complexes can exist above the threshold for simple dissocation but quickly cease to be important with increasing excess energy.

Experimental

Photoionization ionization efficiency curves were determined as described previously⁶ with a microcomputer-controlled photoionization mass spectrometer. Measurements are precise to ± 1 kJ mol⁻¹, but derived thresholds can have larger uncertainties due to thermal energy influences on the PIE curves. Metastable decomposition spectra and translational energy releases were determined by scanning the potential on the second electric sector of a Kratos MS 50TA mass spectrometer.¹⁴ Ethers were syn-

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thesized as described previously.^{5a,b}

Acknowledgment. We thank D. Pavlu for typing, Professor M. L. Gross and the NSF-supported Midwest Center for Mass Spectrometry for use of the MS 50TA mass spectrometer, a referee for extensive suggestions regarding the organization of the manuscript, and the Australian Research Grants Scheme, the Robert A. Welch Foundation (Grant H-609) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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Total $2p^{\pi}$ Spin Density Mapping as a Function of Hydrogen Bonding Involving an Anion Radical

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EPR spectra were utilized to generate a "map" of the 2p^r spin density distribution in the indanetrione anion radical as a function of hydrogen bond formation between this anion radical and water. ¹⁷O substitution followed by computer simulation of natural abundance ¹³C splittings and enriched ¹⁷O splittings allowed measurements of the spin densities on each atom of the radical. The four observable ¹³C hyperfine splittings were found to vary upon hydrogen bond formation, and the equilibrium constant for hydrogen bonding ($C_9H_4O_3^{-+} + HOH = C_9H_4O_3^{---}HOH$) could be evaluated from the variation in these splittings. However, the 2p^{*} spin densities on only three of the seven nonequivalent positions are perturbed. The 2p^{*} spin densities on the two oxygen atoms are invariant even though the formation of the hydrogen bond involves the oxygen atoms.

The most important solvation effect upon anions dissolved in the most common solvent (water) is hydrogen bonding, and the thermodynamic parameters for the formation of hydrogen bonds from water to anions have been determined by use of IR spectroscopy,¹ NMR,² and EPR³ among other techniques. The use of electron spin resonance for such determinations is, of course, limited to paramagnetic proton acceptors. However, it does have the advantage of allowing direct observation of the changes in the electron distribution in the acceptor upon hydrogen bond formation.4

When EPR is used to its fullest advantage, it is almost like having a means to an enlarged image that can be used to monitor changes in the electron distribution in the acceptor as the hydrogen bond forms. Unfortunately, the proton acceptor must be very polarizable so that the electron distribution is altered sufficiently to yield observable EPR coupling constant and/or g-value changes.⁵ This, combined with the fact that the anion radical must endure in the presence of water, means that the system must be substituted with resonance-stabilizing electron-withdrawing groups that enable the system to resist Birch reduction. Since most of these resonance-stabilizing groups contain oxygen atoms and are located on sp²-hybridized carbons, their presence necessarily leads to "blind" positions where spin densities cannot be conveniently measured.

We recently reported an experimental technique for the introduction of ¹⁷O, which has a nuclear spin of 5/2, to the anion radicals of carbonyl-containing anion radical systems.⁶ This technique, coupled with careful observation of the ¹³C splittings from ¹³C's in natural abundance can allow the complete mapping of the $2p^{\pi}$ atomic orbital spin densities of ketyls, semidiones, semiquinones, etc., as a function of the degree of hydrogen bonding.

Solutions of indanetrione readily form an anion radical upon exposure to alkali metal, and this anion radical in hexamethylphosphoramide (HMPA), where it is free of ion association,⁷ is stable in the presence of water.⁸ Due to its polarizability this anion radical system is one of the most studied in terms of environmental effects.⁹ All of these studies are, however, based upon observations of the proton coupling constants, which are determined by only a very small fraction of the total electron spin density.8 The three oxygens and five unprotiated carbon positions contain the vast majority of the spin density, but they have been blind to empirical observation. We now wish to report a complete mapping of the 2p^{*} atomic orbital spin density in this system, and

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Figure 1. Low-field portion of the EPR spectrum of the ninhydrin anion radical (lower) recorded at room temperature in HMPA. The vertical scale is amplified by a factor of 100 to allow easy observation of the ¹³C hyperfine splittings. The computer simulation (upper) was generated by combining five spectra (one for each of the observable ¹³C substitution sites and one for the per-¹²C species in ratios corresponding to their isotopic natural abundance). The arrows indicate the first line for each f ar off scale. However, the splitting from the protons on positions 6 and 7 ($a_{H(6)} = 0.93$ G) can be observed in the ¹³C spectrum where positions 4 and 9 are ¹³C substituted.

the first such mapping for any anion radical system, as a function of hydrogen bond formation. Further, all of the spin densities, quantum mechanical terms, that are perturbed can be used in conjunction with the Benesi-Hildebrand equation⁸ to evaluate the free energy change for hydrogen bonding (reaction 1), a thermodynamic term.

Results and Discussion

The reduction of ninhydrin in HMPA on a sodium metal mirror results in the formation of the very stable corresponding anion radical, which is characterized by two protons with a coupling constant of 1.23 G and two protons with a coupling constant of 0.93 G. Amplification of the outer regions of the spectrum allows the ¹³C satellite components to be clearly observable (Figure 1). The coupling constants of the two proton, two ¹⁷O, and four of the five ¹³C types were measured and confirmed by means of computer simulation of the superimpositions of the EPR spectra of up to five anion radicals of C₉H₄O₃. Since only four ¹³C couplings were observed, the smallest ¹³C splitting must be less than 0.10 G, which is consistent with both McLachlan and Hückel molecular orbital predictions (see below) of $a_{DC(6)} = a_{DC(7)} \approx -0.08$ G for the equivalent carbons at positions 6 and 7 (structure I; Table I).^{10,11} The carbon at position 2 is also easy to assign in that it



TABLE I: Observed Coupling Constants in the Absence of Hydrogen Bonding and ¹³C Coupling Constants Predicted from Eq 2 in Parentheses^a

position	a _H °	allo	a170°
1, 3		2.36 (-2.04)	3.94
2		1.87 (+1.54)	11.63
4, 9		3.06 (-2.62)	
5, 8	1.23	1.07 (+0.80)	
6, 7	0.93	<0.1 (-0.08)	

^{*a*} All values are in G, and the experimental error is estimated to be ± 0.01 .



Figure 2. EPR spectrum (upper) of the ninhydrin anion radical in HMPA at room temperature after the addition of ¹⁷O-labeled water. The spectral amplification was such that the unsubstituted anion radical was recorded off scale. The computer simulation (lower) was generated via the addition of three spectra (one with a ¹⁷O splitting of 11.63 G, one with a ¹⁷O splitting of 3.94 G in a ¹/₂ ratio, and one with no oxygen splitting). Anisotropic effects were not accounted for in the simulation.

is the unique carbon and exhibits only half of the EPR intensity of the other carbons. Again, there is good agreement between the observed coupling and predicted coupling for this carbon (Table I).

The ¹³C assignments were based upon the relationship developed by Karplus and Fraenkel,¹¹ for ¹³C bonded to X_i

$$a_{^{13}\mathrm{C}} = (S^{\mathrm{c}} + \sum Q^{\mathrm{c}}_{\mathrm{CX}_i})\rho^{\pi} + \sum Q_{\mathrm{X},\mathrm{C}}\rho_i^{\pi}$$
(2)

where S^{c} and $Q^{c}_{CX_{i}}$ represent the $\sigma-\pi$ polarization constants for a given carbon with spin density ρ^{π} and ρ_{i}^{π} and $Q_{X,C}$ are the spin density and polarization constants on its neighbors. Following Karplus and Fraenkel,¹¹ values of 14.44, -13.94, and 19.5 G were used for Q^{c}_{CC} , Q_{CC} , and Q^{c}_{CH} , respectively. Following Sioda and Koski,¹⁰ $Q^{c}_{CO} = 17.7$ and $Q_{OC} = -27.1$ G were used.

The spin densities (ρ^{π}) at positions 7 and 8 were obtained by use of the McConnell equation $(a_{\rm H} = Q^{\rm H}\rho^{\pi})$ and the proton coupling constants. When $Q^{\rm H}$ is chosen to be -30 G, the spin densities best agree with the previously calculated McLachlan values.¹⁰ The oxygen spin densities and coupling constants can in principle be related by equations similar in nature to eq 2, but as described by Broze and Luz,¹² these do not lead to improved statistical fits as compared to those from the simple expression¹² $a_{\rm O} = Q^{\rm O}\rho^{\pi}$.

As previously described,⁶ the addition of $5 \ \mu L$ of $20\% \ H_2^{17}O$ to ca. 1 mL of anion radical solution results in the formation of the ¹⁷O-substituted anion radical. In this case, we observed the appearance of two new C₉H₄O₃ anion radicals, both exhibiting the original proton splittings (Figure 2). Each of the two new radicals also exhibits a splitting from an ¹⁷O ($I = \frac{5}{2}$). The larger

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of the two ¹⁷O coupling constants (11.63 G) was assigned to the O at position 2, on the basis of the fact that it was observable only after a significant amount of the species with the smaller ¹⁷O coupling constant (3.94) was formed. Further, the addition of 2.0 μ L of water to the solution did not yield an observable signal for the species with $a_{O(2)} = 11.63$ G, but the species containing the ¹⁷O with the smaller spin density was clearly observable. Letting $Q^{\circ} = 80$ G yields oxygen spin densities that are in good agreement with the McLachlan values, Table I, and this value was used subsequently. The use of a Karplus type equation for the oxygen coupling constant as $a_O = (S^{\circ} + Q^{\circ}_{OC})\rho^{\pi}_O + Q^{\circ}_{CO}\rho^{\pi}_C$ might have the effect of lowering Q° . Trial use of the semiempirical value of Broze and Luz¹² of $Q^{\circ} = 45$ G, however, did not alter the magnitude or the direction of the trends due to hydrogen bonding, as displayed in Figure 4.

At the remaining positions (carbons 1, 2, and 9) the McLachlan values¹⁰ of 0.146, 0.343, and -0.001, respectively, were used for $\rho^{\mathbf{T}}$. The rather large magnitudes of Q^{H} and Q^{o} are needed to gain agreement between the experimental and the McLachlan spin densities and to keep the summation of the spin densities equal to unity. A theoretical value of $S^{c} = -12.75$ G was calculated by Karplus and Fraenkel¹¹ for a carbon atom bonded as in CHC₂ but was shown semiempirically to vary with bonding type. For example, for the ring juncture carbon in naphthalene anion radical they obtained -9.8 G. We performed iterative calculations of ¹³C coupling constants as a function of S^c for all of the significantly varying types of carbons in ninhydrin. A value of -18.75 G proved to be the best average for our empirical purposes, and it was used. The assignments of the ¹³C coupling constants are consistent with the fact that the species containing a ¹³C with a coupling of 1.87 G is present in only half of the concentration of other ¹³C-substituted systems.

With all of the coupling constants and the spin densities of all 12 positions assigned, aliquots of water were added to the anion radical solution to allow observation of how these parameters vary upon the formation of hydrogen bonds to the anion radical. The addition of water did not perturb either of the ¹⁷O coupling constants or the small proton coupling constant ($a_{H(7)}$) up to 6 M water. Thus the formation of the hydrogen bond (reaction 1) between water and presumably the oxygen atoms does not disturb the existing spin densities on either of these atoms.

The spin density at carbon positions 5 and 8 decreased in proportion with the observed decrease in the magnitude of the corresponding proton coupling constant $(a_{H(5)})$ as hydrogen bonding increased. As the concentration of water increased from 0 to 10% by weight (0 to 6 M), $a_{H(5)}$ decreased from 1.23 to 1.03 G.

The magnitudes of the ¹³C coupling constants at positions 1, 2, and 5 also exhibited decreases of about 12%, 63%, and 35%, respectively, while that at the ring juncture $(a_{12}C_{(4)})$ increased by 10%, as the hydrogen-bonding equilibrium (reaction 1) was shifted to the right via the addition of 6 M water. Both oxygen coupling constants were absolutely invariant with the addition of the water.

Each of these coupling constants is intrinsically related to the thermodynamic equilibrium constant for reaction 1. It is well established that anion radicals can be generated free of ion association in HMPA^{2,4,5,7} and that the addition of a proton donor to the solution results in the formation of both hydrogen-bonded HMPA and hydrogen-bonded anion radical.¹³ The problem of dimerization of the proton donor is circumvented by the formation of the strong hydrogen bond between the HMPA and the proton donor, and the exchange of this hydrogen bond to the anion radical (C₉H₄O₃^{\leftarrow}) from the solvent can be monitored via the EPR coupling constants. Since the equilibrium to be studied (reaction 1) is fast on the EPR time scale, the equilibrium constant can be studied by the use of time-averaged EPR coupling constants (eq 3).¹⁴ A simple plot of $1/(a - a^\circ)$ vs 1/[HOH] should yield a

$$1/(a - a^{\circ}) = 1/\{K_{eq}(a' - a^{\circ})[\text{HOH}]\} + 1/(a' - a^{\circ})$$
 (3)



Figure 3. Plots of (absolute values of) reciprocals of $(a - a^{\circ})$ vs reciprocals of the molarity of the added water. The K_{eq} for reaction 1 is obtained from the intercepts divided by the slopes. These ranged from 0.04 to 0.13 due to the intrinsic large percentage errors in very small intercepts.



Figure 4. Plots of spin density on carbon atoms 2, 4, and 5 vs molarity of added water. The spin densities for positions 4 and 5 have been multiplied by a factor of 10 for the presentation. The spin densities of the other atoms remain invariant with the addition of water.

straight line (where *a* is the observed coupling constant in the presence of the donor, a° is that for the anion radical free of hydrogen bonding, and *a'* is the coupling constant for the hydrogen-bonded anion radical. Since the total concentration of water is much larger than that of the anion radical (C₉H₄O₃⁻⁻), the concentration of water not hydrogen bonded to anion radical ([HOH]) is virtually that of the added water. In principle, any coupling constant that undergoes a measurable change upon the addition of water can be use in eq 3.

As predicted when a is replaced by $a_{H(5)}$, $a_{^{13}C(1)}$, $a_{^{13}C(2)}$, $a_{^{13}C(4)}$, or $a_{^{13}C(5)}$, linear plots are obtained (Figure 3). Further, all five plots yield equilibrium constants for reaction 1 that are in reasonable agreement, the average being $K_{eq} = 0.8 \pm 0.4$.

The spin densities at the three oxygen atoms, and carbon centers 6, 7, 5, and 8 having been determined as described above, eq 2 (as expressed for 13 C positions 1 and 2) together with the equation expressing the fact that the sum of the spin densities is unity, provided three independent equations that were used algebraically to obtain the three remaining spin densities, at carbon centers 1, 2, and 4. Utilizing the smoothed coupling constant vs water data represented by Figure 3, a complete spin density map as a function of the degree of hydrogen bonding was obtained (Figure 4). The spin densities for the completely free and completely hydrogen bonded anion radical are qualitatively illustrated in reaction 4.



Surprisingly, the spin densities on only three of the seven nonequivalent positions are perturbed upon the formation of a hydrogen bond with the anion radical. The spin densities on the two oxygen types are invariant even though the formation of the hydrogen bond undoubtedly involves the oxygen atoms. This can be rationalized in view of the fact that a perturbing field, as from

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a hydrogen bond, attracts electron pairs as opposed to polarizing a single electron. The redistribution of the single odd electron upon hydrogen bond formation is evidently not significant at the oxygen atoms. The variation in the spin densities in the anion radical with the formation of the hydrogen bond, of course, reflects the change in the wave function of the LUMO when an electrophilic center approaches the system. These results could, in principle, be predicted by quantum mechanical calculations. However, the complexity of the system, the relatively small perturbation caused by the hydrogen bond, and the consequent approximations that must be made render such calculations of little value.

Experimental Section

HMPA was distilled (from potassium metal) under high vac-

uum directly into the glass apparatus containing the indanetrione which was then reduced to its anion radical on a freshly distilled sodium mirror. Representative samples of this solution, for EPR analysis, were then poured into the EPR sample tubes which were subsequently sealed from the apparatus. Some of these sample tubes contained capillary tubes which were charged with H₂O or $H_2^{17}O$. Agitation of the sample resulted in the rupture of the capillary tubes and subsequent exposure of the anion radical solution to the water. The EPR spectra could then be recorded again. The EPR spectra were recorded on a Bruker-IBM ER-200 spectrometer.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Estimation of Dispersion Relations from Short-Duration Molecular Dynamics Simulations

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Simulation of the motion of particles in large molecular chains is computationally complex, generally involving the solution of large systems of differential equations employing iterative techniques. Generating solutions for even very short time intervals can require significant amounts of computational effort. Though the particle trajectories are significant, further insight into the molecular dynamics is often gained by attempting to predict experimentally verifiable dispersion relations. By use of conventional techniques, however, the accuracy with which frequencies (as a function of wave number) can be estimated is limited by the amount of data available, and often these techniques are completely inadequate with short-duration trajectories. Herein, a new technique (ESPRIT) for obtaining accurate estimates of the complex poles (frequencies of vibration as well as damping coefficients) associated with dominant modes of oscillation present in short-duration molecular dynamics simulations is described. ESPRIT manifests significant performance and computational advantages over previous high-resolution algorithms such as MUSIC.

1. Introduction

The study of nonlinear phenomena in many-particle dynamical systems has recently received a great deal of attention.¹⁻¹¹ This is due largely to the fundamental significance of such problems, coupled with recent advances in computing technology that permit numerical solutions to heretofore untractable problems.^{2,4} A popular technique for analyzing such systems is the power spectra method.¹¹ Therein, the basic idea is to numerically solve Hamilton's equations of motion for a set of time- and space-dependent functions (particle probability density functions) from which particle density correlation functions can be calculated.⁶ Spectral analysis of these correlation functions is then performed using Fourier techniques (i.e., FFTs). This technique has been used to characterize quasi-periodic motion of nonlinear dynamical systems and to compute dispersion relations of many-particle systems.

The major problem with the power spectra method is its limited resolution. Classical Fourier analysis of functions over a finite interval has a resolution capability inversely proportional to the length of the interval. For example, in molecular dynamics (MD) simulations, approximately 33 ps of data are required to achieve 1 cm⁻¹ resolution. In large many-particle systems, MD calculations are very CPU intensity, a fact that has discouraged the use of the power spectra method in such problems. Furthermore, the

dynamics can change as the result of structural changes over long time intervals, invalidating the use of long time intervals for the purpose of increasing resolution. Thus, it might seem that this method is of limited value in such problems.

However, the basic signal processing problem being addressed in the power spectra method is approximately the same, assuming the nonlinear effects are small, as the problem of identifying (damped) sinusoidal components in short-duration time series. In general, this is the case if the quadratic terms in the expansion

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