A Pulse Radiolytic Study of the Acid Dissociation of OH Protons in Radicals Related to Salicylic Acid¹

Q. Sun and Robert H. Schuler*

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (Received: January 26, 1987; In Final Form: March 30, 1987)

The deprotonation of carboxylated benzosemiquinone radicals prepared by pulse radiolytic oxidation of dihydroxybenzoic acids has been examined by time-resolved absorption spectrophotometry. The pK_a for dissociation of the OH proton in 3-carboxy-1,4-benzosemiquinone is found to be 6.47 or 2.4 units higher than that in the unsubstituted radical. This difference presumably reflects internal hydrogen bonding by the carboxy group. This pK_a is, however, well below that of the OH proton in salicyclic acid (13.6) so that hydrogen bonding is appreciably decreased by the delocalization of the unpaired spin in this radical. In the absence of proton acceptors equilibration is relatively slow and in near neutral solutions is controlled by spontaneous loss of the proton from the acidic form with a half-period of 23 μ s. Protonation of the basic form of the radical occurs at the diffusion-controlled rate. The rate constant for deprotonation by OH⁻ is relatively low, $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, so that reaction with base becomes important only above pH 10. As a result this radical provides an excellent system for studying acid-base equilibrium to be examined on the 10- μ s time scale. Deprotonation is also catalyzed by the dihydroxybenzoic acid used as the radical source. Analogous studies on 4-carboxy-1,3-benzosemiquinone give the pK_a as 7.9. In spite of this high pK_a , which indicates the rate constant for spontaneous dissociation of this radical to be >10³ s⁻¹, the rate constant for deprotonation by OH⁻, $4.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, is considerably higher than in the case of 3-carboxy-1,4-benzosemiquinone. This latter comparison again indicates that the nature of the spin delocalization has an appreciable effect on the reaction kinetics.

It is well-known that as a result of hydrogen bonding the pK_a of 13.6 for acidic dissociation of the phenolic proton in salicyclic acid (2-hydroxybenzoic acid) is considerably higher than that in phenol (9.9) or in its isomers, 3-hydroxybenzoic acid (9.9) and 4-hydroxybenzoic acid (9.3).² During the course of pulse radiolytic studies of the semiquinone radicals produced in the oxidation of aqueous solutions of 2,4- and 2,5-dihydroxybenzoic acid we have observed that the pK_{as} for acidic dissociation of their OH protons (6.47 and 7.9, respectively) are several units higher than those for the corresponding unsubstituted semiquinones, reflecting internal hydrogen bonding in these radicals similar to that in salicylic acid. Because of this hydrogen bonding, oxidation of these dihydroxybenzoic acids in acidic solutions leads preferentially, as is shown by ESR studies,^{3,4} to the formation of the isomer of the semiquinone with the salicyclic acid group intact, i.e. oxidation of 2,5-dihydroxybenzoic acid yields only 3-carboxy-1,4-benzosemiquinone 3-carboxy-4-hydroxyphenoxyl radical). In effect



the second OH group in these substrates provides a site for oxidative attack by which intermediates suitable for time-resolved studies of the dissociation of weak acids can be rapidly prepared.

Hyperfine splitting by the OH proton of these radicals is observed in solutions near to neutral, showing that proton exchange with water is relatively slow, i.e. that dissociation of the acidic form



cannot occur on a time scale much shorter than microseconds. In strongly basic solutions these semiquinones deprotonate by reaction with base to form the relatively unreactive carboxylated semiquinone radical dianions, e.g.

$$QH^{*-} + OH^{-} \frac{k_{3}}{k_{-3}} Q^{*2-} + H_{2}O$$
 (3)

We show here that the rate constants for deprotonation of these carboxylated benzosemiquinones by base are several orders of magnitude less than for diffusion-controlled reactions, making it possible to examine the other factors which control deprotonation in near neutral solutions. It is shown, for example, that the azide ion is an efficient proton acceptor by which one can catalyze the otherwise slow equilibration between the acidic and basic forms of the radical. The rate constant for spontaneous dissociation of the OH proton in 3-carboxy-1,4-benzosemiquinone (k_2) is found to be 3×10^4 s⁻¹, indicating that k_{-2} is 8.5×10^{10} M⁻¹ s⁻¹, i.e. that protonation of the radical dianion is essentially controlled by diffusion.

Experimental Section

Time-resolved spectrophotometric studies were carried out by pulse radiolysis methods similar to those used in many recent investigations from these laboratories.⁵ Most studies used N_3° radicals produced by •OH oxidation of sodium azide (Fluka) as a secondary oxidant.⁶ In certain cases $Br_2^{\circ-}$ produced from potassium bromide (Fisher) was used. Formation of these oxidizing radicals at 0.1 M azide or bromide was complete within

⁽¹⁾ This is Document No. NDRL-2926 from the Notre Dame Radiation Laboratory.

⁽²⁾ Serjeant, E. P.; Dempsey, B. Ionization Constants of Organic Acids in Aqueous Solution; Pergamon: Oxford, 1979.
(3) Neta, P.; Fessenden, R. W. J. Phys. Chem. 1974, 78, 523.

⁽⁴⁾ Jinot, C.; Madden, K. P.; Schuler, R. H. J. Phys. Chem. 1974, 70, 525. (4) Jinot, C.; Madden, K. P.; Schuler, R. H. J. Phys. Chem. 1986, 90, 4979.

⁽⁵⁾ For a detailed description of the pulse radiolysis apparatus see: Janata,
E.; Schuler, R. H. J. Phys. Chem. 1982, 86, 2078. A Biomation 8100 was used for digitization of the transient signals in the present experiments.
(6) Alfassi, Z. B.; Schuler, R. H. J. Phys. Chem. 1985, 89, 3359.

TABLE I

| | | | rate constant for oxidation, $M^{-1} s^{-1} \times 10^{-9}$ | |
|----------------------|-------------------------|-------------------|---|---------|
| substrate | pН | form ^a | N3. b | Br2*- c |
| 2,5-dihydroxybenzoic | ~4.5 | monoanion | 2.6 | 0.065 |
| acid | ~11.6 | dianion | 4.2 | |
| 2,4-dihydroxybenzoic | $\sim 5.5 \\ \sim 10.5$ | monoanion | 1.0 | 0.055 |
| acid | | dianion | 3.5 | 0.72 |

^aThe carboxy group of these benzoic acids is fully ionized above pH 5 ($+K_a \sim 3$). pK_{a2} for ionization of the OH proton at C₅ in 2,5-dihydroxybenzoic acid is 10.3 and that at C₄ in 2,4-dihydroxybenzoic acid is 8.9 (see text). ^b From the pseudo-first-order period for production of product radical. ^c From the pseudo-first-order period for loss of Br₂⁻⁻ at an ionic strength of 0.1.

~10 ns of the pulse. The dihydroxybenzoic acids (Aldrich) were present at 0.5 to 5 mM so that there was very little direct oxidation of the substrate by 'OH. This approach largely avoids the intermediary production of hydroxycyclohexadienyl radicals which otherwise complicates the reaction scheme where 'OH is used directly.⁶ Studies were carried out in aqueous solutions which were purged of oxygen and saturated with N₂O to convert e_{aq}^{-} to 'OH. Radical concentrations were ~5 μ M. The pH was adjusted with HClO₄ or KOH and determined with an Orion 801 pH meter calibrated with Fisher buffers. Because of possible ionic strength effects care was used not to introduce extraneous ions so that the rate data are, in most cases, representative of an ionic strength of 0.1.

Results and Discussion

Rate constants for oxidation of 2,4-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid by N_3^{\bullet} and $Br_2^{\bullet-}$ at pH ~5 and ~11 are given in Table I. Oxidation by these secondary radicals takes place by electron transfer from the substrate to the oxidant.⁶ There is no apparent delay in formation of the semiquinone radicals, even in acidic solutions, so that, as with 1,2,4-benzenetriol,⁷ oxidation of the monoanion must be rapidly followed by proton loss. In the case of N₃[•], rate constants were determined from the pseudo-first-order period for growth of the absorption of the product radical and in the case of Br_2^{-} from the period for decay of the latter as measured at 360 nm. The carboxy group of both substrates is somewhat more acidic than that in benzoic acid (pK_a) = 4.2 for benzoic acid, 3.0 for 2,5-dihydroxybenzoic acid, and 3.3 for 2,4-dihydroxybenzoic acid)² so that it should be fully ionized at pH 5 and above. The second pK_a of 2,4-dihydroxybenzoic acid (given in the literature as 9.0)² is similar to the lowest value for resorcinol (9.3) and presumably represents ionization of the OH proton at C_4 . We have determined this pK_a from the pH dependence of the rate constant for oxidation by Br2.- and find a value of 8.9, in good agreement with the literature value. The third pK_a (~14)² is very high and from its similarity to pK_a , for salicylic acid is attributed to ionization of the OH adjacent to the carboxy group. The second and third pK_as of 2,5-dihydroxybenzoic acid are not available in the literature. We have examined its absorption spectrum and find a shift from a maxmum at 320 nm in neutral solution to one at 346 nm in base. The pH dependence indicates pK_{a_2} to be ~10.4. Because the rate constant for oxidation by Br₂^{•-} increases by an order of magnitude on ionization of the OH (see Table I) this oxidation rate also provides a good measure of the relative contribution of the acidic and basic forms. As indicated in Figure 1 the rate constant follows a titration curve very well with an inflection point corresponding to $pK_{a_2} = 10.30$ \pm 0.05 at an ionic strength of 0.1. This value is of the magnitude of the lowest pK_a of hydroquinone (9.9) and is, therefore, attributed to ionization of the OH proton at C5. The carboxy group clearly has a substantial effect on the acidicity of the remote OH proton, increasing its pK_a in the substituted hydroquinone by 0.4 and decreasing its pK_a in the substituted resorcinol by 0.3. The third



Figure 1. Dependence of the rate constant for oxidation of 2,5-dihydroxybenzoic acid by Br_2^{-} on pH. The inflection point corresponds to a pK_{a_2} of 10.3 for the OH proton at position 5. Solid curve is calculated from this pK_a and the limiting rate constants given in Table I.



Figure 2. Absorption spectra of the carboxysemiquinone radicals and their anions observed in the pulse radiolytic oxidation of 1 mM solvents of (A) 2,5-dihydroxybenzoic acid and (B) 2,4-dihydroxybenzoic acid. Spectra were recorded 10 μ s after the pulse. Solid symbols are for studies at pH ~5 and open symbols at pH ~10. Azide radical was used as a secondary oxidant in these studies so that the spectra are free of contributions from H atom addition products (see ref 8).

 pK_a of 2,5-dihydroxybenzoic acid, attributable to the OH proton at C₂, is unavailable but is expected to be similar to that for salicylic acid, i.e. in the region of 13–14. One, therefore, expects that, as indicated by eq 1, oxidation of these substrates will initially yield semiquinone radicals with the oxygen atom adjacent to the carboxy group protonated even up to high pH.

The rate constant for oxidation of the dianionic forms of these substrates by N_3^{\bullet} is comparable to that for oxidation of most phenoxides (i.e., $(4-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁶ Oxidation by N_3^{\bullet} in acidic solutions is also comparable to that for oxidation of hydroquinone $(4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ and resorcinol $(1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ and considerably faster than for oxidation of phenol $(5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$.⁶ Oxidation of these substrates by $Br_2^{\bullet-}$ is slower, particularly in acidic solutions where the oxygen atoms are fully protonated. Where it can be used, N_3^{\bullet} is clearly the better choice as a secondary oxidant for preparing the semiquinone radicals.

Absorption spectra of 3-carboxy-1,4-benzosemiquinone and 4-carboxy-1,3-benzosemiquinone (4-carboxy-3-hydroxyphenoxyl radical) observed at pH \sim 5 (open points) and their corresponding semiquinone radical dianions observed at pH \sim 11 (closed points) are illustrated in Figure 2. These spectra were recorded \sim 10 μ s after pulse irradiating solutions 0.1 M in azide and 1 mM in substrate. From the kinetic data presented below oxidation of

⁽⁷⁾ Qin, L.; Tripathi, G. N. R.; Schuler, R. H. J. Phys. Chem., in press.

Deprotonation of Carboxylated Benzosemiquinones



Figure 3. Fraction of radicals present as dianion: (\bullet) for 3-carboxy-1,4-benzosemiquinone as determined at 432 nm and (O) at 460 nm; (Δ) for 4-carboxy-1,3-benzosemiquinone as determined at 455 nm. Calculated titration curves correspond to pK_{a} s of 6.47 and 7.9, respectively.

the substrates should be complete and equilibrium established between the acidic and basic forms of the radical at the time of these recordings. Because H atoms are removed by reaction with azide ion⁸ these spectra are free of contributions from H atom addition products. Extinction coefficients are based on radical yields of 6.1 in acidic solution and 5.5 in basic solution.⁸

The absorption spectrum of the 2-carboxy-1,4-benzosemiquinone radical dianion is very similar to that of the 1,4-benzosemiquinone radical anion.9 Maxima are observed at 408 and 432 nm which are shifted to the red from those in the unsubstituted radical by ~ 5 nm. Both Raman¹⁰ and ESR³ data show that the carboxy substituent has relatively little effect on the electron distribution over the π system of this radical. In contrast the carboxylated benzosemiquinone observed on protonation exhibits a rather different spectrum than that of either phenoxy¹¹ or 1,4-benzosemiquinone radical.9 In particular, there is appreciable absorption at wavelengths longer than 430 nm. For present purposes the relatively high absorption in the region of 460 nm is important in that it allows one to follow the decay of the protonated radical as well as the growth of the complementary semiquinone anion. The existence of an isosbestic point at 443 nm also allows one to examine the time dependence of the total radical population directly.

The spectrum of 4-carboxy-1,3-benzosemiquinone radical dianion is very similar in structure and intensity to that of 1,3benzosemiquinone radical anion.¹² ESR data¹³ show that the unpaired spin distribution in this radical is essentially unaffected by the presence of the carboxy group. The spectrum of 4carboxy-1,3-benzosemiquinone observed on protonation at pH ~5 is very much weaker and even less intense than that of the 1,3benzosemiquinone radical.¹² As a result there is no isosbestic point and for kinetic purposes one can only follow growth of the completely ionized radical.

The acidic dissociation constants of these radicals were detemined by examining the pH dependence of the absorption spectra. Measurements were made in 0.1 M sodium azide solution at 15 μ s, at which time acid-base equilibrium is established (see below). The data are given in Figure 3 in terms of the fractional contribution of the basic form (the radical dianion) as determined from the intensities observed both at 432 and 460 nm in the case of the 1,4-semiquinone and at 455 nm in the case of the 1,3semiquinone. In the first instance the total radical yield could be monitored at the 443-nm isosbestic point, allowing corrections to be made for the slight changes in yield that occur in the pH range of 5 to 7.⁸ The pK_as observed for dissociation of the OH



Figure 4. Time dependence of the spectrum $(0.2, 0.6, 1.2, 2.0, 3.0, 4.4, and 13 \mu s)$ in the oxidation of 1 mM 2,5-dihydroxybenzoic acid with N₃[•]. Isobestic points are at 396, 402, and 443 nm as indicated by the dashed lines. Spectra at 0.2 and 0.6 μ s are corrected for incomplete oxidation as observed at the 443-nm isobestic point. Arrows indicate directions of absorbance changes with time.



Figure 5. Time dependence of absorbance in the oxidation of 5 mM 2,5-dihydroxybenzoic acid by N_3^{\bullet} in the presence of 0.1 M N_3^{-} at pH 11.1: at (\bullet) 543 nm, (\Box) 443 nm, and (\blacktriangle) 460 nm. The half-period for oxidation as measured at 432 nm is 34 ns and for subsequent deprotonation as measured at 431 and 460 nm is 1.80 μ s.

protons at an ionic strength of 0.1 are 6.47 ± 0.05 for 3carboxy-1,4-benzosemiquinone and 7.9 ± 0.1 for 4-hydroxy-1,3benzosemiquinone. Similar pH dependences were observed for the radicals prepared by $Br_2^{\bullet-}$ oxidation but because of the low oxidation rates and relatively longer equilibration periods the inflection points (p K_a s of 6.5 and 8.1, respectively) have substantial possible errors. The observed p K_a s are several units higher than those for their unsubstituted counterparts (4.0 for 1,4-benzosemiquinone⁹ and 6.43 for 1,3-benzosemiquinone¹⁴). It is clear

⁽⁸⁾ Ye, M.; Madden, K. P.; Fessenden, R. W.; Schuler, R. H. J. Phys. Chem. 1986, 90, 5397.

⁽⁹⁾ Adams, G. E.; Michael, B. D. Trans. Faraday Soc. 1967, 63, 1171. (10) Sun, Q.; Tripathi, G. N. R.; Schuler, R. H., to be submitted for publication.

⁽¹¹⁾ Tripathi, G. N. R.; Schuler, R. H. J. Chem. Phys. 1984, 81, 113.
(12) Tripathi, G. N. R.; Chipman, D. C.; Miderski, C. A.; Davis, H. F.;
Fessenden, R. W.; Schuler, R. H. J. Phys. Chem. 1986, 90, 3968.

⁽¹³⁾ Madden, K. P.; McManus, H. J.; Schuler, R. H. J. Phys. Chem. 1982, 86, 2926.

⁽¹⁴⁾ Jinot, C.; Madden, K. P.; Schuler, R. H. J. Phys. Chem. 1986, 90, 4979.



Figure 6. Dependence of measured first-order deprotonation rate constant on concentration of base for solutions 0.1 M in N₃⁻: (•) 3-carboxy-1,4-benzosemiquinone; (□) 4-carboxy-1,3-benzosemiquinone. Slopes of lines correspond, respectively, to rate constants of 4.9×10^7 and 4.9×10^8 M⁻¹ s⁻¹ for reaction 3.

that hydrogen bonding makes the OH protons in these radicals appreciably less acidic than in the unsubstituted benzosemiquinones. They are, however, much more acidic than the OH proton of salicylic acid ($pK_a = 13.6$).

The spectrum initially observed on oxidation of a 5 mM solution of 2-carboxy-5-hydroxybenzoic acid by N_3^{\bullet} at pH 11 is identical with that found in acidic solutions, assuring that, as expected, the semiquinone radical is initially produced. Figure 4 illustrates the time dependence of the spectrum, as observed at pH 9.6. These spectra exhibit isosbestic points at 396, 402, and 443 nm which indicate that deprotonation occurs without complication. These isosbestic points also make it possible to compare the intensities of the acidic and basic forms of the radical directly without any assumptions as to the pH dependence of the yields.

Typical kinetic traces are given in Figure 5 for a 0.1 M N_3^- solution 5 mM in 2,5-dihydroxybenzoic acid at pH 11.1. It is seen from the trace at the 443-nm isosbestic point (curve 4b) that oxidation is for the most part complete in 200 ns. At longer times the absorption at 432 nm increases and that at 460 nm decreases with measured half-periods of 1.81 and 1.79 μ s, respectively. The first-order rate constant for deprotonation under the conditions for this experiment is, therefore, $3.85 \times 10^5 \text{ s}^{-1}$.

As indicated in Figure 6 similar rate measurements on solutions 0.1 M in sodium azide show a linear dependence of the first-order rate constant on OH⁻ concentration with a slope corresponding to a second-order rate constant for deprotonation by base of 4.9 $\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The intercept of Figure 6 should be less than 3.5 $\times 10^4 \text{ s}^{-1}$ if the rate in neutral solutions is controlled by spontaneous deprotonation. This upper limit is estimated from the pK_a (K₂ = 3.5 $\times 10^{-7}$ M) by assuming a maximum value of $\sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for k_{-2} . The pronounced intercept in Figure 6 (3.6 $\times 10^5 \text{ s}^{-1}$) is, however, an order of magnitude greater, implying that deprotonation occurs by some additional mechanism in solutions near to neutral. To a large extent this intercept can be attributed to deprotonation by azide ion, i.e.

$$QH^{\bullet-} + N_3^{-} \stackrel{k_4}{\underset{k_{\rightarrow}}{\leftarrow}} Q^{\bullet 2^{-}} + HN_3$$
 (4)



Figure 7. Dependence of first-order rate constant on N_3^- concentration at pH ~9: (\bullet) 3-carboxy-1,4-benzosemiquinone (\bullet from Figure 6) and (\Box) 4-carboxy-1,3-benzosemiquinone. Slopes correspond, respectively, to rate constant of 2.0 × 10⁶ and 1.8 × 10⁶ M⁻¹ s⁻¹ for reaction 4.



Figure 8. Time response in the oxidation of 2,5-dihydroxybenzoic acid by Br_2 ⁻⁻ at (\oplus) 432, (\square) 443, and (\blacktriangle) 460 nm. Oxidation half-period as measured at 443 nm is 2.1 μ s.

Determination of the dependence of the pseudo-first-order rate constant on $[N_3^-]$ at pH 8.7 (Figure 7) shows a linear dependence with a slope which corresponds to a rate constant of 2.1×10^6 $M^{-1} s^{-1}$ for reaction 4. At 0.1 M azide ion reaction 4 is the dominant contributor to the deportonation rate pH 10. In effect N_3^- is a catalyst which allows one to examine the equilibrium on the 10 μ s time, as was done in obtaining the data on Figure 3.

The intercept of Figure 7 $(4.6 \times 10^4 \text{ s}^{-1})$ is approximately in accord with the above estimate of the rate constant for spontaneous deprotonation of the semiquinone and in any event gives an experimental upper limit to k_2 . In an attempt to measure k_2 more directly in a case where catalysis is not expected, the semiquinone radical was prepared by Br_2^{-} oxidation. In these studies one must, however, use relatively high concentration of the substrate since oxidation of its acidic form by Br_2^{-} is somewhat slow. From the data of Figure 8 the half-period for deprotonation in a solution 5 mM in 2,5-dihydroxybenzoic acid at pH 9.6 is 22 μ s, or approximately as expected from the intercept of Figure 7.

At this point one must ask whether or not the substrate itself acts as a deportonation catalyst even though one expects any such effect to be small because there is a fairly large mismatch between the pK_{as} of the radical (6.47) and substrate (10.4). Measurements similar to those of Figure 8 made over the 1–10 mM range of 2,5-dihydroxybenzoic acid (see Figure 9) show, in fact, that there is a small contribution from this source. In this figure the observed first-order rate constant is plotted as a function of the equilibrium concentration of the substrate dianion since deprotonation presumably results from reaction of the radical with dianion, i.e.

$$QH^{\bullet-} + S^{2-} \xrightarrow{k_{5}}_{k_{-5}} Q^{\bullet 2-} + HS^{-}$$
 (5)



Figure 9. Dependence of the rate constant for deprotonation of 3carboxy-1,4-benzosemiquinone on the concentration of the dianion of 2,5-dihydroxybenzoic acid; (O) Experiments at pH \sim 8.7 where \sim 3% of the substrate is in the dianionic form, (\oplus) at pH 9.5 where \sim 15% is in the dianionic form.

| TABLE II: | Equilibrium | and Rate | Constants | for E | Deprotonation |
|-----------|-------------|----------|-----------|--------------|---------------|
|-----------|-------------|----------|-----------|--------------|---------------|

| - | - | | | |
|---|------------------------------------|------------------------------------|--|--|
| | 3-carboxy-1,4- benzosemiquinone | 4-carboxy-1,3- benzosemiquinone | | |
| $\overline{K_2}$ equilibrium, M ⁻¹ | 3.4×10^{-7} | 1.2 × 10 ⁻⁸ | | |
| k_2 spontaneous dissociation, s ⁻¹ | 3.4×10^{4} | <10 ^{3a} | | |
| k_{-2} protonation, M ⁻¹ s ⁻¹ | 8.5×10^{10} | | | |
| k_1 deprotonation by base, M ⁻¹ s ⁻¹ | 4.9×10^{7} | 4.9×10^{8} | | |
| $k_{\rm A}$ deprotonation by N ₃ , M ⁻¹ s ⁻¹ | 2.0×10^{6} | 1.8×10^{6} | | |
| k_5 deprotonation by substrate, ^b M ⁻¹ s ⁻¹ | 1.0×10^{7} | $\sim 2 \times 10^7$ | | |

^aEstimated from the equilibrium constant assuming an upper limit for k_{-2} of 10^{11} M⁻¹ s⁻¹. ^bDianion of substrate.

The slope corresponds to a rate constant of $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for reaction 5. Extrapolation gives a limiting value of $3.0 \times 10^4 \text{ s}^{-1}$ at low solute concentration. While this value must still be regarded as an upper limit to k_2 , other possible contributions appear to be small so it is reasonably taken as representing the intrinsic rate constant for acidic dissociation of 3-carboxy-1,4-benzosemiquinone. From this value and that for the equilibrium constant, one obtains the very reasonable value of $8.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for reaction -2, i.e. the radical dianion appears to react with protons at a diffusion-controlled rate.

Measurements similar to the above were also carried out on 2,4-dihydroxybenzoic acid and the rate data obtained are included in Figures 6 and 7. It is seen in Figure 6 that the rate constant for deprotonation of the 1.3-benzosemiquinone by OH⁻ is relatively high (4.9 × 10⁸ M⁻¹ s⁻¹). Deprotonation by N₃⁻ (Figure 7; $k_4 =$ $1.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is comparable in rate to that for its 1,4-isomer. The intercept noted for the this plot in Figure 7, 4.5×10^4 s⁻¹, appears to be almost entirely attributable to reaction 5 which is more important here than for 3-carboxy-1,4-benzosemiquinone because of the close match of the pKs of the radical and the substrate. In this latter case, the relatively high pK_a of the radical indicates that the rate constant for spontaneous dissociation must be less than 10^3 s⁻¹, i.e. one expects the intrinsic lifetime of the protonated radical to approach 1 ms. However, the maximum lifetime that we were able to demonstrate was only 60 μ s in an experiment 0.5 mM in 2,4-dihydroxybenzoic acid at pH 9.5. Under these conditions deprotonation is controlled by contributions of $\sim 5 \times 10^3$ s⁻¹ from both reactions 3 and 5. Basically, it was not possible to design a practical experiment to determine the rate for spontaneous decay of this radical with any accuracy and we could only show that k_2 cannot be significantly greater than the upper limit of 10³ s⁻¹ estimated from the equilibrium constant.

The various kinetic data are summarized in Table II. The carboxylated 1,4-benzosemiquinone produced on oxidation of 2,5-dihydroxybenzoic acid provides a particularly good system for studying the factors influencing the dissociation of an OH proton in the salicylic acid configuration. In this case the ionization equilibrium is controlled by dissociation on the 10- μ s time scale and protonation at a diffusion-controlled rate. Ionization of 4-carboxy-1,3-benzosemiquinone is somewhat slower. Because of the relatively low rates intrinsic to these reactions, catalysis by even modest concentrations of donors and acceptors becomes important. Internal hydrogen bonding is important in controlling the ionization, as is illustrated by the relatively high pK_as and low rates for deprotonation by base. Comparison of the data on these two radicals shows that the delocalization of the unpaired spin in 3-carboxy-1,4-benzosemiquinone increases the dissociation rate considerably over that for its 1,3-benzosemiquinone isomer.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Department of Energy.

Registry No. 3-Carboxy-1,4-benzosemiquinone, 34496-50-9; 4carboxy-1,3-benzosemiquinone, 109282-17-9; 2,4-dihydroxybenzoic acid, 89-86-1; 2,5-dihydroxybenzoic acid, 490-79-9.