molecules and later the intermediates until the composition of the gas approaches a steady state of the stable molecules  $(H_2, C_2H_2, C_2H_4, HCN)$ . Under laboratory pyrolysis conditions, the endothermicity of the reaction leads to a substantial temperature drop; in flame pyrolysis, the temperature profile would be governed by other processes.

The product distribution for CH<sub>3</sub>NH<sub>2</sub> pyrolysis is a function of pressure. As described above, the high-pressure result of Dorko et al.—about half of the CH<sub>3</sub>NH<sub>2</sub> forming NH<sub>3</sub>—is well accounted for by the Table I mechanism and rate constants. To test its predictive ability at low pressure, we modeled the Peel and Willett<sup>4</sup> conditions (ignoring the probable participation of wall reactions) of P = 1.2 Torr and T = 1543 K. In 50-ms reaction time about 27% of the CH<sub>3</sub>NH<sub>2</sub> had decomposed to give products in the ratio H<sub>2</sub>/HCN/CH<sub>2</sub>NH/CH<sub>4</sub>/NH<sub>3</sub> = 25/9/9/1/1. Their photoelectron spectroscopic result showed H<sub>2</sub>, HCN, and a small amount of NH<sub>3</sub>.

Of reactions 1–12, the only one for which an experimental rate constant has been provided is reaction 3, for which Gray and Thynne<sup>16</sup> give  $k_3 = 10^{11} \exp(-8700 \text{ cal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . At 1600 K the Table I expression gives a value 40 times larger than this expression. If the Gray and Thynne expression were used in modeling, reaction 3 would make no contribution to the decomposition process. While some of the difference would be normal Arrhenius graph curvature,<sup>18</sup> it appears more reasonable

(18) Zellner, R. In Combustion Chemistry; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984; p 135. to adopt the Table I expression, based upon the analogy to reaction 22, for decomposition modeling at this time. Further refinement of the rate constant expressions should be readily possible if shock tube experiments would be undertaken to obtain the high-temperature product distributions: stable products by single-pulse experiments and the intermediates  $CH_3$  and  $NH_2$  by absorption spectroscopy.

#### Conclusions

The high-temperature thermal decomposition of  $CH_3NH_2$  is a combination of two processes: unimolecular scission of the C–N bond and H-atom-catalyzed stripping of four H atoms from the parent molecule to form HCN and H<sub>2</sub>. The relative contributions of the two pathways depend upon pressure and temperature. Because the stripping process is a sequential one combining two abstraction reactions with two unimolecular decompositions, only its overall rate is determinable through measuring the overall decomposition rate; measurements of intermediate concentrations would be required for assignment of rate constant expressions to the actual elementary steps. The initiation reaction 1 is, for the conditions studied, a normal bond-scission unimolecular decay in the falloff region.

Acknowledgment. This research was supported by the Robert A. Welch Foundation. We acknowledge a helpful discussion with C. F. Melius. T.H. expresses appreciation for financial support of the Ministry of Education, Science, and Culture of Japan. Registry No.  $CH_3NH_2$ , 74-89-5.

# Radiolytic Oxidation of 1,2,4-Benzenetriol. An Application of Time-Resolved Resonance Raman Spectroscopy to Kinetic Studies of Reaction Intermediates<sup>1</sup>

Ling Qin, G. N. R. Tripathi, and Robert H. Schuler\*

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (Received: September 19, 1986)

In acidic solution, 1,2,4-benzenetriol is rapidly oxidized by 'OH or  $N_3$ ' to form a mixture of neutral 2,4- and 3,4-dihydroxyphenoxyl radicals. At higher pH these radicals deprotonate ( $pK_a(1) = 4.75$ ) to form the 2-hydroxy-*p*-benzosemiquinone radical anion which exhibits a prominent resonance Raman band at 1625 cm<sup>-1</sup> attributable to the Wilson 8a ring stretching mode. In basic solutions this radical subsequently reacts with OH<sup>-</sup> to form the radical dianion ( $pK_a(2) = 8.85$ ) in which the 8a band is shifted to an appreciably lower frequency (1587 cm<sup>-1</sup>). While the absorption spectra of these latter radicals are very similar and do not allow ready examination of their interconversion by absorption spectrophotometry, the difference between these 8a frequencies is sufficiently great that the Raman method can be used to examine the acid-base equilibrium between the two forms of the radical and to follow the deprotonation kinetics. It is shown that even at high pH the radical monoanion is initially formed on oxidation by  $N_3^{\bullet}$  and that deprotonation subsequently occurs by its reaction with base with a rate constant of ( $9.6 \pm 1.5$ ) × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. These studies illustrate very well the application of time-resolved resonance Raman spectroscopy as a complement to kinetic spectrophotometry in sorting out the details of secondary processes in pulse radiolysis studies.

To date time-resolved resonance Raman studies of radiolytically produced free radicals have largely been devoted to their qualitative identification and to determination of their spectroscopic properties.<sup>2</sup> Because Raman spectroscopy provides an approach by which one can follow individual components in a reaction mixture it is of interest to use time-resolved Raman methods as a complement to kinetic spectrophotometry in pulse radiolysis experiments, particularly in cases where intermediates have complex and overlapping absorption spectra.<sup>3</sup> In the following we illustrate the potential of this approach with results from a recent study of the oxidation of 1,2,4-benzenetriol (hydroxyhydroquinone) where the singly and doubly charged forms of the semiquinone intermediate present in neutral and basic solutions have very similar absorption spectra, making it virtually impossible to carry out meaningful studies of their interconversion by spectrophotometric methods. However, their Raman spectra are sufficiently different that, as is demonstrated here, this interconversion can be followed readily by time-resolved resonance Raman spec-

<sup>(1)</sup> The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2905 from the Notre Dame Radiation Laboratory.

<sup>(2)</sup> Wilbrandt, R. Faraday Discuss. Chem. Soc. **1984**, 213. Earlier studies on the application of Raman methods in pulse radiolysis studies are summarized.

<sup>(3)</sup> Tripathi, G. N. R.; Schuler, R. H. Proceedings of the VI Tihany Conference on Radiation Chemistry; Budapest, Hungary, in press. Application and limitations of time-resolved resonance Raman methods in radiation chemistry are summarized.

troscopy. Auxiliary information in more acidic solutions, where the neutral radical is produced, is also presented to give a comprehensive picture of the radiolytic oxidation of this substrate in aqueous solutions.

#### **Experimental Section**

The time-resolved spectrophotometric and resonance Raman pulse radiolytic approaches used here have been described in detail previously.<sup>4</sup> In the Raman studies a  $\sim 100$ -ns pulse of 2-MeV electrons from a Van de Graaff accelerator was used to produce an initial radical concentration  $\sim 10^{-4}$  M. These radicals were then probed with an excimer pumped dye laser operated at a wavelength within an absorption band of the intermediate of interest. The Raman emission was examined with a mediumresolution spectrograph using a gated ( $\sim 20$  ns) intensified diode array, synchronized with the laser, as the detector (OMA). Time resolution was obtained by a controlled delay between the accelerator and laser pulses with the relative delays being known to better than the laser pulse width ( $\sim 10$  ns). Signal averaging methods were employed extensively with experiments being carried out at a pulse rate of 7.5 Hz. In most cases the OMA was read out after integration of the Raman emission from  $\sim 100$  pulses and recorded after accumulation of data from  $\sim 1000$  pulses in the OMA controller. Recordings were further averaged and appropriate backgrounds subtracted offline with a VAX 11/780 processor. Raman frequencies were determined by reference to spectra of cyclohexane and for well-resolved bands are accurate to  $\sim 1 \text{ cm}^{-1}$ .

Absorption spectra of the transients were recorded with pulse radiolysis methods as previously described.<sup>5-7</sup> A 5-ns pulse of 8-MeV electrons from a linear accelerator was used to produce an initial radical concentration of  $\sim 3 \,\mu$ M. Extinction coefficients were determined by reference to the thiocyanate dosimeter.<sup>8</sup> Data on the nanosecond time scale were recorded with a Biomation 6500 (2 ns/channel) and on the microsecond time scale with a Biomation 8100 (10 ns/channel). ESR measurements were made by in situ radiolysis methods as previously described<sup>9,10</sup> in order to provide auxiliary information on the structure of the intermediates. These experiments took advantage of recent improvements which include digital recording of the ESR signals.<sup>11</sup>

Solutions of 1,2,4-benzenetriol (Aldrich) were prepared in water purified in a Millipore Milli Q system and the pH was adjusted with HClO<sub>4</sub> or KOH. pH measurements were made with an Orion 811 pH meter calibrated with Fisher reference buffers and are generally accurate to  $\pm 0.02$ . In most cases the radicals were prepared by using N<sub>3</sub><sup>•</sup> produced by the <sup>•</sup>OH oxidation of 0.1 M NaN<sub>3</sub> (Fluka) as a secondary oxidant.<sup>12</sup> Solutions were purged of dissolved air and saturated with  $N_2O$  to convert  $e_{aq}$  to •OH.

## **Results and Discussion**

In these studies it is important to know the state of ionization of the substrate being oxidized. The literature<sup>13</sup> gives only two acid dissociation constants for 1,2,4-benzenetriol ( $pK_a = 9.1$  and 11.9). Since these values are similar to the values for dihydroxybenzenes and also the lowest two  $pK_a$  values for 1,2,3benzenetriol it is clear that they represent the first and second acid dissociation constants. The third  $pK_a$  of 1,2,4-benzenetriol, while not given in the literature, is presumably considerably greater

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Figure 1. Acid-base equilibria of 1,2,4-benzenetriol and between radical intermediates produced on oxidation.



Figure 2. Absorption spectra observed in the pulse radiolytic oxidation of 1,2,4-benzenetriol at (A; O) pH 2.8, (B; ●) pH 7.2, and (C; △) pH 11.0. A represents a composite of the spectra of three neutral dihydroxyphenoxyl radicals (see text), B that of the 2-hydroxy-p-benzosemiquinone radical anion, and C that of the radical dianion.

than 12. We have examined the absorption spectrum up to pH 13 and find no evidence for a change representing the third ionization so it appears to be higher and likely is of the magnitude of 14 estimated for its 1,2,3-trihydroxy isomer.<sup>13</sup> The substrate, therefore, should exist predominately in its neutral form below pH 9 and as the monoanion in the pH range of 9 to 12. Oxidation of the dianion will become important only above pH  $\sim 11$  and direct oxidation of the trianion should not be of importance in any of the experiments reported here. The various equilibria involved are illustrated in Figure 1.

The optical absorption spectra observed in pulse radiolysis of  $N_2O$ -saturated 2 mM solutions of 1,2,4-benzenetriol at pH 2.8, 7.2, and 11.0 are given in Figure 2. Spectra were recorded  $\sim 5$  $\mu$ s after the pulse. At the lowest pH the substrate was oxidized directly by the 'OH radicals produced in a N<sub>2</sub>O-saturated solution so that, as with phenoxy,<sup>4,14</sup> one expects a contribution in the 340-380-nm region from the cyclohexadienyl radicals produced by H atom addition. The absorption observed in the region of 400 nm is, however, largely attributable to the radicals produced by oxidation. At the higher pH  $N_3$  was used as a secondary oxidant<sup>12</sup> so that the H atoms are effectively scavenged by the  $N_{3}^{-}\ensuremath{\text{ present}}^{15}$  and the spectra should not have any significant contribution from H atom addition products. Spectra taken above

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Figure 3. pH dependence of the absorbance at 430 nm in the oxidation of 1,2,4-benzenetriol. Measurements were made at 10  $\mu$ s with 0.1 M phosphate being used to accelerate equilibration between the neutral and anionic forms of the radical. The sigmoidal curve corresponds to a simple acid-base equilibrium with a  $pK_a$  of 4.75.

pH 12 are complicated by the presence of products from the autooxidation of the benzenetriol in the irradiated solutions.

The spectrum observed at pH 2.8 (Figure 2, spectrum A) has a maximum at 401 nm and an overall appearance similar to most simple phenoxyl radicals and neutral semiquinones.<sup>4,14,16</sup> It is readily attributable to the fully protonated radical which can, in fact, exist in three isomeric forms, 2,4-, 3,4-, and 2,5-dihydroxyphenoxyl radical. Since the protonation equilibria are rapid at this pH the observed spectrum represents an appropriately weighted average of contributions from each of the possible forms. On increase in pH to 7.2 the spectrum shows, as with the simple semiquinones, a pronounced shift in the principal absorption maximum toward the red (to 431 nm) as the result of deprotonation of the neutral radical. From the pH dependence of the absorption at 430 nm (Figure 3) the  $pK_a$  for loss of the first proton is  $4.75 \pm 0.05$ . This pK<sub>a</sub> is somewhat above that of the o- and p-benzosemiquinones (4.3 and 4.1, respectively)<sup>17,18</sup> but considerably below that for *m*-benzosemiquinone (6.40).<sup>19</sup> The low value of the  $pK_a$  indicates that the OH proton at the 2 position is retained in the neutral radical.

Raman and ESR data (see below) show that the radical loses its second proton only in much more basic solutions so that the spectrum observed at pH 7.2 (Figure 2, spectrum B), which has a strong absorption band at 431 nm resembling that of the pbenzosemiquinone radical anion, represents the singly ionized form of the radical. A very similar, but somewhat less intense, spectrum is observed above pH 10 (Figure 2, spectrum C) where the Raman and ESR data clearly show that the radical present is different from that in neutral solution. This spectrum which has a maximum at 427 nm, is attributed to the radical dianion. Since spectra B and C are so similar it is difficult to determine the second acid dissociation constant of the radical accurately from absorption data although spectral changes in the region of pH 8-10 suggest that it is in the region of 9. Without the Raman data in hand the observed changes can, in fact, be as well attributed to minor complications in the chemistry and one cannot be sure, even qualitatively, that one is dealing with further ionization of the radical.



Figure 4. Time dependence of absorbance as observed (O) at 405 nm and (•) at 430 nm (pH 7; N<sub>2</sub>O saturated solution 10<sup>-1</sup> M in NaN<sub>3</sub>; 10<sup>-2</sup> M in 1,2,4-benzenetriol). The time dependence at the 405-nm isosbestic point represents exponential growth ( $t_{1/2} = 13.8$  ns) corresponding to an oxidation rate of  $5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The ~12-ns delay in the signal at 420 nm, where only the monoanion absorbs, was numerically simulated assuming a pseudo-first-order rate constant of  $8 \times 10^7 \text{ s}^{-1}$  for deprotonation of the neutral radical.

A rate constant of  $5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for oxidation of the neutral substrate by N<sub>3</sub><sup>•</sup> was determined at pH 6.5 from growth of the signal at 405 nm (the isosbestic point between spectra A and B) for solutions 10<sup>-4</sup> M in the benzenetriol. Measurements at 420 nm (the isosbestic point between B and C) at pH 10.5 gave a somewhat lower rate constant  $(4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ . Similar rate constants were also found for 10<sup>-2</sup> M solutions so this difference appears real although one expects from observations on less highly oxygenated systems<sup>12</sup> that oxidation rates should increase on ionization. Although complicated by autooxidation, measurements at pH 12.5 indicate a comparable rate for oxidation of the dianionic form. In any case the oxidation rate is, as with hydroquinone,<sup>12</sup> not strongly dependent on the state of ionization of the substrate.

We find no indication either in the spectra or in the reaction kinetics that the radical cation produced by oxidation of the neutral substrate has any significant lifetime. Presumably oxidation is immediately followed by proton loss to form the neutral radical. Comparison of the time dependences of the absorption at 405 and at 430 nm at pH 7 (Figure 4) do show that above  $pK_a(1)$  subsequent formation of the radical monoanion is delayed by  $\sim 12$ ns. The observed time dependence can be simulated very well by assuming that the pseudo-first-order rate constant for deprotonation of the neutral radical is  $8 \times 10^7$  s<sup>-1</sup>. Since this rate constant is more than an order of magnitude greater than that for spontaneous dissociation expected from the equilibrium constant and an upper limit of  $\sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$  for protonation of the anion, it would appear to represent catalysis by the azide present. A coefficient of this magnitude is reasonable in view of the fact that the  $pK_a$  of the radical is almost identical with that of hydroazoic acid (4.7). ESR experiments also indicate that at pH 4 exchange with water occurs in the presence of azide at a frequency  $\sim 10^8$  Hz. It should be noted that catalysis of deprotonation of the neutral radical, which is estimated to have a lifetime  $\sim$  500 ns toward spontaneous dissociation, is important in these experiments in order to avoid delay in formation of the radical anion which would otherwise seriously complicate the kinetic studies of the subsequent chemistry.

Raman spectra in the 1300-1800-cm<sup>-1</sup> region for the radicals produced on oxidation are given in Figure 5. The spectrum of the neutral radical (Figure 5, spectrum A) was obtained 0.2  $\mu$ s after the pulse at pH 4.1 with excitation in the radicals' principal absorption band at 401 nm. It has complex structure in the 1514-1535-cm<sup>-1</sup> region which clearly indicates that several of the possible protonated forms of this radical are simultaneously

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Figure 5. Raman spectra of (A) a mixture of dihydroxyphenoxyl radical produced by oxidation of 1,2,4-benzenetriol at pH 4.1; (B) the 2-hydroxy-*p*-benzosemiquinone radical anion at pH 7.2; (C) the radical dianion at pH 10.5. The most intense bands are at 1619, 1625, and 1587 cm<sup>-1</sup>, respectively.

present. It is particularly noted that the Wilson 8a ring stretching vibration observed at  $1617 \text{ cm}^{-1}$  is considerably more intense than is found with most phenoxyl radicals and, in particular, that the features in the  $1400-1700\text{-cm}^{-1}$  region contrast with the Raman spectrum of 3-hydroxyphenoxyl radical where the intensity of the ring stretching vibration observed at  $1625 \text{ cm}^{-1}$  is very weak.<sup>16</sup> The similarities to the Raman spectrum of the 4-hydroxyphenoxyl radical<sup>20</sup> indicate that the neutral radical is predominantly present in its 2,4- and 3,4-dihydroxylated forms (radicals Ia and Ib, respectively, Figure 1).

The Raman spectrum of the radical monoanion, observed 0.5  $\mu$ s after the pulse (Figure 5, spectrum B) at pH 7.2, is very similar to that of the *p*-benzosemiquinone radical anion with the Wilson 8a ring stretching vibration being shifted upward slightly to 1625 cm<sup>-1</sup> (1620 cm<sup>-1</sup> in the *p*-benzosemiquinone anion).<sup>21</sup> The spectral pattern is very different from the *m*-benzosemiquinone radical anion where the CO stretching vibration at 1519 cm<sup>-1</sup> dominates the spectrum, and the 8a vibration is not appreciably enhanced.<sup>16</sup> It is clear, therefore, that this radical can be properly represented as the 2-hydroxy-*p*-benzosemiquinone radical anion (radical II, Figure 1) with the unpaired spin being distributed over the semiquinone system. This aspect bears importantly on the detailed description of the deprotonation kinetics, as is discussed below.

The Raman spectrum of the radical dianion (radical III; Figure 5, spectrum C) shows that the increase in charge and/or delocalization of the unpaired spin over the three oxygen atoms perturbs the Wilson 8a ring mode appreciably. The large decrease in frequency, from 1625 cm<sup>-1</sup> in the monoanion to 1587 cm<sup>-1</sup> in the dianion, provides the specificity necessary to apply Raman methodology to studies of the deprotonation equilibrium and kinetics.

Qin et al.

Figure 6. pH dependence of the Raman spectra observed at 30  $\mu$ s with excitation at 430 nm.

ESR spectra of the neutral form of the radical taken at pH 1, where the OH protons are rapidly exchanging with water, show three nonequivalent ring protons which have hyperfine constants of 1.13, 1.95, and 3.21 G. These values are of the magnitude of the averaged value of 2.3 G observed for the ring protons in the p-hydroxyphenoxyl radical, again indicating that the radical is protonated on the 2 position and that there is very little contribution from the structure corresponding to the 2,5-dihydroxyphenoxyl radical. ESR spectra taken at pH 4.3 are complicated by exchange of the OH protons but show definitively that the radical must be present in more than one form. At pH 7 the ESR spectrum of the monoanion manifests three ring protons with hyperfine constants of 0.44, 1.84, and 3.66 G showing that the unpaired spin is delocalized over a p-semiquinone system, i.e. that, in agreement with the Raman data, the radical is protonated at the 2 position. Much larger values would be expected if the radical had significant o- or m-semiquinone character such as would be expected if protonation was at either of the other oxygen portions. The radical dianion, in which the unpaired spin is delocalized over the entire oxygen systems, has hyperfine constants of 0.62, 1.35, and 4.85 G.22 Comparison with the hyperfine constants of the monoanion shows clearly that there is substantial interaction of the third oxygen atom with the electronic system of this radical. This interaction apparently results in the pronounced decrease in the ring stretching frequency from 1625 to 1587 cm<sup>-1</sup> noted above.

The substantial difference in the frequencies of the ring stretching vibrations shown in Figure 5, B and C, makes it readily possible to examine the equilibrium and kinetics of the interconversion between the monanionic and dianionic forms of the radical, particularly since the resonance Raman spectra of both can be excited at 430 nm. It is seen in Figure 6 that as the pH is increased the intensity of the band at  $1625 \text{ cm}^{-1}$  decreases and that of the band at  $1587 \text{ cm}^{-1}$  increases in a complementary fashion. Measurements of the relative intensities were made at  $30 \ \mu s$ , at which time equilibrium is established. Since at the pH

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Figure 7. pH dependence of the fractional contribution of the monoanionic form of the radical as determined from the relative intensities of the 1625- and 1587-cm<sup>-1</sup> Raman bands at 30  $\mu$ s (see text for calculation method). The sigmoidal curve corresponds to a simple equilibrium with  $pK_a = 8.85$ .



Figure 8. Raman spectrum observed at 0.3  $\mu$ s at pH 8.6. Reference spectrum of the monoanionic form of the radical obtained at pH 7.2 is given by the dotted spectrum. Note that there is very little contribution from the dianionic form of the radical at 1587 cm<sup>-1</sup>.

of these experiments the radicals decay somewhat on this relatively long time scale we have plotted in Figure 7 the fractional contribution of the monoanion taking into account its 15% greater sensitivity as compared with the dianion when excited at 430 nm. A correction has also been made for a contribution of 5.7% of the signal of the dianion at 1625 cm<sup>-1</sup> and for a 7.5% contribution of the signal of the monoanion at 1587 cm<sup>-1</sup>. The data very nicely follow the sigmoidal curve expected for a simple acid-base equilibrium with an inflection point corresponding to a  $pK_a(2)$ of 8.85  $\pm$  0.05. At this point it is noted that the radical monoanion is about as acidic as is phenol and that the  $pK_as$  are, respectively, 5 and 3 units below the first and second  $pK_as$  of the parent compound, as is common for OH groups in most radicals.<sup>23</sup>

The Raman spectrum observed at pH 8.6 at 0.3  $\mu$ s (Figure 8) is very similar to that found at pH 7.2, clearly showing that the neutral radical, which presumably is the species initially formed, rapidly loses its first proton. At short times there is essentially no contribution from the dianionic form of the radical. At higher pH the signal of the radical monoanion increases for about 0.5  $\mu$ s and then decreases as a result of deprotonation, as is indicated in Figure 9. The initial increase is about as expected from the ~100-ns oxidation period. At the longer times the total signal is essentially constant. As a result an "isosbestic" point appears



Figure 9. Raman spectra observed at pH 9.9 (a) in order of increasing intensity of the 1625-cm<sup>-1</sup> band at 0.3, 0.4, and 0.5  $\mu$ s and (b) in order of decreasing intensity of the 1625-cm<sup>-1</sup> band at 0.5, 0.7, 1.2, 2.2, and 5.2  $\mu$ s.



**Figure 10.** Time dependence of the Raman signal attributable to the radical dianion at ( $\Delta$ ) pH 9.05, ( $\Delta$ ) pH 9.43, (O) pH 9.89, and ( $\oplus$ ) pH 10.34 for a solution 2 mM in the benzenetriol. Excitation was at 430 nm. The observed growths can be simulated very well (solid curves) with the pseudo-first-order rate constant for deprotonation of the radical monanion taken as  $4 \times 10^5 + 9.6 \times 10^9$  [OH<sup>-</sup>].

in Figure 9b at  $1604 \text{ cm}^{-1}$  where the two Raman signals overlap. The dianion signal grows in complementary to the decay of the monoanion but decays slightly at very long times as the result of second-order reactions.

The time dependence for the fractional contribution of the radical dianion observed in a number of experiments in the pH 9 to 10.5 region is illustrated in Figure 10. The reaction period is strongly dependent on the OH<sup>-</sup> concentration so that it is clear that deprotonation occurs to a large extent by attack of base on the OH group. A plot of the pseudo-first-order rate constants as a function of base concentration is linear with, however, an intercept of  $4 \times 10^5$  s<sup>-1</sup>. This intercept is attributed to catalysis of the deprotonation by N<sub>3</sub><sup>-</sup>. The second-order rate constant for this catalysis ( $4 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>) is of the order of magnitude



Figure 11. Time dependence of the absorbance at 431 nm for an N<sub>2</sub>Osaturated solution 10 mM in 1,2,4-benzenetriol at pH 10.4 (0.1 M in NaN<sub>3</sub>). Solid curve represents numerical simulation of the sum of the contributions from radicals II and III based on rate information from the Raman experiments.

expected from the difference (4 units) between the  $pK_a$  of the radical and that of hydrazoic acid.<sup>24</sup> The slope of this plot, 9.6  $\times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, represents the second-order constant for deprotonation of the radical monoanion by base at an ionic strength of 0.1 and is estimated to be accurate to  $\pm 1.5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. This value approaches that for most diffusion-controlled reactions of OH<sup>-</sup> with acids<sup>24</sup> so it is clear that hydrogen bonding does not play any important role in determining the deprotonation rate even though the OH proton is adjacent to an oxygen atom with some formal negative charge. On combining this value with the equilibrium constant the rate constant for protonation of the radical dianion is estimated to be 7  $\times 10^4$  s<sup>-1</sup>. Such a high value shows that in basic solutions protonation of the dianion mainly involves its reaction with water.

Since the radical monoanion absorbs slightly more strongly in the region of 430 nm than does the dianion we have attempted to follow the deprotonation kinetics by absorption spectrophotometry. Simulations of the expected time dependences using the rate and spectroscopic information given above show that at high

substrate concentrations (<5 mM) and at a pH of  $\sim 10.5$  one should see a small ( $\sim 10\%$ ) decay on the microsecond time scale in the signal at 430 nm which is attributable to the difference in the absorption of the monoanionic and dianionic forms of the radical. Data obtained at pH 10.4 for a solution  $10^{-2}$  M in the substrate (N<sub>2</sub>O saturated; 0.1 M in NaN<sub>3</sub>) are illustrated in Figure 11 along with the numerical simulations of each of the contributions to the total absorbance (II + III in Figure 11). It is seen that the agreement of the data with the latter is excellent although the absorbance appears to decay  $\sim 20\%$  more rapidly than predicted by the rate information obtained from the Raman experiments. Comparison of data taken at 420 and 405 nm shows that the rate for deprotonation of the neutral radical at this pH is about as noted in Figure 4, i.e.  $t_{1/2} \sim 10$  ns, so that this step, although included in the simulations, does not complicate the kinetic treatments in any important way. Interpretation of the small differences in the spectrophotometric results can be complicated by contributions from minor products, particularly in view of the fact that  $\sim 10\%$  of the oxidation involves direct attack of OH on the benzenetriol at the high solute concentration used in this experiment. The data from the Raman experiments, where one is able to follow a specific intermediate, should provide a more reliable measure of the reaction rate. In effect the Raman data are essential to the design of appropriate spectrophotometric experiments and to provide assurance that one is not, in fact, looking at some artifact in the latter.

### Summary

Oxidation of the various forms of the 1,2,4-benzenetriol by 'OH or N<sub>3</sub>' is essentially diffusion controlled and, as indicated in Figure 1, yields the neutral radical below pH 4.75. The radical dianion is formed above pH 8.85 and the 2-hydroxy-*p*-benzosemiquinone radical anion in the intermediate region. In 0.1 M sodium azide solution loss of the first proton from the neutral radical occurs with a first-order rate constant of  $8 \times 10^7 \text{ s}^{-1}$  which largely reflects catalysis by azide. It is found that the rate constant for deprotonation of the monoanion by base is  $9.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Measurement of this deprotonation rate by time-resolved resonance Raman spectroscopy illustrates the power of this tool in providing specific information on the relative importance of products and reactants in cases where they cannot be readily distinguished by absorption spectrophotometric approaches.

Acknowledgment. The authors thank Dr. K. P. Madden for his assistance in carrying out ESR studies on the radicals of interest here.

<sup>(24)</sup> Eigen, M. Angew. Chem., Int. Ed. Engl. 1964, 3.