Solvent Effects on the Electron Spin Resonance Spectrum of p-Benzosemiquinone-1-C^{13}

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The dependence of the C^{13} isotropic coupling constant ($a_1{}^C$) of p-benzosemiquinone-1-C^{13} on solvent composition has been measured in the systems dimethyl sulfoxide–water and acetonitrile–water. The absolute sign of $a_1{}^C$ was determined to be negative in the nonaqueous solvents but it decreases in magnitude and is interpreted to change sign in water-rich mixtures. The $a_1{}^C$ dependence on solvent composition is found to be in excellent quantitative agreement with activity data on the dimethyl sulfoxide–water system, provided three complexes are assumed to be in equilibrium. These complexes are RD_2, RWD, and RW_2, where R is the radical anion, D is a dimethyl sulfoxide molecule, and W is a water molecule. Equilibrium constants were obtained for the solvation reactions leading to these species. These results serve to verify the solvent effect theory of Gendell, Freed, and Fraenkel, provided solvent activities rather than concentrations are employed in the calculations. Comparable agreement with theory could not be obtained in the acetonitrile–water system, perhaps because of inadequate activity data. The detailed synthesis of p-benzoquinone-1-C^{13} from sodium acetate-1-C^{13} is given.

I. Introduction

The sensitivity of nuclear hyperfine coupling constants of free radicals to changes in solvent composition have previously been noted for semiquinones[2a] and aromatic nitro anions.[2b] Recently, an interesting effect of alkali or alkali earth ion concentration on the N^{14} hyperfine coupling constant in p-chloronitrobenzene anion has also been observed.[3]

In the e.s.r. spectrum of p-benzosemiquinone in dimethyl sulfoxide (DMSO) we previously detected[2a] satellite lines which were consistent with the hyperfine interaction of the unpaired electron with C^{13} in natural abundance at the 1-position. The absolute value of the coupling constant $a_1{}^C$ was determined to be 2.13 gauss, in contrast to the value of 0.4 gauss observed by Das and Venkataraman,[4] who measured the spectrum of an isotopically enriched sample in alkaline aqueous ethanol (AAE). We ascribed this discrepancy to a solvent effect, analogous to that observed for the proton hyperfine coupling constants in several p-semiquinones.[2a] Gendell, Freed, and Fraenkel[5] (GFF) subsequently proposed a theory to account for these solvent effects,

based on the assumption that the solvent forms localized complexes with the oxygen atoms, altering their electronegativity and consequently redistributing the spin density within the π-system of the semiquinone free radical. GFF applied this theory and molecular orbital calculations of spin densities to the observed solvent effects on proton hyperfine splittings with good quantitative agreement. GFF also measured the variation of C^{13} satellite splittings in various mixtures of H_2O–DMSO, C_2H_5OH–DMSO, and D_2O–DMSO. The observed variations were shown to be qualitatively consistent with the solvent effect theory.

In order to confirm the assignment of the satellite lines to C^{13} in the one position and to extend the range of the data in mixed solvents, we have prepared p-benzoquinone-1-C^{13} isotopically enriched to 56% and have observed e.s.r. spectra of electrochemically generated semiquinone in the mixed solvent systems water–DMSO and water–acetonitrile (ACN) at several compositions in the range 0–100% water.

The high signal-to-noise ratio resulting from isotopic enrichment permitted accurate measurement of the variation of the splitting constant $a_1{}^C$ with solvent composition, and it also revealed alternations in the width of the C^{13} lines which allowed determination of the sign of $a_1{}^C$, as well as a change in sign with change in solvent composition. We have attempted to explain these data quantitatively in terms of the GFF theory, using a simple model in which the radical is distributed between three types of solvated species, RD_2, RWD, and RW_2, where R is the radical anion, D is a non-aqueous solvent molecule, and W is a water molecule.

II. Experimental

Preparation of p-Benzoquinone-1-C^{13}. Barium acetate-1-C^{13} monohydrate (I) was prepared by the method of Dauben and Vaughan[6] from 1.024 g. of sodium acetate-1-C^{13} (II) of isotopic purity 56.3%, obtained from Merck, Ltd., Montreal. The yield of I was 1.627 g., or 95.8%.

Acetone-2-C^{13} (III) was prepared[6] by pyrolysis of I at 490–510° *in vacuo*, was collected in a liquid nitrogen trap, and was immediately diluted with 5 ml. of distilled water upon warming to room temperature. An unidentified impurity formed during the pyrolysis, imparting a yellow color and acrid odor to the product, but the crude III reacted in the next step with as high a yield as reagent grade acetone.

p-Nitrophenol-1-C^{13} (IV) was prepared by condensing III with sodium nitromalonaldehyde monohydrate (V) by a modification of the method of Hill and Torrey.[7]

(1) (a) Arthur D. Little, Inc.; (b) University of California.

(2) (a) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962); (b) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962); J. Q. Chambers, III, T. Layloff, and R. N. Adams, *J. Phys. Chem.*, **68**, 661 (1964).

(3) T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

(4) M. R. Das and B. Venkataraman, *J. Chem. Phys.*, **35**, 2262 (1961).

(5) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).

(6) W. G. Dauben and C. W. Vaughan, Jr., *J. Am. Chem. Soc.*, **75**, 4651 (1963).

(7) H. B. Hill and J. Torrey, Jr., *Am. Chem. J.*, **22**, 89 (1899).

V was prepared according to Fanta[8] from mucobromic acid, which was prepared from furoic acid by the method of Allen and Spangler.[9] In a 50-ml. erlenmeyer flask, 0.85 g. of IV was dissolved in 9 ml. of water, the aqueous solution of II was added, followed by 2.4 ml. of 1 M NaOH. The stoppered flask was stored in a refrigerator for 75 hr., during which time the reaction mixture developed a deep red color. The sodium salt of IV was recovered by gradual addition with stirring of 4.9 g. of NaOH pellets, accompanied by a temperature rise to 80°. Upon chilling to 5°, a dark brown precipitate appeared, was filtered by vacuum on a glass frit, and was dissolved in 20 ml. of water in the original flask to prevent losses. To purify the salt, 4.5 g. of NaOH was added gradually as before, the solution chilled, and the light brown precipitate filtered. This recrystallization was repeated twice more, with heating to 85°, the final time. The hot solution was left to stand undisturbed and yellow needles of product formed within 10 min. After chilling, the needles were filtered off and dissolved in 4 ml. of water. Then 6 ml. of 1 M HCl was added and the solution was made just acid with concentrated HCl, precipitating IV, which was recrystallized from the same solution, collected by filtration, and air dried. The filtrate was extracted twice with ether; the extracts were dried with a saturated solution of NaCl and then evaporated to collect a small second crop. The total yield of IV (m.p. 113–114°) was 0.306 g., or 36.8% based on I.

p-Aminophenol-1-C^{13} HCl (VI) was prepared from 0.306 g. of IV by reduction with Sn and HCl. IV was dissolved in 2.7 ml. of 95% ethanol in a 25-ml. erlenmeyer flask, and 0.54 g. of Sn shot and 1.65 ml. of concentrated HCl were added. The flask was left on a steam bath, with occasional swirling, for 1 hr., during which time all of the Sn dissolved. The solution was transferred to a 50-ml. flask with 30 ml. of water, heated to 80°, and saturated with H_2S for 10 min. to remove the Sn as the sulfide, which was filtered off. The filtrate was carefully evaporated to collect 0.310 g. of large needles of VI, for a yield of 96.4%.

p-Benzoquinone-1-C^{13} (VII) was prepared from 0.310 g. of VI by oxidation with sodium dichromate. VI was dissolved in 3 ml. of water in a 25-ml. erlenmeyer flask, to which 5 ml. of 5 M H_2SO_4 was added. A solution of 0.40 g. of $Na_2Cr_2O_7 \cdot H_2O$ in 1.8 ml. of water was added dropwise, with constant swirling, during 2–3 min. The reaction mixture turned deep blue, some dark solids separated; then near the end of the addition of dichromate, the solids dissolved and the solution turned deep orange-red. Upon standing for 10 min., shiny platelets of VII separated and were filtered off and washed with a few drops of ice–water. A small second crop was recovered by ether extraction of the filtrate. The combined product was sublimed at 105° and atmospheric pressure to give 0.109 g. of clear yellow needles of VII, m.p. 115–116°. The yield of the oxidation step was 47.4% and the over-all yield was 16% based on II. Das[10] previously prepared VII from II by a different method, with a reported over-all yield of 2%. The isotopic abundance of C^{13}

(8) P. E. Fanta, Org. Syn., 32, 95 (1952).
(9) P. Allen and F. Spangler, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 621.
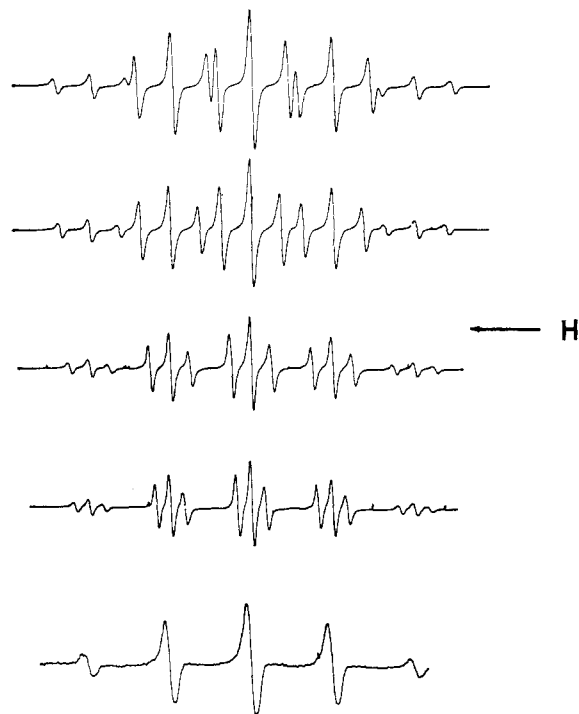(10) M. R. Das, Current Sci. (India), 30, 370 (1961).

Figure 1. Observed spectra of p-benzosemiquinone-1-C^{13} in solutions of DMSO and water with the mole fraction of water equal to (top to bottom): 0.0, 0.137, 0.442, 0.613, and 1.00. The magnetic field increases from right to left.

in VII was determined from intensity measurements of the e.s.r. spectrum of the semiquinone to be 54 ± 3%, in good agreement with the specified 56.3% for the starting material II.

E.s.r. Spectra of p-Benzosemiquinone-1-C^{13}. The semiquinone was generated by diffusion-controlled electroreduction[11] within the microwave cavity of 2–5 × 10^{-4} M solutions of the quinone in deoxygenated DMSO, ACN, and various mixtures of these solvents with distilled water. The reduction potential was −0.7 v. vs. a modified saturated calomel electrode, which incorporated saturated sodium chloride instead of potassium chloride. The supporting electrolyte was 0.05 M tetra-n-propylammonium perchlorate or sodium perchlorate in solutions with mole fractions of water less than or greater than 0.5, respectively. E.s.r. spectra were determined at 9.7 kMc./sec. using the previously described spectrometer.[11]

III. Results

Spectra of the semiquinone in DMSO, in distilled water, and in several mixtures of these solvents are shown in Figure 1. Each spectrum is clearly a superposition of the hyperfine structures of two radical species, p-benzosemiquinone and p-benzosemiquinone-1-C^{13}, the latter of mole fraction 0.54 ± 0.03. It is evident that the C^{13} coupling constant a_1^C changes by a much larger amount than the proton coupling constant a^H upon addition of water to DMSO. In water the value of a^H is 2.357 ± 0.005 gauss, compared to 2.417 ± 0.003 gauss in DMSO, 2.42 ± 0.01 gauss in ACN, and 2.368 ± 0.001 gauss in AAE.[12]

(11) D. H. Geske and A. H. Maki, J. Am. Chem. Soc., 82, 2671 (1960); A. H. Maki and D. H. Geske, J. Chem. Phys., 33, 825 (1960).
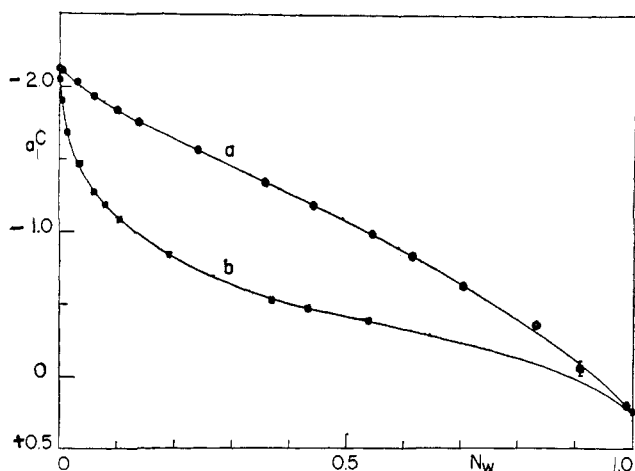(12) G. Vincow and G. K. Fraenkel, ibid., 34, 1333 (1961).

Figure 2. Observed C^{13} coupling constant a_1^C vs. mole fraction of water N_w in solutions of (a) DMSO–water and (b) ACN–water.

With the mole fraction of water in the range 0.137–0.613, as shown in Figure 1, all of the lines in the spectrum are clearly resolved, and it is evident that the high-field component of each C^{13} doublet is narrower than the low-field component. Only a rather small variation in line width with magnetic field among the components of the proton quintet was observed.

This information permits the determination of the sign of a_1^C, the isotropic hyperfine coupling constant of the C^{13} nucleus. The approach has been recently described by de Boer and Mackor[13] in determining the absolute signs of the C^{13} coupling constants in naphthalenide anion. A more complete theory of linewidth alternations in free-radical spectra has been recently developed by Freed and Fraenkel.[14] For the case of p-benzosemiquinone, C^{13} satellites with $M_I = +\frac{1}{2}$ should be narrower than those with $M_I = -\frac{1}{2}$, and the sign of a_1^C is consequently negative in all solvent mixtures in which we were able to resolve the C^{13} satellites. It should be noted that the signal-to-noise ratio of the spectrum of p-benzosemiquinone-1-C^{13} previously determined by Das and Venkataraman[4] in AAE is too low to permit determination of the variation of line width with magnetic field and thus the sign of a_1^C in AAE.

Table I lists the experimental values of a_1^C for a number of values of N_w, the mole fraction of water, in mixtures with DMSO and ACN. In pure water and in mixtures of DMSO–water with $N_w > 0.9$, it was not possible to resolve the splitting from the a_1^C hyperfine interaction. However, the line width in water of each of the five lines in the e.s.r. spectrum was found to be 0.34 ± 0.02 gauss, compared to the value of 0.16 gauss determined from a spectrum of ordinary p-benzosemiquinone in the same concentration (5 × 10^{-4} M) in water. In mixtures of DMSO–water the observed line width w' (in gauss) of the C^{13}-enriched sample, and the natural line width w of ordinary semiquinone, are given in Table II. These data were used to estimate the values of a_1^C listed in Table II for $N_w > 0.9$ by the following procedure: for several small values of the ratio $|a_1^C|/w$, a theoretical spectrum was calculated by the previously described[15] computer

(13) E. de Boer and E. L. Mackor, J. Chem. Phys., 38, 1450 (1963); Mol. Phys., 5, 493 (1962).
(14) J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 39, 326 (1963).

Table I. Carbon-13 Coupling Constant, a_1^C, of p-Benzosemiquinone-1-C^{13} in Mixtures of Water with Dimethyl Sulfoxide (DMSO) and Acetonitrile (ACN)

—DMSO–water—		—ACN–water—	
N_w[a]	$-a_1^{C\ b}$	N_w[a]	$-a_1^{C\ b}$
0.000	2.130 ± 0.007	0.000	2.057 ± 0.005
0.006	2.120 ± 0.007	0.004	1.907 ± 0.005
0.031	2.040 ± 0.007	0.013	1.686 ± 0.003
0.060	1.938 ± 0.005	0.034	1.473 ± 0.003
0.100	1.841 ± 0.003	0.060	1.282 ± 0.003
0.137	1.759 ± 0.003	0.081	1.193 ± 0.005
0.240	1.57 ± 0.01	0.104	1.09 ± 0.01
0.357	1.348 ± 0.005	0.189	0.843 ± 0.005
0.442	1.19 ± 0.01	0.368	0.53 ± 0.01
0.543	0.989 ± 0.003	0.431	0.476 ± 0.007
0.613	0.837 ± 0.008	0.538	0.39 ± 0.02
0.703	0.632 ± 0.003	1.000	-0.24 ± 0.03
0.832	0.36 ± 0.02		
0.909	±0.06 ± 0.04		
0.990	-0.20 ± 0.03		
1.000	-0.24 ± 0.03		

[a] Mole fraction of water; average error is ±0.003. [b] Expressed in gauss.

Table II. Observed Line Widths of p-Benzosemiquinone Anion in H_2O and Mixtures with DMSO

N_w[a]	w'[b]	w[c]	w'/w
1.000	0.34 ± 0.02	0.16 ± 0.01	2.12
0.990	0.28 ± 0.02	0.16 ± 0.01	1.75
0.909	0.15 ± 0.01	0.13 ± 0.01	1.15

[a] Mole fraction of H_2O ±0.003. [b] p-Benzosemiquinone-1-C^{13}, 56%, full width between derivative maxima. [c] p-Benzosemiquinone, full width between derivative maxima.

program SESRS, with an assumed Lorentzian line shape and 56% isotopic enrichment. From these calculated spectra, the value of w'/w was measured and plotted vs. $|a_1^C|/w$. From this theoretical plot and the above data for w'/w and w, the value of a_1^C for each water concentration in the range $0.909 < N_w < 1.000$ was obtained. Since it has been shown that a_1^C is negative for low N_w, the data indicate that a_1^C either reaches a maximum or changes sign at $N_w \sim 0.9$. We have assumed a change in sign, as shown in Table I, since it seems more reasonable that the dependence of a_1^C upon N_w should be monotonic than unimodal. Figure 2 is a plot of the experimental a_1^C vs. N_w for mixtures of DMSO and of ACN with water.

IV. Discussion

According to the solvent effect theory of GFF,[5] the changes in splitting constants upon change of solvent are caused by a redistribution of spin density in the π-system of a semiquinone. Thus the familiar McConnell relation

$$a_i^H = Q_{CH}^H \rho_i^C$$

is expected to be valid for proton coupling constants a_i^H, with $Q_{CH}^H \sim -24$ gauss,[16] but ρ_i^C will in general vary as the solvent is changed. Since the heteroatom hyperfine coupling constants also depend upon the spin density distribution in the radical,[17] it is expected and found that these are solvent dependent, as well.

(15) E. W. Stone and A. H. Maki, ibid., 38, 1999 (1963).
(16) A. D. McLachlan, Mol. Phys., 3, 233 (1960).
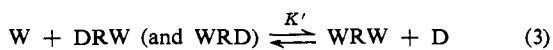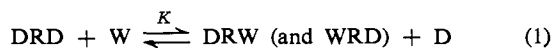(17) M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961).

The theory of GFF assumes that the spin densities are affected by radical–solvent complexing, and that each type of complex is characterized by a unique spin density distribution. The formation and decomposition of complexes is sufficiently rapid in our case that only a single averaged coupling constant, $\bar{a}$, is observed for each nucleus, i.e.

$$\bar{a} = \sum_i p_i a_i \left(\text{with } \sum_i p_i = 1\right)$$

where a_i is the coupling constant characteristic of the ith solvent–radical complex with represents the fraction p_i of the total concentration of the radical. It is further assumed that the p_i can be evaluated, in principle, in terms of a series of solvent–radical association equilibria.

At first it might seem reasonable to assume that the ion does not complex with the nonaqueous solvent molecules, since the C^{13} hyperfine interaction is observed to be the same in ACN and DMSO. It was found, however, that quantitative agreement with the GFF theory could not be obtained for either solvent system if radical–nonaqueous solvent complexing was ignored.[18]

The postulated equilibria are

$$\text{DRD} + \text{W} \overset{K}{\rightleftharpoons} \text{DRW (and WRD)} + \text{D} \qquad (1)$$

$$\text{DRW} \overset{K''}{\rightleftharpoons} \text{WRD} \qquad (2)$$

$$\text{W} + \text{DRW (and WRD)} \overset{K'}{\rightleftharpoons} \text{WRW} + \text{D} \qquad (3)$$

We have ignored mono- and nonsolvated species for simplicity. DRW and WRD refer to complexes in which the water molecule is complexed with the labeled carbonyl and nonlabeled carbonyl, respectively, and we assume $K'' = 1$. If all the equilibria are rapid the single C^{13} coupling constant is given by

$$\bar{a} = \frac{a_1 + Ka_2S + KK'a_3S^2}{1 + KS + KK'S^2} \qquad (4)$$

where $S = a_w/a_D$, the ratio of the activities. Activities are used here, rather than concentrations, because of the large deviations from ideality of the solvent systems investigated. a_1, a_2, and a_3 are the coupling constants of DRD, the *average* of DRW and WRD, and WRW, respectively.

Using a calculation similar to that employed by GFF,[5] in which the oxygen Coulomb integral in a LCAO-MO spin density calculation was assumed to be changed by solvation, we have found that the relationship

$$2\rho_2{}^j = \rho_1{}^j + \rho_3 \qquad (5)$$

holds very well for the π-electron spin densities in the 1-C atom position as well as for the three adjacent atom positions, where j labels the atom position. The subscripts 1, 2, and 3 refer to the spin densities of DRD, the *average* of DRW and WRD, and WRW, respectively. The theory of Karplus and Fraenkel[17] gives the linear relationship

$$a^i = \sum_j q_i{}^j \rho^j \qquad (6)$$

(18) We are indebted to J. Freed for suggesting that the agreement with theory might be improved by assuming radical complexes with DMSO and ACN.
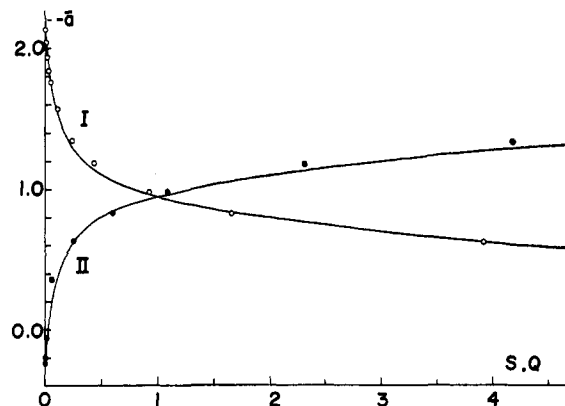

Figure 3. Calculated (solid lines) behavior of the C^{13} coupling constant $\bar{a}$ vs. the parameters $S \equiv a_w/a_{DMSO}$ and $Q \equiv S^{-1}$. Curve I is eq. 8 vs. S, while curve II is eq. 9 vs. Q. Values of the parameters are $a_1 = -2.130$, $a_3 = 0.24$ gauss, $K = 8.98$, and $K' = 0.105$. Points are the experimental data, with solvent activities obtained from ref. 19.

for heteroatoms such as C^{13}, where the $q_i{}^j$ are constants and the sum is taken over the π-atomic orbitals of atom i and all adjacent atoms. Equations 5 and 6 enable us to simplify eq. 4, since they imply

$$a_2 = (a_1 + a_3)/2 \qquad (7)$$

Equation 4 simplifies to

$$\bar{a} = \frac{a_1(2 + KS) + a_3(KS + 2KK'S^2)}{2(1 + KS + KK'S^2)} \qquad (8)$$

Since we have ignored the presence of mono- and nonsolvated species, a_1 and a_3 may be interpreted as the experimental C^{13} hyperfine coupling constants in the pure nonaqueous solvent, and in pure water, respectively. In order to verify eq. 8 experimentally, we have used the data of Kenttämaa and Lindberg[19] on the activities of the water–DMSO system. We found that the data of Vierck[20] on the activities of the water–ACN system gave spurious results when compared with the water–DMSO system.

Since in our experiments $0 < S < \infty$, it is helpful for comparison of all the experimental data with theory, to obtain an equation equivalent to eq. 8, but with the parameter $Q \equiv S^{-1}$ as the variable. The equivalent equation is found to be

$$\bar{a} = \frac{a_3(2 + K'^{-1}Q) + a_1[2(KK')^{-1}Q^2 + K'^{-1}Q]}{2[1 + K'^{-1}Q + (KK')^{-1}Q^2]} \qquad (9)$$

Taking the experimental values -2.130 and $+0.24$ gauss for a_1 and a_3, respectively, we obtain $K = 8.98$ from the initial slope

$$\frac{d\bar{a}}{dS}\bigg|_{S=0} = K(a_3 - a_1)/2$$

Although the remaining parameter K' could in principle be obtained from the initial slope of eq. 9

$$\frac{d\bar{a}}{dQ}\bigg|_{Q=0} = (a_1 - a_3)/2K'$$

the values of $\bar{a}$ near $Q = 0$ are subject to a great deal of experimental uncertainty. K' was obtained, in-

(19) J. Kenttämaa and J. J. Lindberg, *Suomen Kemi.*, **33B**, 98 (1960).
(20) A. L. Vierck, *Z. anorg. Chem.*, **261**, 283 (1950).

stead, by fitting eq. 8 to the experimental values of $\bar{a}$ and S^{19} for a single experimental point, $N_w = 0.703$. From this single data point, we obtained $K' = 0.105$. We have plotted both eq. 8 and 9 in Figure 3 with S and Q as common abscissa. All data points obtained in the water–DMSO system are thus included in Figure 3 at least once. The excellent agreement of experimental points with eq. 8 *and* 9 over the entire range of solvent composition lends support to the radical-solvent complexing theory of GFF, as well as to the specific solvation model employed in this work. The

symmetry of the two curves in Figure 3 is an accidental consequence of the result that $KK' \sim 1$, and is not a general consequence of the theory.

The failure of the data of the water–ACN system to agree quantitatively with the theory may reflect an oversimplification of the solvation model for this particular system, errors in the activity measurements, or both.

Molecular Complexes and Their Spectra. XVIII. Iodine Complexes with Tertiary Amine N-Oxides[1a,b]

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The 1:1 iodine complexes of aromatic and aliphatic tertiary amine N-oxides were studied spectrophotometrically in carbon tetrachloride for the former and in dichloromethane for the latter. The typical compounds used are pyridine N-oxide (I) and N-methylbenzaldoxime (II) for the former, and for the latter tribenzylamine N-oxide (III) and trimethylamine N-oxide (IV). The visible iodine band shifted to 441, 446, 393–394, and 391–392 mμ on complex formation with I, II, III, and IV, respectively. The following values of K (l./mole), ΔH (kcal./mole), and ΔS (e.u.) for the complexes were determined by intensity measurement of these shifted iodine bands: 77.9 (at 23°), −5.85, and −11.0 for I; 35.8 (at 15°), −5.25, and −11.2 for II; 3470 (at 20°), −10.5, and −19.6 for III; and 5660 (22°), −10.0, and −16.9 for IV, respectively. These values are discussed and compared with the iodine complexes with other oxo compounds; it is concluded that the oxygen atom in the N→O bond is the active center for complex formation, and that the complexes with aliphatic tertiary amine N-oxides are more stable than those with the aromatic N-oxides, while the latter complexes in turn are more stable than the iodine complexes of other usual oxo compounds. Ultraviolet absorption spectra as affected by complex formation were recorded under various conditions and are discussed from the viewpoints of hydrogen bonding and salt formation effects on these N-oxides, the spectra of the donors themselves in the complexes, and the effect of complex formation in eliminating the contact charge-transfer band between iodine and dichloromethane. Various spectral constants pertinent to the shifted iodine bands, charge-transfer bands, etc., are shown in Table II.

Introduction

Since tertiary amine N-oxides contain the semipolar bond $>N\rightarrow O$ and show a large dipole moment,[3] the oxygen atom here is doubtless more negative than in usual oxo compounds like alcohols, ethers, amides, and so on, whose iodine complexes were studied spectroscopically by many workers,[4] and a comparative study of the characteristics of the iodine complexes with these N-oxide compounds is then of special interest. In the present paper, we report quantitative spectroscopic and thermodynamic studies of iodine complexes with pyridine N-oxide (I), N-methylbenzaldoxime (II), tribenzylamine N-oxide (III), and trimethylamine N-oxide (IV). Compounds I and II are typical conjugated amine N-oxides as shown in $I_{a,b,c}$ and $II_{a,b,c}$ where oxygen 2pπ-electrons can conjugate with the rest of the π-electron systems.[3,5,6] On the other hand, compounds III and IV, which are aliphatic tertiary amine N-oxides, seem to be different from those of the conjugated type, because in these molecules the N^+–O^- dative bond cannot conjugate with another π-electron system. The oxygen atom in the aliphatic type of amine oxides should then be more negative and a stronger donor for iodine than that in the conjugated type, an expectation which is confirmed by the much larger values of pK_a[7] and

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