concentration increases to approximately its concentration in the combined reactant streams, which is also its concentration in the flow branch at high reciprocal residence times.

Figure 2 shows the appearance of an isola when the flow of buffer is increased. With increased solvent flow, the mushroom is squeezed off at the base leaving an isolated branch of steady states. Now as the reciprocal residence time is increased from the minimum possible value k_0', the system moves along a continuous branch of steady states. At appropriate reciprocal residence times, microliter injections of KI reagent result in perturbation-induced transitions from the continuous branch to the isola branch. Steady-state iodide concentrations and extinction points of the isola branch can then be determined by variation of reciprocal residence time. A slight maximum in steady-state iodide concentration is displayed in the continuous branch below the isola. The conversion of iodate to iodide at this maximum is less than 1.0%; however, in the isola branch at the same reciprocal residence time (3.05×10^{-3} s^{-1}), the conversion is over 41.0%.[12]

The patterns of multiple steady states reported here have potential ramifications for commercial tank reactor processing. Thus, the conversion of reactants to products in the isola branch is many times greater than that in steady states ordinarily accessible by variation of system constraints. A simple model of the iodate–arsenous acid reaction[11] provides a near quantitative description of the patterns of steady states in this system. A detailed study of washout effects in the iodate–arsenous acid system will appear in another paper.[13]

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Registry No. Iodate, 15454-31-6; arsenous acid, 13464-58-9.

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(12) Here, conversion is defined simply as $([I^-] - [I^-]_0)/[IO_3^-]_0$. An alternate definition of conversion which accounts for washout of reactants and products is $((k_0 + k_0')[I^-] - k_0[I^-]_0)/k_0[IO_3^-]_0$.[13]

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Powder ENDOR Analysis of the *p*-Benzosemiquinone Anion Radical

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EPR and ENDOR spectroscopies have been used extensively in the study of biological free radical systems.[1,2] Quinones, which perform various functions in biological systems, have represented an intense area of study for many years.[3] EPR analysis of the free radical signals arising from these quinones suffers, however, from the immobilized character and resulting lack of spectral resolution in the signals observed.[4,5] The investigator is therefore usually confined to spectral quantities such as line width, line-shape characteristics, and average *g* value determinations. Important parameters, such as the nuclear hyperfine interaction, are usually lost in the inhomogeneously broadened spectrum. The infeasibility of single-crystal studies, particularly in biological membrane systems, therefore puts severe limitations on the amount of information available from such studies.

Although the ENDOR technique has been used to considerable advantage in the investigation of other biological radicals (e.g., the chlorophylls[6-8]), such studies have been principally concerned with β-proton interactions. For the more highly anisotropic α protons, a severe broadening of the ENDOR band over a wide spectral range usually occurs. A buildup of intensity at the principal hyperfine tensor values is expected for α protons.[9] Unfortunately, the quality of the spectra so far obtained have precluded such an analysis.[10,11]

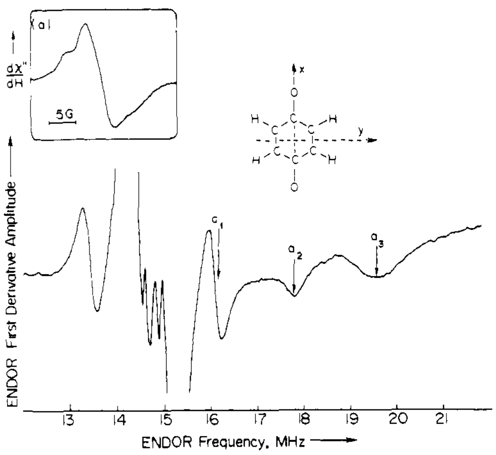

Figure 1. ENDOR spectrum of the *p*-benzosemiquinone anion radical at 123 K: mW powder, 6.3 mW; rf power, 150 W at 12 MHz; FM modulation, ±150 kHz; time constant, 2 s; sweep time, 500 s; average of 17 scans. For explanation of spectral region 14–16 MHz, see ref 20. Inset a: EPR spectrum: mW power, 200 μW; modulation amplitude, 2.0 G; time constant, 50 ms; sweep time, 100 s. Inset b: *g* tensor principal axes as described by Hales.[16]

Table I. Principal Values of Hyperfine Tensor for the α-CH Proton of *p*-Benzosemiquinone Anion Radical Compared with Theoretical Dipole-Dipole Interaction Values for an Isolated C-H Fragment[a,17,18]

	$T_\perp$	T_{CH}	T_π	ρ[c]	angle of hf axis and C-H bond direction
theory[b]	−13.6	15.4	−1.7	1.0	0°
	−1.1	1.2	−0.1	0.08[d]	0°
experimental	−1.2	1.3	0.0	0.08[d]	

[a] All values are in gauss (G). $T_i = a_i + 2.2$ (isotropic value). All a_i values are taken as negative. [b] From ref 17 and 18. [c] Spin density. [d] Determined by using the relationship a_i(isotropic) = $Q\rho_i$ using $Q^{CH} = -27$ G.[21]

We report here that as the result of increased sensitivity of detection, we have been successful in obtaining the principal hyperfine tensor values of the *p*-benzoquinone anion radical from its powder ENDOR spectrum (Figure 1). The formation of fixed hydrogen bonds between the quinone carbonyls and the ethanol hydroxyl group, originally proposed by Hales[15,16] from EPR line-width broadening and anisotropic saturation effects, is confirmed by the presence of an intense band in the ENDOR spec-

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(11) For radicals in which a large *g* factor or hyperfine (*a*) anisotropy does exist orientation selection can be carried out by monitoring the so-called turning points of the EPR spectrum while sweeping through the desired RF frequency range.[12,13] For simple carbon-based organic radicals, which exhibit relatively low anisotropy in their *g* and *a* values, species selection such as the above is not possible at X-band frequencies.

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trum which is substantially decreased in intensity on deuteration of the alcohol hydroxyl group.

The radical species was prepared by air oxidation of the parent quinol (Aldrich reagent grade) in a slightly basic ethanol solution (10^{-2} M). The X-band EPR and ENDOR spectra were recorded at 123 K with a Bruker ER200D spectrometer equipped with a Bruker ENDOR accessory by using procedures similar to those already described.[8] In recording the spectrum of the benzosemiquinone anion radical shown in Figure 1, we used a microwave power of 6.3 mW and 12.5-kHz frequency modulation of the incident microwave frequency radiation.

Hyde[14] has shown that, when the *p*-benzosemiquinone anion radical is rapidly rotating in liquid solution, an ENDOR band is observed at the isotropic coupling value of 2.37 G. On immobilization, however, three distinct bands are observed as illustrated in Figure 1, having absolute coupling values of 0.9 ± 0.1, 2.2 ± 0.1, and 3.4 ± 0.1 G. The EPR spectrum is also illustrated (inset a, Figure 1) and is identical with that already described by Hales.[15,16] The conclusion that the coupling values obtained represent the principal values of the hyperfine tensor is supported by the following observations: (i) The values are in the ratio 0.4:1.0:1.5, i.e., the expected ratio for the principal values of an α-proton hyperfine tensor.[9] (ii) The average value of 2.2 ± 0.1 G obtained from the sum of the three values is in good agreement with the isotropic value given above determined from the solution spectrum. (iii) Table I compares the experimental ENDOR hyperfine tensor values with theoretical values calculated by Atkins,[17] assuming that one principal axis of the local hyperfine tensor lies along the C–H bond direction (T_{CH}) with another axis parallel to the carbon p orbital (T_π). The excellent agreement between the experimental and theoretical values indicates that the principal axis system of the local hyperfine tensors do indeed lie along these directions.[18]

Figure 1 also illustrates an important difference in the shape of the bands observed for the principal components. a_2 and a_3 are relatively weak and broad bands when compared with a_1, which is present as a sharp and clearly defined band. Deuteration of the ethanol hydroxyl group leads to a considerable decrease in intensity of the a_1 band (unpublished data). We therefore attribute the intensity of the band in the protonated solvent to indicate hyperfine interaction from the solvent hydroxyl group. This confirms the original proposal of Hales, who attributed the increased EPR line width in protonated solvent to the formation of rigid hydrogen bonds between the alcohol hydroxyl and quinone carbonyl groups.[15,16]

The results presented here demonstrate the feasibility of obtaining the principal hyperfine tensor values from an organic radical's powder spectrum. The formation of rigid hydrogen bonds between the alcohol hydroxyl and the quinone carbonyl groups is also confirmed. Similar studies of in vivo radicals in powder type samples should prove valuable in elucidating the structure, environment, and orientation of these molecules in their biological habitat.

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Registry No. *p*-Benzosemiquinone anion radical, 3225-29-4.

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[20] The strong absorption in the region 14–15.5 MHz can be attributed to the matrix peak usually observed in powder ENDOR spectra.[2] In contrast to previously reported matrix bands, it is composed of four resolved peaks. The sharp bands seen at the center in Figure 1 are slightly overmodulated. Observation at lower FM modulation (±30 KHz) shows the presence of four distinct bands (O'Malley, P. J.; Babcock, G. T., unpublished data). Observations of a structural matrix peak has previously been reported by Möbius et al.[19] and may be associated with the increased spectral resolution attainable by FM modulation and phase-sensitive detection.

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Conversion of η^4,η^6-Bis(arene)ruthenium(0) Complexes to Cyclohexadienyl Analogues of Ruthenocene

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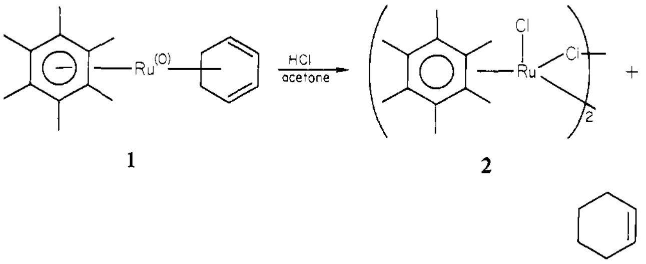
The reaction of (η^4-cyclohexadiene)(η^6-hexamethylbenzene)ruthenium(0) (**1**) with concentrated hydrochloric acid in acetone gives cyclohexene and the dimeric chloride **2**.[2] Previously, we have described using this basic reaction as a key step in a new, general method for synthesizing (η^6-[2_n]cyclophane)ruthenium(II) solvates and bis(η^6-[2_n]cyclophane)ruthenium(II) compounds.[3] Since, η^4,η^6-bis(arene)ruthenium(0) complexes are also well-known,[4-7] we have since investigated how such ruthenium(0) compounds behave toward acid. We now report that η^4,η^6-bis(arene)ruthenium(0) complexes react to yield cyclohexadienyl derivatives. These, in turn, readily undergo hydride reduction, so that the two-step sequence provides a convenient route for preparing cyclohexadienyl analogues of ruthenocene.



1 **2**

As shown in Scheme I, our first experiments were with (η^4-[2_2](1,4)cyclophane)(η^6-hexamethylbenzene)ruthenium(0) (**4**), which was prepared from **3** by reduction with aluminum in an aqueous sodium hydroxide–hexane mixture.[8,9] Treatment of **4** with concentrated hydrochloric acid in acetone then gave **5**. The skeletal structure assigned **5** was clearly suggested from its NMR spectra. However, elemental analysis of **5** showed the unexpected presence of the additional elements of hydrogen chloride. A single-crystal X-ray analysis confirmed the correctness of the skeletal assignment for **5** and showed the counterion to be the unusual hydrogen dichloride anion. This anion can readily be exchanged for other counterions such as PF_6^- and so is not an integral part of the organic moiety. In Figure 1 the molecular structure of **5** ($X^- = HCl_2^-$), as deduced from X-ray analysis, is presented.[9]

Reduction of **5** with Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride) resulted in hydride attack on the hexa-

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[9] All new compounds being reported have been fully characterized and thier composition and spectral properties are in agreement with their assigned structures. Compound **5** crystallized in the monoclinic system, $P2_1/n$ with a = 18.362 (2) Å, b = 14.946 (2) Å, c = 9.219(1) Å, β = 94.79 (1)° (T = 24 °C, Mo Kα, λ_{a1} = 0.7093 Å) U = 2521.2 Å^3, Z = 4, D_m = 1.43 (1), D_x = 1.434 g cm^{-3}. The structure was solved by the heavy-atom method and refined to R = 0.044 for 6242 reflections with $T > 3\sigma(I)$. Key information regarding the properties of these new compounds and the details of the X-ray crystallographic analysis of **5** are given in the supplementary material.

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