

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 88, NUMBER 18

SEPTEMBER 20, 1966

Physical and Inorganic Chemistry

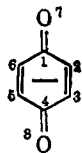
Electron Spin Resonance Study of Oxygen-17 Enriched *p*-Benzoquinone Anion Radical

Wilson M. Gulick, Jr., and David H. Geske¹

Contribution from the Department of Chemistry, Cornell University,
Ithaca, New York. Received April 7, 1966

Abstract: *p*-Benzoquinone-7-¹⁷O was prepared by equilibration of *p*-benzoquinone with H₂¹⁷O. The ¹⁷O-enriched *p*-benzoquinone (PBSQ) anion radical was generated electrochemically and the oxygen-17 isotropic coupling constant, *a*₀, was measured in various solvents. The values ranged from -9.54 ± 0.05 gauss in 1,2-dimethoxyethane to -8.70 ± 0.05 gauss in water. Values of *a*₀ were also measured in various acetonitrile-water mixtures. The sign of the coupling constant was determined on the basis of line-width variations. The oxygen atoms in PBSQ were found to undergo rapid exchange with water. The variation of *a*₀ with solvent composition was rationalized on the basis of π -electron spin densities calculated on the basis of ¹³C and ¹H coupling constants for PBSQ available in the literature.

The *p*-benzoquinone (PBSQ) anion radical has been the subject of intensive study by electron spin



PBSQ

resonance (esr) spectroscopy over the past 10 years. Since the original reports by Venkataraman and Fraenkel^{2,3} in 1955, almost 20 papers have been published presenting experimental esr data for PBSQ.⁴⁻²¹

The observation of coupling with ¹³C present in PBSQ in natural abundance (1.1%), first reported by van Roggen,⁷ was extended by subsequent workers.^{8,11,15,21} Two studies of PBSQ enriched with ¹³C have also been reported.^{14,20}

The proton coupling constants observed for PBSQ have served as the basis for the comparison of experimental spin densities with calculated values.^{18,17,21-27} The rationalization of ¹³C coupling constants in PBSQ on the basis of π -electron spin densities has also been examined.^{12,14,17,20,24} PBSQ has served as a model system for the theoretical treatment¹⁷ of solvent effects.

- (1) Alfred P. Sloan Foundation Fellow.
- (2) B. Venkataraman and G. K. Fraenkel, *J. Am. Chem. Soc.*, **77**, 2707 (1955).
- (3) B. Venkataraman and G. K. Fraenkel, *J. Chem. Phys.*, **23**, 588 (1955).
- (4) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *ibid.*, **30**, 1006 (1959).
- (5) J. E. Wertz and J. L. Vivo, *ibid.*, **23**, 2441 (1955).
- (6) M. Adams, M. S. Blois, Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958).
- (7) A. van Roggen, *ibid.*, **33**, 1589 (1960).
- (8) D. C. Reitz, F. Dravnieks, and J. E. Wertz, *ibid.*, **33**, 1880 (1960).
- (9) J. E. Bennett, *Nature*, **188**, 485 (1960).
- (10) T. Nakamura, *Biochem. Biophys. Res. Commun.*, **2**, 111 (1960).
- (11) J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 756 (1961).
- (12) H. L. Strauss and G. K. Fraenkel, *ibid.*, **35**, 1738 (1961).

- (13) R. W. Brandon and E. A. C. Lucken, *J. Chem. Soc.*, 4273 (1961).
- (14) M. R. Das and B. Venkataraman, *J. Chem. Phys.*, **35**, 2262 (1961).
- (15) E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962).
- (16) V. M. Kazakova and Ya. K. Syrkin, *Zh. Strukt. Khim.*, **3**, 536 (1962); *J. Struct. Chem. (USSR)*, **3**, 518 (1962).
- (17) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).
- (18) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **41**, 949 (1964).
- (19) E. A. C. Lucken, *J. Chem. Soc.*, 4234 (1964).
- (20) E. W. Stone and A. H. Maki, *J. Am. Chem. Soc.*, **87**, 454 (1965).
- (21) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).
- (22) Y. Matsunaga, *Bull. Chem. Soc. Japan*, **33**, 1436 (1960).
- (23) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).
- (24) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).
- (25) J. C. Shug, T. H. Brown, and M. Karplus, *ibid.*, **37**, 330 (1962).
- (26) A. Fairbourn and E. A. C. Lucken, *J. Chem. Soc.*, 258 (1963).
- (27) G. Vincow, *J. Chem. Phys.*, **38**, 917 (1963).

The recent study by Stone and Maki²⁰ of PBSQ in dimethyl sulfoxide-water mixtures is consistent with the theoretical treatment.

We regarded the measurement of isotropic coupling constants for oxygen-17, a_0 , as of significant interest since this would complete the measurement of esr coupling constants for all four kinds of atoms in PBSQ. Since molecular orbital calculations indicated that the spin density on the oxygen atoms in PBSQ is 0.15–0.18, we felt confident that, with sufficient enrichment in ^{17}O , the coupling constant could be measured. Furthermore, in view of the strong solvent dependence of the coupling constant²⁰ for C-1, it seemed likely that the oxygen coupling constant might also exhibit a solvent dependence which would be of assistance in estimating σ - π parameters for that nucleus. We report here the realization of these possibilities.^{27a}

Experimental Section

p-Benzoquinone-7- ^{18}O was prepared by the method described by Becker, *et al.*,²⁸ for preparation of the oxygen-18 enriched compound: 83 mg of freshly sublimed quinone dissolved in 1.3 ml of benzene was mixed with 0.50 g of water enriched to 14.03 atom % ^{17}O and 44.0 atom % ^{18}O (YEDA Research and Development Co., Ltd.). The mixture was sealed in a tube under reduced pressure and then shaken at room temperature for 10 days. The liquid layers were then allowed to separate, and the benzene layer was transferred to a cold finger vacuum sublimation apparatus. Benzene was removed quantitatively by distillation at *ca.* 25 mm at 40°. The system was then isolated from the pump, and the quinone was sublimed onto the cold finger by heating to 70–75°. The red-brown, nonvolatile residue was discarded. The yield of quinone was 60 mg or 72%. Assuming complete randomization of oxygen during the exchange procedure, the ^{17}O content of the quinone is calculated to be 13.2 atom %. Analysis of the product by high-resolution mass spectrometry gave the ^{17}O content as 11.8 ± 1.1 atom % and the ^{18}O content 35.7 ± 2.2 atom %.

Radicals were generated by electrolytic reduction of 1–2 mM solutions of enriched *p*-benzoquinone by the *intra muros* technique.²⁹ In general, a mercury cathode was employed, but the reduction was equally well carried out on platinum. When water was the primary solvent, esr spectra were obtained using a Varian 0.25-mm flat electrolysis cell in the Varian V-4531 multipurpose cavity; all other spectra were examined using a 3-mm o.d. cylindrical cell in a cylindrical cavity. Both the cavity²⁹ and the Varian spectrometer system³⁰ employed have been described previously. Magnetic field calibration markers were placed directly on recorded spectra using a Harvey Wells Model 502 gaussmeter in conjunction with a Hewlett-Packard Model 524D frequency counter.

Tetraethylammonium perchlorate (Distillation Products Industries) at a concentration of 0.1 M was used as supporting electrolyte in all solutions except dimethoxyethane and absolute ethanol in which the tetrabutyl salt was employed. Both salts were recrystallized several times and dried before use. Acetonitrile (Sohio) was purified by method E of Coetzee, *et al.*³¹ Dimethyl sulfoxide (Crown Zellerbach) was distilled *in vacuo*; absolute ethanol was redistilled from Drierite through a 4-ft packed column; dimethoxyethane (DPI) was distilled from sodium benzophenone ketyl in an atmosphere of argon. Anhydrous methanol (Mallinckrodt) was used as received.

In order to obtain esr spectra containing signals due to enriched radicals in aqueous solution, it was found necessary to purify the ^{17}O water used in the original exchange reaction (*vide infra*). This was accomplished by bulb-to-bulb distillation of the recovered

(27a) NOTE ADDED IN PROOF. The esr spectrum of PBSQ- ^{17}O has also been studied by B. L. Silver, Z. Luz, and C. Eden, *J. Chem. Phys.*, **44**, 4258 (1966). These authors have carried out a highly detailed consideration of the line-width variation and conclude that a_0 is negative, a conclusion with which we concur.

(28) E. D. Becker, H. Ziffer, and E. Charney, *Spectrochim. Acta*, **19**, 1871 (1963).

(29) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(30) K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

(31) J. F. Coetzee, G. Cunningham, D. McGuire, and G. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

aqueous layer under reduced pressure. The distillate, which was collected in a calibrated tube, separated into two discrete layers. The upper layer, benzene, was drawn off and discarded. In this way 0.3 ml of purified, enriched water was recovered. This proved to be sufficient volume to fill the Varian flat esr cell to a point above the resonance cavity stack. In this experiment, after degassing the aqueous quinone solution with nitrogen introduced *via* a capillary, contact to the solution was made by direct insertion of the salt bridge of an aqueous saturated calomel reference electrode. The cell was then sealed with tape to minimize ingress of air.

In all spectra, four of the six expected ^{17}O multiplets were clearly distinguishable, two at each end of the spectra. The two-center multiplets were largely obscured by signals from unlabeled radicals. Coupling constants were measured between the pairs of multiplets at the two ends of the spectra; the values reported are averages of these high- and low-field measurements. Uncertainties are given for the 95% confidence level. Widths of the lines involving interaction with the ^{17}O nucleus were somewhat larger than those for the unlabeled radicals with typical values for acetonitrile solutions being 0.55 and 0.35 gauss, respectively.

Observation of the spectrum of ordinary PBSQ under conditions similar to those used for the labeled material revealed only the expected proton and ^{13}C splittings. There exists no possibility of confusing ^{13}C and ^{17}O hyperfine structure.

Results

The esr spectrum shown in Figure 1 was obtained by reduction of a 1.17 mM acetonitrile solution of enriched quinone and is typical of the spectra obtained in various solvents. Data are given in Table I. Data given in Table II for the variation of a_0 as water or alcohol is added to acetonitrile are also displayed in Figure 2.

Table I. Oxygen-17 Coupling Constants in PBSQ Anion Radical

Solvent	$-a_0$, gauss
1,2-Dimethoxyethane	9.54 ± 0.05^a
Acetonitrile	9.48 ± 0.03
Dimethyl sulfoxide	9.46 ± 0.04
Absolute ethanol	9.12 ± 0.03
Water (^{17}O enriched)	8.70 ± 0.05

^a Uncertainties are given for 95% confidence level.

Table II. Oxygen-17 Coupling Constants for PBSQ in Solvent Mixtures

Mole fraction water in acetonitrile	$-a_0$, gauss	Mole fraction methanol (ethanol) in acetonitrile	$-a_0$, gauss
0.000	9.48 ± 0.03^a	0.000	9.48 ± 0.03
0.010	9.43 ± 0.10	0.004	9.44 ± 0.04
0.019	9.41 ± 0.08	0.013	9.41 ± 0.06
0.037	9.32 ± 0.02	0.025	9.30 ± 0.03
0.055	9.31 ± 0.10	0.071	9.31 ± 0.13
0.071	9.32 ± 0.10	0.149	9.25 ± 0.03
0.089	9.34 ± 0.12	0.257	9.18 ± 0.04
0.553	8.93 ± 0.03	0.306	9.21 ± 0.54
0.744	8.93 ± 0.06	0.341	9.18 ± 0.07
0.897	8.83 ± 0.04	0.376 (ethanol)	9.18 ± 0.05
0.943	8.80 ± 0.04	0.409	9.20 ± 0.05
1.000	8.70 ± 0.05	0.464	9.22 ± 0.06
		0.473 (ethanol)	9.19 ± 0.03
		0.545 (ethanol)	9.19 ± 0.04
		1.000 (ethanol)	9.12 ± 0.03

^a Uncertainties are given at 95% confidence level.

The phenomenon exhibited in Figure 1, where the high-field oxygen multiplet appears less intense than

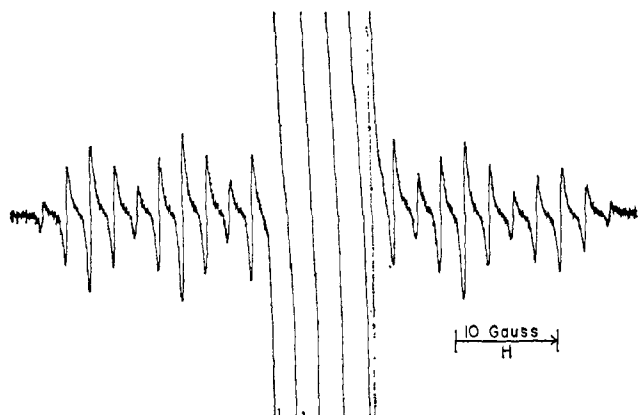


Figure 1. First-derivative esr spectrum of ^{17}O -enriched PBSQ in acetonitrile solution. Radicals were generated by electroreduction of a solution initially 1.17 mM in enriched quinone. The central portion of the spectrum, that due to unlabeled radicals, is off-scale at the gain employed.

the corresponding low-field signal, was observed in all solvents studied. It is reproducible and not associated with radical decay. It is also observed at very low power levels.

In view of the results of Stone and Maki³⁰ regarding the solvent dependence of the coupling constant for C-1, our first attempts were to obtain the limiting values for a_{O} in an aprotic solvent (acetonitrile) and in water. Having obtained spectra similar to that in Figure 1 from acetonitrile solutions, we were puzzled to discover that reduction of the enriched quinone in unbuffered distilled water failed to reveal any esr signals except those attributable to normal proton splittings with satellites due to naturally abundant ^{13}C at position 2 (*i.e.*, two lines of about 2.2% of the unlabeled intensity). The latter coupling constant had an absolute value of 0.713 ± 0.013 gauss.³² Only two explanations for this result seemed possible: either the value of a_{O} had been reduced to the point that oxygen hyperfine structure was obscured by signals from unlabeled radicals, or the ^{17}O had exchanged with the water. Addition of methanol to acetonitrile solutions showed, as indicated in Table II, that the diminution of a_{O} with increasing polarity of the solvent medium was not excessively rapid, thus suggesting that the exchange phenomenon was indeed important. Having recovered sufficient ^{17}O -enriched water to obtain the esr spectrum of PBSQ therein, we did, in fact, observe the anticipated oxygen hyperfine structure. Addition of acetonitrile to this aqueous solution provided data in the region of large mole fraction of water. It proved possible to study a_{O} in the region of low water content using ordinary water, although beyond $N_{\text{water}} = 0.089$ exchange was too rapid to permit measurement of a_{O} with reasonable accuracy.

As a matter of ancillary interest, we have verified on the basis of the experiment described below that exchange of oxygen is rapid only through the anion PBSQ and not through the neutral quinone. A 1.16 mM solution of enriched quinone in acetonitrile containing 0.9 M water was reduced at a mercury

(32) This value is different from the value of -0.594 gauss previously reported for ethanol-water mixtures.¹²

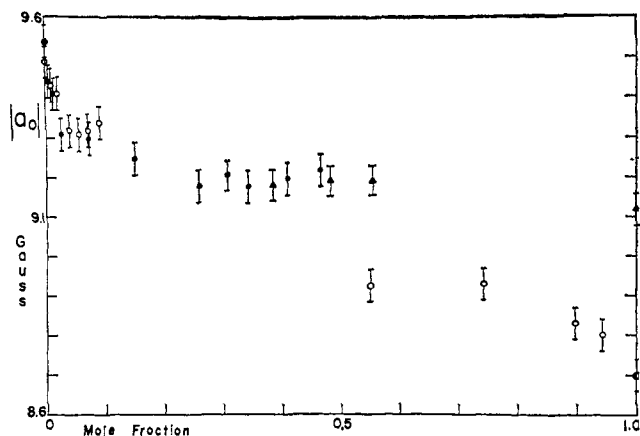


Figure 2. Variation in oxygen coupling constant, a_{O} , with solvent composition. Points represent mole fraction of a second solvent added to acetonitrile, and the heights of the lines represent approximately 1% uncertainty. Open circles indicate N_{water} , solid circles N_{methanol} , and triangles N_{methanol} . The solid hexagon shows the coupling constant in dimethoxyethane.

cathode. The intensity of the low-field oxygen multiplet $|M_I| = 3/2$ was observed as a function of time by repetitive scans and was observed to decrease markedly over a period of *ca.* 40 min. During this time the intensity of the signal from unlabeled radicals did not change. When the intensity of the multiplet had decreased to the point that meaningful measurements could no longer be made, the solution was stirred with nitrogen, thus removing the electrolyzed solution from the vicinity of the electrode and replacing it with fresh solution. Electrolysis of this fresh solution again yielded ^{17}O signals. The intensity of the $|M_I| = 3/2$ multiplet in the initial scan of the second electrolysis was nearly identical with that of the initial scan in the first electrolysis, and the decay of this signal intensity proceeded at the same rate, within reasonable experimental uncertainty. The solution was then allowed to stand for 8 hr, whereupon the water was removed by purging with a stream of nitrogen saturated with acetonitrile. Electrolysis of the solution after this treatment produced oxygen signals in the esr spectrum which were slightly more intense than either of the initial scans obtained when water was present. Moreover, the intensity of these signals did not decay with time. In estimating the rate constant for exchange, the intensity observed in this last experiment was used as the zero time value. Because of the large excess of water present, the reaction was treated as pseudo first order. The exchange reaction has a rate constant of 0.192 hr^{-1} for 0.9 M H_2O in acetonitrile. Qualitatively similar results were obtained when water-acetonitrile solutions were reduced on a platinum spiral cathode instead of mercury.

Radicals were not sufficiently stable for accurate measurement of a_{O} in acetonitrile solutions in which the mole fraction of methanol, N_{methanol} , was greater than 0.464. Consequently, it was necessary to resort to absolute ethanol for the extreme point in the alcohol-acetonitrile study. Further investigation of ethanol-acetonitrile mixtures showed that the values of a_{O} obtained were identical with those containing similar mole fractions of methanol.

Discussion

Sign of a_O . Examination of the esr spectrum of a radical in solution permits (on the basis of line positions) the assignment of only the absolute values of coupling constants. The task of determining the sign of the coupling constant on the basis of line-width studies is examined here as a preface to the discussion of the sign of a_O in PBSQ.

McConnell³³ recognized that the anomalous relaxation of hyperfine lines involved a dependence on the nuclear magnetic quantum number. Subsequent theoretical developments³⁴⁻³⁸ provided the basis for the expression in eq 1 for the line width of lines characterized by only one total nuclear quantum number, M_I . T_2^{-1} is the line-width parameter, and K , L , and C are constants. The KM_I^2 term in eq 1 arises from aniso-

$$T_2^{-1} = KM_I^2 + LM_I + C \quad (1)$$

tropic intramolecular dipolar interactions of electron and nuclear spins whereas the LM_I term involves anisotropy of both the g tensor and the hyperfine tensor. It should be noted that the KM_I^2 term contributes symmetrically to line-widths at high and low fields. By contrast the LM_I term introduces asymmetry. If the sign of L is known, the proper sign for M_I for a particular hyperfine line can be derived. This would permit determination of the sign of the coupling constant since the position of a particular hyperfine line to first order is

$$H = H_0 - a_i M_I \quad (2)$$

given by eq 2, where H is the magnetic field strength necessary for resonance and H_0 is the field strength at the center of the spectrum.

The recognition by de Boer and Mackor³⁹ that the sign of L could be determined was based on the assumption⁴⁰ that the component of the g tensor perpendicular to the molecular plane, g_z , is always less than the mean of the two g terms in the plane of the ring, $\frac{1}{2}(g_x + g_y)$ for planar hydrocarbon radicals. An abbreviated expression⁴¹ for L is written in eq 3,

$$L = kg_1 \rho_1^\pi (2g_z - g_x - g_y) \quad (3)$$

where k is a positive proportionality constant which embodies the hyperfine anisotropy under the assumption of an oxygen p_z orbital perpendicular to the plane of the ring, g_i is the magnetogyric ratio for the particular nuclear species,⁴² and ρ_1^π is the π -electron spin density on the atom in question. On the basis of the argument presented above it is expected that the term $(2g_z - g_x - g_y)$ will be negative.

de Boer and Mackor employed the theoretical strategy outlined above together with experimental spectra to determine that the ^{13}C coupling constant

(33) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

(34) M. J. Stephen and G. K. Fraenkel, *ibid.*, **32**, 1435 (1960).

(35) D. Kivelson, *ibid.*, **33**, 1094 (1960).

(36) M. J. Stephen, *ibid.*, **34**, 484 (1961).

(37) J. W. H. Schreurs and G. K. Fraenkel, *ibid.*, **34**, 756 (1961).

(38) J. H. Freed and G. K. Fraenkel, *ibid.*, **39**, 326 (1963).

(39) E. de Boer and E. L. Mackor, *ibid.*, **38**, 1450 (1963). See also E. de Boer and E. L. Mackor, *Mol. Phys.*, **5**, 493 (1962).

(40) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(41) A more detailed exposition of the evaluation of L is available in ref 39 and 42.

(42) Since both L and the isotropic coupling constant are directly proportional to g_i , the asymmetry of the spectrum is independent of the sign of g_i .

for the α -carbon atom in naphthalene anion radical enriched in ^{13}C is positive. Signs of nitrogen coupling constants in nitroaromatic anion radicals⁴³ and ^{13}C constants in anthracene cation and anion radicals⁴⁴ and PBSQ^{14,15} have been determined on the basis described above.

A general feature of the ^{17}O hyperfine structure in esr spectra (Figure 1) of enriched PBSQ is a field-dependent variation in the amplitude of the derivative signal. One would anticipate that the six multiplets arising from interaction of the unpaired electron with a nucleus of $I = \frac{5}{2}$ would be of equal intensity; however, we find relative derivative amplitudes for the four resolved multiplets of 0.92, 1.0, 0.97, 0.83, in order of increasing external field. The line-width behavior of the ^{17}O signals from PBSQ is at least qualitatively rationalized if both K and L in eq 1 differ appreciable from zero. In fact, on this basis the narrower low-field line, $|M_I| = \frac{5}{2}$, must correspond to a negative value for LM_I . The evaluation of L by eq 3 proceeds as follows. On the basis of all theoretical spin density calculations^{13,17,21-27} the oxygen spin density, ρ_O^π , is positive. The term involving g values was previously noted as negative. Since the magnetic moment for ^{17}O is negative the magnetogyric ratio, g_O , is also negative. Thus L must be positive and the low-field line corresponds to $M_I = -\frac{5}{2}$. From examination of eq 2 it is clear that a_O must be negative. It is on this basis that the algebraic sign in Tables I and II has been affixed.

π -Electron Spin Densities in PBSQ. We now proceed to examine the a_O values in PBSQ in terms of π -electron spin densities. This discussion follows rather closely the recent evaluation of spin densities for PBSQ by Das and Fraenkel.²¹ These workers have estimated spin densities for PBSQ in various dimethyl sulfoxide-water mixtures utilizing ^{13}C and ^1H coupling constants together with σ - π parameters from the Karplus-Fraenkel²⁴ treatment of isotropic carbon-13 coupling constants.

In order to delineate the way in which our evaluation of spin densities in PBSQ differs slightly from previous work²¹ it will be necessary to trace through the calculations in some detail. Evaluation of spin densities in PBSQ is based on experimental carbon-13 and proton coupling constants. The latter quantity can be directly related to the spin density on the contiguous carbon atom, ρ_j^π , by McConnell's⁴⁵ relationship (eq 4). While there are indications that a_H is slightly

$$a_H = Q_{\text{CH}}^H \rho_j^\pi \quad (4)$$

dependent on the excess charge density⁴⁶ on the carbon atom, this refinement will be omitted in this treatment. According to the Karplus-Fraenkel²⁴ treatment the carbon-13 coupling constant for the C-2 carbon atom in PBSQ is given by eq 5. In this and subsequent ex-

$$a_2^{\text{C}} = 21.7\rho_2^\pi - 13.9\rho_1^\pi \quad (5)$$

pressions the π -electron spin density on atom i is written as ρ_i^π , where the numbering scheme shown for PBSQ

(43) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

(44) J. R. Bolton and G. K. Fraenkel, *ibid.*, **40**, 3307 (1964).

(45) H. M. McConnell, *ibid.*, **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(46) J. R. Bolton, *ibid.*, **43**, 309 (1965), and references cited therein.

Table III. Calculated Spin Densities and Experimental Coupling Constants for PBSQ in Acetonitrile-Water Mixtures

Mole fraction water	$-a_H$, gauss ^a	ρ_2^π ^b	$-a_1^C$, gauss ^c	ρ_1^π ^d	ρ_7^π ^d	Calcd ^e $-a_O$, gauss	Obsd $-a_O$, gauss
0.00	2.42 ^f	0.0896	2.057	0.1469	0.1739	9.48	9.48
0.010	2.42	0.0896	1.760	0.1521	0.1687	9.36	9.43
0.019	2.42	0.0896	1.625	0.1544	0.1664	9.30	9.41
0.037	2.42	0.0896	1.451	0.1574	0.1634	9.23	9.32
0.055	2.42	0.0896	1.318	0.1597	0.1611	9.18	9.31
0.071	2.42	0.0896	1.236	0.1611	0.1597	9.14	9.32
0.089	2.414	0.0894	1.157	0.1627	0.1585	9.12	9.34
0.553	2.385	0.0883	0.378	0.1765	0.1469	8.88	8.93
0.744	2.373	0.0879	0.109	0.1813	0.1429	8.80	8.93
0.897	2.364	0.0876	-0.10	0.1851	0.1397	8.73	8.83
0.943	2.361	0.0874	-0.162	0.1862	0.1390	8.72	8.80
1.000	2.357 ^f	0.0873	-0.24	0.1876	0.1378	8.70	8.70
DME ^g	2.395 ^h	0.0887	2.21 ^h	0.1447	0.1779	9.60	9.54
DMSO ⁱ	2.417 ^f	0.0895	2.13	0.1457	0.1753	9.52	9.46

^a Estimated from $-a_H = 2.42 - 0.063N_{H_2O}$. ^b Calculated from eq 4 with $Q_{CH^H} = -27$ gauss. ^c From ref 15 with linear interpolation where necessary. ^d From solution of eq 6 and 7. ^e Calculated using eq 10 with $Q_{CO^O} = -40.41$ gauss and $Q_{CO^O} = -16.69$ gauss. ^f From ref 15. ^g Dimethoxyethane. ^h From ref 21. ⁱ Dimethyl sulfoxide.

is in use. The conservation of spin density is stated in eq 6.

$$\sum_i \rho_i = 1 \quad (6)$$

For the sake of illustration the spin densities for PBSQ in water are evaluated here using eq 4-6. Taking Q_{CH^H} as -27 gauss⁴⁷ and a_H as -2.357 gauss,¹⁵ $\rho_2^\pi = 0.0873$. Taking $a_2^C = -0.713 \pm 0.016$ gauss⁴⁸ $\rho_1^\pi = 0.1876$ and $\rho_7^\pi = 0.1378$.

Thus within the validity of this model the spin densities on all of the atoms in PBSQ in a particular solvent environment can be estimated if a_H and a_2^C are known. Unfortunately, a_2^C has been measured in only a few instances. The reason for this is that the constant probably is quite small in aprotic solvents. For instance, a value of -0.123 gauss is estimated²¹ for a_2^C in dimethyl sulfoxide. Where data for a_2^C in a particular solvent mixture are lacking, the evaluation of spin densities can be accomplished on the basis of a_H and a_1^C as outlined below.

An expression similar to eq 5 for a_1^C is written⁴⁹ as eq 7. The evaluation of Q_{CO^C} and Q_{OC^C} in eq 7

$$a_1^C = 16.1\rho_1^\pi - 27.8\rho_2^\pi + Q_{CO^C}\rho_1^\pi + Q_{OC^C}\rho_7^\pi \quad (7)$$

proceeds as follows. Substituting the spin densities for PBSQ in water into eq 7 and taking $a_1^C = +0.24 \pm 0.03$ as evaluated by Stone and Maki¹⁵ yields eq 8.

$$0.1876Q_{CO^C} + 0.1378Q_{OC^C} = -0.353 \quad (8)$$

The related equation for the 2,5-dioxy-1,4-benzosemiquinone (DOSQ) ion is given^{21,50} as eq 9. Simul-

$$0.2021Q_{CO^C} + 0.0625Q_{OC^C} = 1.779 \quad (9)$$

(47) The choice of $Q_{CH^H} = -27$ gauss is made on the basis of its usage in ref 21.

(48) Since a_2^C for PBSQ in ethanol-water is -0.594 gauss, we assume a negative sign for a_2^C in water.

(49) There appears to be a typographical error in eq 1.2 of ref 21. The first coefficient on the right-hand side of the equation should be 16.1, not 16.2.

(50) Our numbers in eq 9 differ slightly from those reported in ref 21.

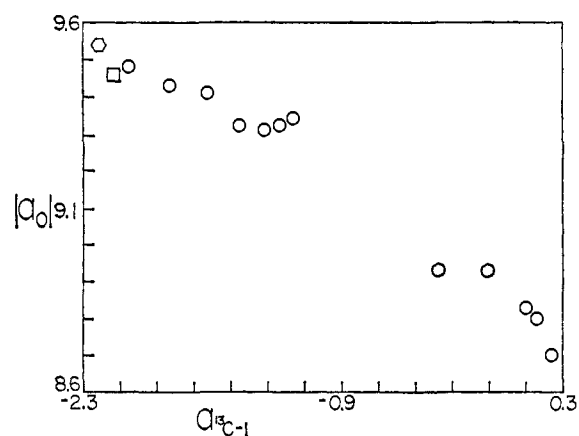


Figure 3. Oxygen coupling constants for various solvent mixtures plotted vs. the carbon-13 coupling constant for C-1 (data from ref 15). Circles indicate acetonitrile-water mixtures. The hexagon and square represent, respectively, values in dimethoxyethane and dimethyl sulfoxide. All values are given in gauss.

taneous solution of eq 8 and 9 yields $Q_{OC^C} = -25.12$ gauss and $Q_{CO^C} = 16.57$ gauss.⁵¹

The estimation of spin densities for PBSQ in those acetonitrile-water mixtures for which we have measured oxygen-17 coupling constants was of particular interest. Such calculations are possible on the basis of eq 7 and the experimental values of a_1^C measured by Stone and Maki.¹⁵ Results of these calculations are presented in Table III. Values of a_1^C for water compositions not exactly corresponding to values examined by Stone and Maki¹⁵ were estimated by linear interpolation.

A graphic comparison of a_O and a_1^C is given in Figure 3. These data can be rationalized in terms of a solvent-induced perturbation of spin density on the carbonyl

(51) These constants are presented with four significant figures for the sake of a self-consistent model. We do not imply that Q_{CO^C} and Q_{OC^C} are accurately known to four significant figures. For instance, if Q_{CH^H} is taken as -26 gauss instead of -27 gauss, the values are $Q_{OC^C} = -32.2$ gauss and $Q_{CO^C} = 19.2$ gauss. The largest uncertainty in the experimental data, ± 0.03 gauss in a_1^C for PBSQ in water, generates an uncertainty of only ± 0.5 gauss in Q_{OC^C} and ± 0.15 gauss for Q_{CO^C} . Calculations in ref 21 are based on data for PBSQ in dimethyl sulfoxide with 0.81 mole fraction water present. Their values of Q_{OC^C} and Q_{CO^C} are -27.1 and 17.7 gauss, respectively.

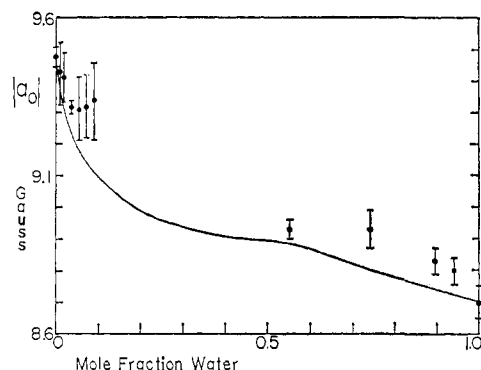


Figure 4. Variation of a_O with mole fraction of water added to acetonitrile. Points represent experimental values and the heights of the lines indicate the 95% confidence level of the measurements. The solid curve indicates the calculated solvent dependence of the oxygen coupling constants (see text).

oxygen and carbon atoms, a statement which is formulated as eq 10. We have chosen to evaluate the two

$$a_O = Q_{OC}^O \rho_{7\pi} + Q_{CO}^O \rho_{1\pi} \quad (10)$$

constants in eq 10 using the calculated spin densities and observed oxygen coupling constants for PBSQ in water and acetonitrile. The values are $Q_{OC}^O = -40.41$ gauss and $Q_{CO}^O = -16.69$ gauss.⁵² Having fixed the extreme conditions of pure water and pure acetonitrile, values of a_O were calculated for intermediate conditions and are given in Table III. A graphic comparison of calculated and observed oxygen-17 coupling constants is presented in Figure 4.

It is far too early to assess the validity of eq 10 as a description of oxygen-17 coupling constants. There

(52) While the individual spin densities are substantially dependent on the particular choice of Q_{CH}^H , the values of Q_{OC}^O and Q_{CO}^O only change to -44.56 and -15.99 gauss when Q_{CH}^H is changed to -26 gauss.

is at least a strong indication that a_O is responsive to changes of spin density on the carbonyl carbon atom.

Exchange Reaction. As indicated previously, the rate constant for the exchange of the oxygen atoms in PBSQ with the water in an acetonitrile solution at 25°, 0.19 hr⁻¹, is significantly larger than the constant for the exchange of water with neutral *p*-benzoquinone in the same medium. Kinetic data for the exchange of *p*-benzoquinone with pure water are limited to the report⁵³ that *p*-benzoquinone undergoes 5.8% exchange in 5 min at 20°. Total exchange in 10 days has also been reported.⁵⁴ The rate constant for exchange of the oxygen atoms in hydroquinone with water⁵⁵ at 25° is 1.9×10^{-6} hr⁻¹. In view of the rapid exchange through the anion radical in acetonitrile we are surprised by the report⁵⁴ that the addition of *p*-benzoquinone does not influence the speed of exchange of hydroquinone in water.

The occurrence of the exchange reaction suggests that a_O in various semiquinones may be accessible without the necessity of synthesizing gross quantities of the corresponding quinone. Thus reduction of quinones in aprotic solvents containing small quantities of ¹⁷O-enriched water should permit the occurrence of the "back-exchange" reaction with the anion and eventual observation of a_O .

Acknowledgments. The authors gratefully acknowledge support from the National Science Foundation through Grant GP-4906 as well as through Grant GP-1687 for partial support for purchase of the esr spectrometer. We are also indebted to Professor F. W. McLafferty for providing the mass spectrometric analysis of the enriched quinone and to Miss Marion Apter for translating a Russian paper.

(53) E. Adler, I. Falkehag, and B. Smith, *Acta Chem. Scand.*, **16**, 529 (1962).

(54) V. V. Fesenko and I. P. Gragerov, *Dokl. Akad. Nauk SSSR*, **101** 695 (1955).

(55) This value was estimated from the data in ref 54.

The Crystal and Molecular Structure of Disodium β -Glycerolphosphate Pentahydrate ($\text{Na}_2\text{PO}_4\text{C}_3\text{H}_5(\text{OH})_2 \cdot 5\text{H}_2\text{O}$)

Mazhar Ul-Haque and C. N. Caughlan

Contribution from the Department of Chemistry, Montana State University, Bozeman, Montana. Received May 5, 1966

Abstract: The structure of disodium β -glycerolphosphate has been determined by X-ray diffraction study. The crystals are monoclinic, $a = 7.943$, $b = 12.104$, $c = 6.167$ Å, $\beta = 107^\circ$, space group $P2_1$ with one molecule in the asymmetric unit. The first Fourier synthesis was based on phosphorus phases; the rest of the structure emerged gradually from four more Fouriers. The phosphorus-oxygen distances are normal and are 1.62, 1.53, 1.52, and 1.46 Å. Each of the phosphate oxygens is involved in hydrogen bonding or coordinated to sodium. Both sodium atoms are six coordinated. A strong network of hydrogen bonding and sodium coordination holds the crystal together.

Glycerolphosphates are involved in the biosynthesis and degradation of phospholipids, the synthesis of fats from fatty acids, the exchange of hydrogen in biological systems, as well as in a variety of other

biologically important processes. Since most of these functions involve hydrolysis of the P-O-C bond at one step or another, precise structural information is significant in understanding the processes. Thus, in