenol ( $pK_a = 9.9$ ), which is fully protonated at this pH, is two orders of magnitude lower than with phenoxide ion. Spectral studies show that for a  $1.1 \times 10^{-2}$  M phenol solution phenoxyl is produced with a half-period of 1.24  $\mu$ s. The rate constant,  $5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>, is several orders of magnitude greater than the contribution from the remaining phenoxide (<0.01%)so it appears that  $N_3$ , does oxidize the neutral molecule directly, though slowly. The difference observed between aniline and phenol provides the basis for the selective oxidation of tryptophan compared to tyrosine found below pH 7.6.6 One also sees in Table III very pronounced dependences on substitution. While reaction with phenol is very slow, reaction with o- or p-hydroxy- or methoxy-substituted phenol approaches rates observed in basic solution. Typical spectra observed in acidic solution are given for the cresols in Figure 3. These spectra also agree with those reported for oxidation by persulfate<sup>21</sup> showing that the products are the methyl-substituted phenoxyls. In general, spectra obtained on the microsecond time scale at pH 5.8 are similar to those found in more basic media and under other oxidation conditions showing that oxidation of these solutes by  $N_3$  is, indeed, rapid. For these groups rate constants are ordered in the direction para > ortho > meta. Comparison of the cresols with phenol shows that methyl substitution has a surprisingly large effect.

#### **Oxidation Mechanism**

The observed selectivity suggests that N<sub>3</sub> oxidizes primarily by electron transfer. That this is the case is demonstrated very

<sup>(19)</sup> O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. J. Phys. Chem. 1975, 79, 2773.

<sup>(20)</sup> Hasegawa, K.; Neta, P. J. Phys. Chem. 1978, 82, 854.
(21) Bansal, K. H.; Fessenden, R. W. Radiat. Res. 1976, 67, 1.



Figure 3. Absorption spectra of  $(-) o_{-}, (---) m_{-}$ , and  $(\cdots) p$ -methylphenoxyl radicals prepared by the  $N_3$ - oxidation of the corresponding cresols in acidic solution.



Figure 4. Absorption spectrum of ( $\bullet$ ) *p*-fluorophenoxy radical prepared by N<sub>3</sub> oxidation of a N<sub>2</sub>O-saturated 1 mM solution of *p*-fluorophenol at pH 11.2. The principal absorption maximum at 390 nm (extinction coefficient = 2920 ± 100 M<sup>-1</sup> cm<sup>-1</sup>) is shifted 10 nm to the blue from that of phenoxyl. The spectrum observed following oxidation of *p*fluorophenol by OH (O) exhibits a major contribution (~24%) from *p*-benzosemiquinone radical anion, as is manifest by the absorption at 428 nm. Spectra are uncorrected for contribution from H atom addition.

nicely in Figure 4 where spectra observed in the oxidation of *p*-fluorophenol by  $N_3$  and OH at pH 11 are compared. In the latter case oxidation to p-fluorophenoxyl proceeds largely by addition followed by OH<sup>-</sup> elimination. Attack of OH at the fluorine position, however, results in loss of HF and production of the p-benzosemiquinone radical anion, as is manifest by the appreciable absorption observed at 428 nm.<sup>22</sup> This band is characteristic of the semiquinone and is not affected when ascorbic acid is added to reduce the phenoxyl radical.<sup>22</sup> We estimate that 24% of •OH adds at the fluorine position. When p-fluorophenol is oxidized by N<sub>3</sub>, the spectrum observed is almost entirely attributable to the p-fluorophenoxyl radical with a typically narrow phenoxyl band at 390 nm ( $E_{390} = 2920 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ ) and very little absorption above 400 nm. From the initial absorption at 428 nm we can place an upper limit of 1% on the yield of semiquinone. The small absorption in Figure 4 at wavelengths longer than 400 nm is almost entirely attributable to secondary



Figure 5. Decay of N-methylaniline radical cation at pH 9.7 ( $\bullet$ ) and at pH 10.2 (O). Decay corresponds to a rate constant for deprotonation of the radical cation by OH<sup>-</sup> of 3 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>.

products which result from radical combination. Absorption in this region becomes more pronounced at longer times. There is, in fact, no evidence for semiquinone formation over and above that attributable to the •OH expected to react directly with the phenol in this experiment. We conclude that  $N_{3^*}$  reacts with *p*-fluorophenoxide entirely by electron transfer, i.e.

$$F \longrightarrow 0; - + N_{3}, \longrightarrow F \longrightarrow 0, + N_{3}^{-} (5)$$

Similarly semiquinones are not produced in the  $N_3$  oxidation of the methoxyphenols whereas appreciable yields are observed when OH is used as the oxidant. It would appear that this conclusion is generally applicable to the oxidation of oxyanions by  $N_3$ . In view of the importance of  $N_3$  attack on the oxygen of the phenoxides it is somewhat surprising that  $N_3$  reacts so relatively slowly with certain of the phenols in acidic solution and not observable with the methoxy derivatives.

In the case of aniline, oxidation also appears to occur via electron transfer. The radical cation is rapidly formed in acidic solution, bypassing the relatively stable hydroxycyclohexadienyl radical produced initially when  $\cdot$ OH is used as the oxidant. In basic solution the radical cation deprotonates to form the anilino radical, also very rapidly. In modestly basic solutions (pH 9–10) one can take advantage of the absence of absorption by N<sub>3</sub>. to demonstrate that even above the  $pK_a$  of the radical (i.e., above pH 7) the cation is, in fact, the precursor to the anilino radical.<sup>12</sup> This approach is illustrated in Figure 5 for *N*-methylaniline at pH 9.7 and 10.2 where the buildup and decay of absorption at 450 nm which is attributable to the radical cation is illustrated. The decay has half-periods of 500 and 211 ns which correspond to a rate constant of  $\sim 3 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for deprotonation of the radical cation by OH<sup>-</sup>.

$$\cdot AH^{+} + OH^{-} \xrightarrow{\kappa_{5}} A \cdot + H_{2}O$$
 (6)

There is no evidence from our experiments that either the anilino or N-methylanilino radicals is produced directly without the intermediate production of their radical cations, i.e., in these cases reaction is via electron transfer and not H-atom abstraction.

Butler et al.<sup>9</sup> found that the deprotonation of TrpH<sup>+</sup>. is catalyzed by N<sub>3</sub><sup>-</sup>. We, however, find that at pH 7.0 transformation to the neutral *N*-methylanilino radical is not observed even at 100  $\mu$ s, indicating that N<sub>3</sub><sup>-</sup> catalysis contributes very little. The difference between the radiation chemistry of *N*-methylaniline and tryptophan may be due to the difference in the pK<sub>a</sub> of the radical cations (4.3 for tryptophan and 7.05 for anilin).<sup>12</sup> Since the pK<sub>a</sub> of HN<sub>3</sub> is much closer to the former, N<sub>3</sub><sup>-</sup> is expected to

<sup>(22)</sup> Schuler, R. H. Radiat. Res. 1977, 69, 417.



Figure 6. Production of p-methoxyphenoxyl radical following oxidation of 0.02 M p-methoxyphenol by N<sub>3</sub> at pH 5.95 ( $\oplus$ ), 5.52 (O), 5.19 ( $\Delta$ ) and 4.75 ( $\Delta$ ). Measurements were at 417 nm in a N<sub>2</sub>O-saturated 0.5 M NaN<sub>3</sub> solution. Approximately 2/3 of this radical is produced within 100 ns as expected from the rate constant measured in mM solution. The half-life for growth of the slow component decreases from 530 ns at the highest pH to 64 ns at the lowest. The [H<sup>+</sup>] dependences of the pseudo-first-order rate constant of this component is given in the insert. Spectra taken at ~100 ns, normalized for the observed growth, are very similar to those found at microsecond times.

be a much better catalyst for the deprotonation of the tryptophan radical cation than for the deprotonation of aniline or N-methylaniline radical cation.

In studies of the oxidation of N,N-dimethylaniline by N<sub>3</sub>, similar spectra were obtained at pH 6.2 and 12.0, with both corresponding to the known spectrum of the radical cation.<sup>23-25</sup> This radical does not demethylate to any significant extent. Holchman and Sehested<sup>26</sup> found that this radical reacts slowly with base ( $k \sim 10^5 \text{ M}^{-1}$ ) to form C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>c</sub>H<sub>2</sub> but because of deprotonation this pathway is not available in the less than fully N-substituted radicals.

Oxidation of p-Methoxyphenol. Oxidation of p-methoxyphenoxide in basic solution by N<sub>3</sub> results, as expected, in the rapid production of the p-methoxyphenoxyl radical which has absorption band at 417 nm ( $E_{417} = 7030 \text{ M}^{-1} \text{ cm}^{-1}$ ) that is about twice as intense as the absorption of phenoxy at 400 nm.<sup>27</sup> As with p-fluorophenoxyl there is no manifestation of any significant yield of p-semiquinone radical anion. At low concentration in acidic solution p-methoxyphenoxyl oxidized to p-methoxyphenoxyl radical in what appears to be a single step with a rate constant of  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . At high concentration, however, two steps in the oxidation are observed (Figure 6) and it becomes clear that the reaction mechanism is more complicated. Spectral measurements show that for a 0.02 M p-methoxyphenol solution the

rapid step, which as expected from the rate constant measured in more dilute solutions is complete in  $\sim 100$  ns, results largely in the formation of the *p*-methoxyphenoxy radical. Additional radical is, however, produced more slowly. The spectra observed at 100 ns and at 3  $\mu$ s are similar with the latter being 50% more intense and essentially identical with that observed in basic solution. As is illustrated in Figure 6 the slow step is acid catalyzed, being an order of magnitude more rapid at pH 4.75 than at pH 5.95. The insert in Figure 6 shows that the first-order growth rate is proportional to the acid concentration with a small intercept which corresponds to a half-life of the precursor in neutral solution of ~10  $\mu$ s. In terms of [H<sup>+</sup>] concentration the acid catalysis coefficient is  $6 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup>. Since this coefficient is very high it seems likely that the reaction is at least partially catalyzed by HN<sub>3</sub> which is present at a three order of magnitude higher concentration than is  $H^+$ . The fact that this additional production of *p*-methoxyphenoxyl radical is acid catalyzed points very strongly to the production, in part, of a hydroxycyclohexadienyl radical such as is important in the OH oxidation of phenol. While such a component is not apparent in the spectrum it absorbs in the 300-nm region<sup>19</sup> and a minor contribution at higher wavelengths would be largely masked by the more intense absorption of the *p*-methoxyphenoxyl radical.

We tentatively suggest that  $N_3$  oxidizes *p*-methoxyphenol by electron transfer to form the radical cation, which rapidly, but only in part, eliminates the OH proton to form the phenoxyl radical directly. This proton is represented by the fast step in Figure 6. Apparently the cation reacts competitively with water to form a hydroxycyclohexadienyl radical which produces additional radical in a delayed process involving OH<sup>-</sup> eliminations. We expect to carry out additional studies to examine this interesting observation in more detail. For purposes of the present discussion the importance is that complications become very apparent which are not discernable if one follows the disappearance of a secondary oxidant such as  $Br_2^{-}$ . One must, of course, be sure that these complications do not influence interpretation of other aspects of the chemistry involved.

## Summary

In summary, the  $N_3$  radical appears to be a relatively mild and selective oxidant that can be used to advantage to oxidize aromatic oxyanions and amines rather directly. It has been shown that reaction with both of these types of substrates proceeds directly by electron transfer and that complications such as result from •OH addition to aromatic rings are absent. Reaction of  $N_3$  with phenols or aromatic ethers is more complicated. For practical purposes use of  $N_3$  is largely limited to the pH range of 4–13.

**Registry No.** NaN<sub>3</sub>, 26628-22-8; OH-, 3352-57-6; N<sub>3</sub>-, 12596-60-0; phenoxide, 3229-70-7; hydroquinone dianion, 48100-05-6; *p*-methoxy-phenoxide, 29368-59-0; *p*-fluorophenoxide, 32376-34-4; *o*-cyanophenoxide, 14609-76-8; *p*-hydroxybenzoic acid, 99-96-7; aniline, 62-53-3; *N*-methylaniline, 100-61-8; *N*,*N*-dimethylaniline, 121-69-7; *m*-dimethoxy-benzene, 151-10-0; *p*-dimethoxybenzene, 150-78-7; benzene, 71-43-2; toluene, 108-88-3; anisole, 100-66-3; benzoic acid, 65-85-0; pyridine, 110-86-1; phenol, 108-95-2; catechol, 120-80-9; resorcinol, 108-46-3; hydroquinone, 123-31-9; *o*-methoxybenol, 90-05-1; *m*-methoxybenol, 150-19-6; *p*-methoxybenol, 150-76-5; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; *m*-cyanophenol, 873-62-1; *p*-cyanophenol, 767-00-0; *o*-methylphenoxyl, 20217-30-5; *m*-methylphenoxyl, 20227-79-6; *p*-methoxyl, 3174-48-9; *p*-fluorophenoxyl, 2145-21-3; *p*-methoxyl phenoxyl, 29368-59-0.

<sup>(23)</sup> Porter, G.; Land, E. J. Trans. Faraday Soc. 1963, 59, 2927.

<sup>(24)</sup> McKellar, J. F. Photochem. Photobiol. 1967, 6, 287.

<sup>(25)</sup> Christensen, H. Int. J. Radiat. Phys. Chem. 1972, 4, 311

<sup>(26)</sup> Holçman, J.; Sehested, K. Proc. Tihany Symp. Radiat. Chem. 5th 1982, 693.

<sup>(27)</sup> Schuler, R. H.; Buzzard, G. K. Int. J. Radiat. Phys. Chem. 1976, 8, 563-574.