A Ring-H^+ Bonded Semiquinone Dication Radical Observed by Time Resolved Resonance Raman Spectroscopy

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The *p*-benzosemiquinone radical is a prototype of redox intermediates of quinone−hydroquinone (Q/QH_2) systems that occur in a variety of chemical and biochemical processes.[1,2] We have examined the reaction of this radical with the proton in water, in mild to extreme acid conditions, by time-resolved resonance Raman spectroscopy. Here we present spectroscopic evidence of a previously unknown ring-protonated dication form of the radical.

The relationship between the resonance Raman spectra, structure, and protonation chemistry is helpful in understanding the results obtained on the *p*-benzosemiquinone radical. The frequency of the CO stretching mode (Wilson mode 7a), 1435 cm^{-1}, in the basic form of the aqueous radical ($Q^{\bullet -}$)[3] is comparable to that in the acetate anion,[4] implying that the electronic charge added to *p*-benzoquinone gets equally distributed between the two oxygen atoms, and that there is very little of it on the ring. Therefore, there is a strong electrostatic attraction for the proton to the oxygen atoms and not to the ring. The pK_a of the oxygen-bound proton in the radical ($pK_a = 4$)[5] is comparable to that of acetic acid ($pK_a \sim 5$),[1] as expected from the charge distribution. Once a proton attaches to one oxygen atom, the effective electronic charge on the other is altered. If the effective electronic charge becomes lower, that should reflect in a higher CO stretching frequency, and a greater proton concentration in solution would be required to induce H^+-bonding. Whether the proton addition occurs on the oxygen atom or on the ring can be readily discriminated by examining the relative intensities of the ∼1600 cm^{-1} (1620 cm^{-1} in $Q^{\bullet -}$) and ∼1170 cm^{-1} (1161 cm^{-1} in $Q^{\bullet -}$)[3,6] bands in the resonance Raman spectra. The former is a ring vibration (Wilson mode 8a), largely involving the stretching motion of the central CC bonds, and the latter is largely a CH bending vibration (Wilson mode 9a).[4] It has been shown previously that the 9a CH bending mode is enhanced due to coupling with the 8a ring mode.[6] Proton bonding with the ring will induce nonplanarity in the radical structure, reducing this coupling, and thus the resonance enhancement of the CH bending mode.

The *p*-benzosemiquinone radical was prepared by pulse radiolytic oxidation of 2 mM hydroquinone (QH_2) in oxygen-free water containing 0.2 to 16 M acid.[3,7,8] Radiolysis of oxygen-free water produces $^{\bullet}OH$ radical and hydrated electron (e_{aq}^-) in almost equal concentrations on the 100-ns time scale.[3,7] In acidic solutions, e_{aq}^- reacts with H^+ to form $H^{\bullet}$ atom which is a reducing species that adds to the ring.[7] The $^{\bullet}OH$ radical is a strong oxidant that reacts with hydroquinone by addition followed by rapid elimination of water, to produce the neutral *p*-benzosemiquinone ($QH^{\bullet}$) radical in mildly acidic solutions.[9,10] At pH < 2, the oxidation is complete in less than 100 ns (see ref 9 for rate constants). The known protonation forms of the *p*-benzosemiquinone radical absorb in the 380−440 nm region ($\lambda_{max} = 428$ nm for $Q^{\bullet -}$, 415 nm for $QH^{\bullet}$ ($pK_a = 4$) and 423 nm for $QH_2^{\bullet +}$ ($pK_a = -0.8$)).[3,5,6] The absorption spectrum obtained 5 μs after electron pulse irradiation of an N_2-saturated aqueous solution containing 2 mM hydroquinone and 14 M H_2SO_4 exhibits maxima at ∼380 and ∼422 nm. The Raman spectra, in resonance with these absorption bands, were obtained 1 μs after electron pulse. The solvent background was digitally subtracted (for experimental procedure, see ref 3). At very high acid concentration, the subtraction leads to considerable noise in the transient Raman spectra, particularly in the low frequency region, and very weak signals cannot be unambiguously attributed to the transients formed. Therefore, the spectra were monitored in the 800−1800 cm^{-1} spectral region.

The transient Raman spectra, excited at 418 nm in the 1300−1800 cm^{-1} region, are displayed in Figure 1. With 0.4 M H_2SO_4 in solution (Figure 1a), the spectrum obtained is that of the neutral *p*-benzosemiquinone radical ($QH^{\bullet}$),[3,9] with prominent bands at 1613 and 1511 cm^{-1}. The 1511 cm^{-1} 7a CO stretching frequency in $QH^{\bullet}$ is 76 cm^{-1} higher, and the 1613 cm^{-1} 8a ring stretching frequency is 7 cm^{-1} lower than in $Q^{\bullet -}$.[3] With increase in the acid concentration in solution, the $QH^{\bullet}$ spectrum converts into that of the $QH_2^{\bullet +}$ species (Figure 1a−c).[3,9] The 1511 cm^{-1} CO frequency shifts to 1400 cm^{-1}, and the 1613 cm^{-1} ring frequency to 1644 cm^{-1}, on proton addition to $QH^{\bullet}$, indicating that the proton adds to the oxygen atom. Between 6.5 and 12 M acid in solution, there is no apparent change in spectral features, except for a slight increase in the 1644 cm^{-1} signal intensity. However, an examination of the spectra in the 830−1300 cm^{-1} region (Figure 2) provides evidence for further protonation.

Between 0.4 and 6.5 M H_2SO_4 in solution the spectral changes in the 830−1300 cm^{-1} region (Figure 2) follow the same pattern as in the 1300−1800 cm^{-1} region. In hydrated $QH^{\bullet}$, the 9a CH bending mode appears at 1162 cm^{-1}, and in $QH_2^{\bullet +}$ at 1172 cm^{-1}, with enhancement almost similar to that in the anion form of the radical.[3,9] Between 6.5 and 12 M acid in solution, the intensity of the CH bending mode (1172 cm^{-1}) gradually decreases and the band becomes unobservable in 12 M H_2SO_4 (Figure 2c−e). On the other hand, no new band of appreciable intensity appears in the 1100−1200 cm^{-1} region (Figure 2e). The overtone band (932 cm^{-1}, Figure 2c) of the 468 cm^{-1} planar ring distortion mode (Wilson mode 6a) of $QH_2^{\bullet +}$ [9] also disappears and is replaced by a new band at 959 cm^{-1} (∼2 × 480 cm^{-1}?). A similar trend was seen on substituting $HClO_4$ for H_2SO_4. This extreme acid form of the *p*-benzosemiquinone radical, with transient absorption (∼422 nm) similar to that of $QH_2^{\bullet +}$, has not been identified previously. We could not observe a transient Raman spectrum by 380-nm excitation, presumably due to photodissociation, a problem that we have encountered with most $^{\bullet}H$ and $^{\bullet}OH$ adducts. The 380-nm species can be tentatively attributed to the protonated

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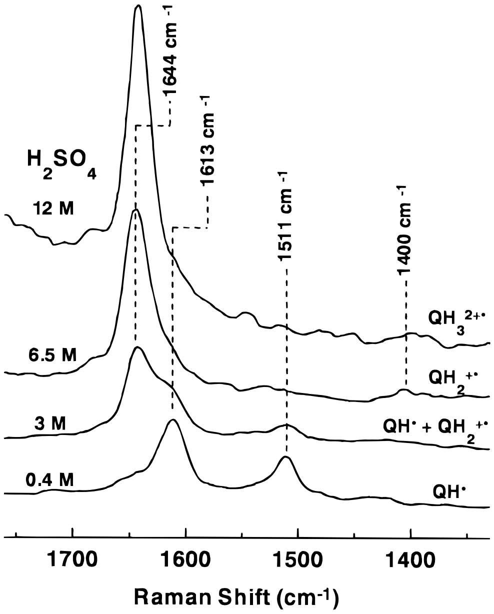

Figure 1. Transient Raman spectra in the 1300−1800 cm^{-1} region (see text).

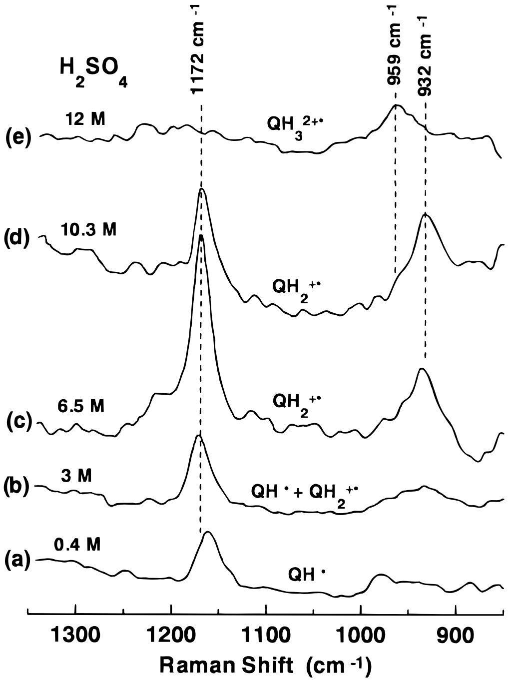

Figure 2. Transient Raman spectra in the 800−1300 cm^{-1} region (see text). The intensity scale is different from Figure 1.

form of the $H^{\bullet}$ atom adduct of QH_2. The $H^{\bullet}$ adducts generally absorb in the 300−400 nm region.[7,11]

The disappearance of the 9a CH bending mode in the 418 nm transient Raman spectra in extreme acidic conditions, and independence of this observation on the nature of the acid used, is a clear indication of ring protonation. The positive charge in hydrated $QH_2^{\bullet+}$ is almost entirely on the oxygen atoms, as indicated by the CO stretching frequency of 1400 cm^{-1} that corresponds to a bond order of ~1.5.[9] Therefore, proton addition occurs on the ring. The π-electron cloud on the ring provides electrostatic attraction to the proton. The proton bonds by sharing the unpaired π-electron on $QH_2^{\bullet+}$.[3,12]

If a proton bonded with an unpaired π-electron localized on a ring C site, the C atom would acquire a valence close to sp^3, with the adjacent H atom out of the ring plane.[1] In $QH_2^{\bullet+}$, the unpaired π-electron that bonds with the proton is equally delocalized over the central C atoms.[12] Therefore, all four central H atoms would be displaced out of the ring plane. This nonplanarity of the structure disrupts the ability of the CC stretch and CH bend vibrations to couple and leads to the observed loss of intensity of the 9a CH bending mode in the transient Raman spectrum.

On removal of the unpaired π-electron from the ring, the Wilson mode 8a is observed to increase in frequency (e.g., by ~45 cm^{-1} from $Q^{\bullet-}$ to Q).[3,13] Since π-H^+ bonding amounts to partial loss of the unpaired π-electron from the ring to H^+ (strengthening of the central CC bonds), one may anticipate an upward shift in the 8a frequency. However, an offsetting downward shift in the frequency can occur due to reduction of the CH bending component in the mode (the 8a frequency in $Q^{\bullet-}$ decreases by 23 cm^{-1} on ring deuteration).[3] Thus, the frequency change for the 8a mode on π-H^+ bonding is expected to be small. It is within the experimental error (±2 cm^{-1}) for the $QH_2^{\bullet+}$ and $QH_3^{\bullet 2+}$ species (Figure 1).

In summary, we have reported the first spectroscopic identification of an π-H^+ bonded dication radical in water. The behavior of particular spectral features is a sensitive probe for the interactions between ring molecules and their environments. The downward shift of 35 cm^{-1} in the 1435 cm^{-1} CO frequency (Wilson mode 7a) and the upward shift of 24 cm^{-1} in the 1620 cm^{-1} ring frequency (Wilson mode 8a) on conversion of hydrated $Q^{\bullet-}$ into $QH_2^{\bullet+}$ are the spectral consequences of replacing the coordinating solvent water molecules with directly bound protons at the two oxygen sites. At the other extreme, an aprotic (and thus more weakly coordinating) solvent should reverse the trend seen here, leading to an upward shift in the 1435 cm^{-1} CO frequency and a comparable (~70%) downward shift in the 1620 cm^{-1} ring frequency of hydrated $Q^{\bullet-}$. This explains some recent observations.[13] The strength of the chemical interactions operating on the ring are indicated by the change in the relative intensity of the CH bending mode in the 1100−1200 cm^{-1} region in the resonance Raman spectra, for which the spectrum in water can be used as standard. In rigid molecular environments, which are often present in biochemical systems, the geometrical constraints lead to chemical interactions much stronger than in water.[14] This work provides valuable guidelines for recognizing and quantifying such interactions by time-resolved resonance Raman spectroscopy.

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[11] The transient absorption spectra of $H^{\bullet}$ atom adducts of benzene derivatives in strongly acidic aqueous solutions have rarely been examined. Since the observed absorption is red-shifted with respect to the $H^{\bullet}$ adducts of hydroquinone (ref 7), this assignment is a good possibility.

[12] The proton is symmetrically situated with respect to the unpaired π-electron distribution (see ref 5 for ESR constants). The effective positive charge on the oxygen atoms of the radical is likely to increase on π-H^+ bonding.

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