Isotropic Oxygen-17 Coupling Constant in the Nitrobenzene Anion Radical

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Synthesis of ^{17}O-nitrobenzene was accomplished from benzene and nitrogen dioxide enriched in ^{17}O. It was thus possible to measure the ^{17}O isotropic coupling constant, a_O, in the nitrobenzene anion radical. In acetonitrile a_O was 8.86 gauss; in dimethylformamide a_O increased from 8.84 to 8.99 gauss as the water content was increased from 0 to 10%. These results are compared to earlier molecular orbital calculations of nitrogen and oxygen spin densities, $\rho_N{}^\pi$ and $\rho_O{}^\pi$. The possibility is considered that a_O may be described in terms of the equation $a_O = Q_1\rho_O{}^\pi + Q_2\rho_N{}^\pi$.

Introduction

Considerable attention has been lavished on the electron spin resonance (e.s.r.) spectrum of the nitrobenzene anion radical over the past 12 years. A ten-line spectrum was first reported by Weissman and co-workers[1] in 1953. On the basis of the e.s.r. spectrum of nitrobenzene anion enriched in ^{15}N and ^2H, Ward and Klein[2] were able to assign coupling constants to molecular positions. Line widths were sufficiently large that the coupling constant corresponding to the *meta* protons was not resolved.

The electrolytic reduction of nitrobenzene in acetonitrile by the *intra muros* technique[3] permitted observation of e.s.r. spectra uncomplicated by the presence of alkali cations. Resolution of all 54 hyperfine components anticipated from interaction of the unpaired electron with one ^{14}N nucleus and the five ring protons was achieved. Specific deuteration then permitted unambiguous assignment of all the splittings to molecular positions. Well-resolved spectra of the electrolytically generated nitrobenzene anion have more recently been observed in water,[4] N,N-dimethylformamide,[5] and in acetonitrile–water and N,N-dimethylformamide–water mixtures.[6]

Radical anions produced by electroreduction of various substituted nitrobenzenes have been the subject of detailed studies in various solvent media.[5-8] In these investigations, hyperfine splittings have ordinarily been observed for ^1H, ^{14}N, and, in some favorable cases, for naturally abundant ^{15}N and ^{13}C as well.[8]

Observation of splittings due to oxygen, however, has not been even remotely possible in previous studies. Since an important fraction of the unpaired spin is presumed to reside on the oxygen atoms of the nitro group, observation of isotropic coupling constants for these nuclei would be a helpful step in the comparison of theoretical spin-density calculations with experimental results. Das and Fraenkel[9] have recently pointed to the hazards of estimating spin densities at "blind" positions, *i.e.*, those for which no experimental coupling constants are obtainable.

The lack of observed coupling to oxygen is, of course, due to the very low natural abundance (0.039%) of ^{17}O, the only isotope of that element which has a nuclear spin. The problem is compounded by the fact that the spin of ^{17}O is large ($^5/_2$) and six hyperfine lines are produced by coupling to it, thus reducing the intensity of the lines by a factor of six. The feasibility of observing ^{17}O coupling constants for radicals in solution was established by Baird[10] who found a coupling constant of 19.71 gauss for ^{17}O in enriched di-*sec*-butyl nitric oxide. Just recently Dimroth and co-workers[11] observed a coupling constant of 9.7 gauss for ^{17}O in the 2,4,6-triphenylphenoxyl radical. The prospect of ^{17}O coupling constants large enough for comfortable measurement was further enhanced by the calculation[12] that an unpaired electron in a 2s-orbital of ^{17}O would have a coupling constant of 1650 gauss.

We wish to report here the synthesis of nitrobenzene enriched in ^{17}O and the observation of hyperfine coupling to this nucleus in the nitrobenzene anion radical. Solvent effects on the hyperfine coupling constant have been investigated as have the effects of sodium and potassium ion.

Experimental

Reagents. Acetonitrile, N,N-dimethylformamide (DMF), and tetraethylammonium perchlorate were prepared as described previously.[8,13] Nitric oxide was obtained from the Matheson Co. and oxygen gas enriched to 37.8 atom % ^{17}O was obtained from YEDA Research and Development Co., Ltd. (Rehovoth, Israel). Anhydrous aluminum chloride, benzene, and sodium and potassium nitrates were Mallinckrodt analytical reagents; the latter two compounds were dried for 12 hr. at 120° *in vacuo* before use.

(1) T. E. Chu, G. E. Pake, D. D. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953).

(2) R. L. Ward and M. P. Klein, *J. Chem. Phys.*, **28**, 518 (1958); **29**, 678 (1958); R. L. Ward, *ibid.*, **30**, 852 (1959). A better resolved e.s.r. spectrum of the potassium salt of nitrobenzene was reported later by R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961).

(3) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

(4) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **83**, 3909 (1961); **84**, 4212 (1962).

(5) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

(6) (a) P. Ludwig, T. Layloff, and R. N. Adams, *J. Am. Chem. Soc.*, **86**, 4568 (1964); (b) J. Q. Chambers, T. Layloff, and R. N. Adams, *J. Phys. Chem.*, **68**, 661 (1964).

(7) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); *J. Am. Chem. Soc.*, **83**, 1852 (1961); D. H. Geske and J. L. Ragle, *ibid.*, **83**, 3532 (1961); J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1156 (1962).

(8) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

(9) M. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

(10) J. Baird, *ibid.*, **37**, 1879 (1962).

(11) K. Dimroth, F. Bär, and A. Berndt, *Angew. Chem.*, **77**, 217 (1965).

(12) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

(13) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

[17]O-Nitrobenzene. Preparation of [17]O-enriched nitrobenzene by direct nitration of benzene with nitrogen dioxide or dinitrogen tetroxide minimizes the possibility of exchange dilution intrinsic to the conventional procedure using nitric acid in sulfuric acid. Furthermore molecular oxygen enriched in [17]O, a commercially available form, is readily incorporated into nitrogen dioxide by the reaction in eq. 1. Singer, *et al.*,[14]

$$NO + 0.5O_2 \longrightarrow NO_2 \tag{1}$$

have demonstrated 99% conversion of nitrogen dioxide to nitrobenzene in the gas phase reaction of benzene and nitronium ion. Nitronium ion was generated by electron bombardment of nitrogen dioxide. We, however, chose to employ the more conventional chemical techniques of Schaarschmidt[15] for the reaction of nitrogen dioxide and benzene.

Enriched oxygen gas (2.23 mmoles) was allowed to mix with nitric oxide (4.46 mmoles) in a vacuum system and the resulting nitrogen dioxide was condensed in a trap maintained at liquid nitrogen temperature. The nitrogen dioxide was then distilled into a reaction tube which contained 2 ml. of benzene and 1.23 g. of aluminum chloride. The reaction tube was stoppered and warmed to 35° for *ca.* 20 min. The reaction mixture was then poured into ice–water and 15 ml. of benzene was added to facilitate handling the organic layer in subsequent manipulations. The organic layer was extracted with one portion of dilute sodium hydroxide and several small portions of water. These operations were done rapidly to minimize possible exchange reactions. The benzene layer was separated, dried by filtration through magnesium sulfate, and evaporated to 0.75 ml. Benzene and nitrobenzene were then separated by preparative gas chromatography. The yield of nitrobenzene was 93.6 mg., which is 17.1% calculated on the basis of molecular oxygen.

The mass spectrum of the enriched nitrobenzene was examined at moderate resolution and compared to a similar spectrum of ordinary nitrobenzene. Significant increase in the intensities of peaks at masses 124, 125, and 126 was observed, although superficial examination of the spectrum could account for only about 10% enrichment in [17]O. However, comparison of integrated intensities of corresponding e.s.r. lines from the labeled and unlabeled portions of the same e.s.r. spectrum with correction for the sixfold decrease in intensity of the lines due to [17]O interaction gave an average value of [17]O content of 17%, or nearly the value of 18.9% anticipated from the stated enrichment of the original oxygen gas.

Electron Spin Resonance Spectra. Solutions of [17]O-nitrobenzene were reduced electrolytically in the resonance cavity of the spectrometer by the *intra muros*[3] technique. Where mixed solvents were used, the volume per cent of water is given under the assumption of additivity of volumes. The spectrometer system employed has been described previously.[13]

Reported values of [17]O coupling constants are the average of at least two separate scans. In a typical case of three scans, the standard deviation from the

mean was calculated to be ±0.46% and the other cases are all presumed to contain experimental uncertainties of ±1% or less. The introduction of a single [17]O nucleus into the nitrobenzene anion splits each resonance line into six equally spaced lines of equivalent intensity. Radicals containing two [17]O nuclei were not detected. The experimentally measured quantity was the distance between the low-field end line due to the isotopically enriched nitrobenzene anion radicals and the low-field end line due to the unlabeled nitrobenzene anion radicals. This distance represents 2.5 times the [17]O coupling constant.

Observation of the e.s.r. spectrum of ordinary nitrobenzene anion under the same experimental conditions used for [17]O spectra showed that ^{13}C present in natural abundance produced only two small satellite lines on each end of the spectrum.[16] There existed no possibility of confusing [17]O and ^{13}C splittings. The e.s.r. spectrum of the isotopically enriched radical was simulated using a slightly modified version of the SESRS program developed by Stone and Maki[17] executed on a Control Data Corporation 1604 computer. Since the program does not accept spin values greater than 1, the [17]O lines were generated by substitution of one spin with $I = 1$ and a coupling constant of $2a_O$ and one spin with $I = 1/2$ and a coupling constant of a_O.

Results

E.s.r. spectra of [17]O-enriched nitrobenzene anion radical have been obtained in DMF, DMF–water mixtures, acetonitrile, and acetonitrile–water. The effect of alkali metal cations has been observed by substitution of sodium or potassium nitrate for the usual tetraethylammonium perchlorate supporting electrolyte.

As indicated by the data summarized in Table I, the [17]O coupling constant, a_O, was evaluated in solutions of

Table I. Electron Spin Resonance Data

Solvent compn., vol. %[a]	a_O, gauss	a_N, gauss	Line width,[b] gauss	Nitrobenzene concn., mM
100% DMF	8.84	9.67	0.283	1.81
DMF–0.2% H₂O	8.84	9.84	0.226	1.81
DMF–0.6% H₂O	8.85	10.15	0.215	1.81
DMF–1.0% H₂O	8.93	10.39	0.200	1.80
DMF–5.0% H₂O	8.99	11.17	0.193	1.83
DMF–10.0% H₂O	8.99	11.78	0.128	1.73
100% Acetonitrile	8.86	10.29	0.233	1.67
Acetonitrile–2% H₂O	9.02	11.80	0.225	1.64
DMF–0.098 *M* NaNO₃	8.94	10.98	0.367	1.49
DMF–0.094 *M* KNO₃	8.93	10.43	0.279	3.17

[a] Tetraethylammonium perchlorate (0.1 *M*) supporting electrolyte except where alkali metal salts were employed. [b] Width between derivative extrema of the low-field end line of unlabeled spectrum.

varying water content. The amount of water which could be added to these solutions was limited by the fact that the radicals were somewhat less stable in the

(14) S. Singer, N. G. Kim, A. W. Merkel, and M. Farber, *J. Phys. Chem.*, **69**, 799 (1965).
(15) A. Schaarschmidt, *Chem. Ber.*, **57**, 2065 (1924).

(16) It is possible to assign a ^{13}C coupling constant of 4.7 gauss to one carbon atom in the nitrobenzene anion radical. The coupling constant did not change upon addition of up to 4% water to DMF.
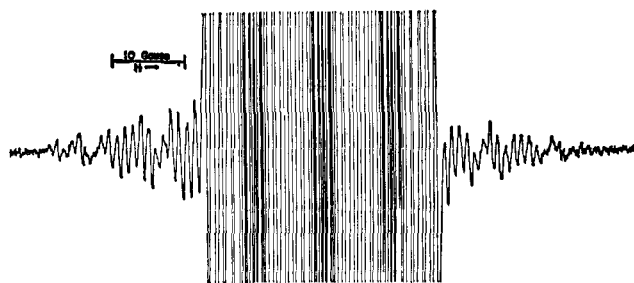(17) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

Figure 1. E.s.r. spectrum of ¹⁷O enriched nitrobenzene anion produced by electrolytic reduction of a 1.81 mM solution of enriched nitrobenzene in 100% DMF. Hyperfine lines due to ¹⁷O are seen at both ends of the spectrum. The center portion of the spectrum, that due to unlabeled radicals, is off scale at the gain employed.
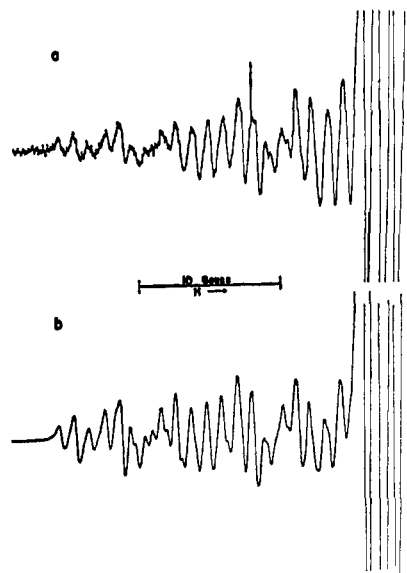

Figure 2. (a) Low-field portion of the e.s.r. spectrum of ¹⁷O-enriched nitrobenzene anion. The solution employed is the same as that described in Figure 1, but the scan rate is one-half as large. (b) Computed spectrum using two spins of one-half with $a = 3.36$ gauss, two spins of one-half with $a = 1.07$ gauss, one spin of one-half with $a = 4.03$ gauss and one spin of one with $a = 9.67$ gauss for the unlabeled species. Identical coupling constants were used for the labeled species with the addition of one spin of five-halves (see text) with $a = 8.84$ gauss. Line widths of 0.35 and 0.42 gauss were employed for the unlabeled and labeled species, respectively. The labeled species was considered 15% abundant. The interval of computation was 0.01 gauss with a Lorentzian line shape assumed.

presence of water. Thus, while the nitrobenzene anion signal is in fact observable even in 100% water,[4] at 15% water in DMF or 5% water in acetonitrile, the intensity of signals from labeled radicals was too low to make meaningful measurements of the ¹⁷O coupling constant.

The complete e.s.r. spectrum of the enriched radical in 100% DMF solution is shown in Figure 1. The low-field end of this same spectrum, scanned more slowly, is shown in Figure 2a and a computed spectrum is given in Figure 2b. Figure 1 serves to demonstrate that the intensities and thus presumably the line widths of the ¹⁷O lines differ between the low-field and the high-field ends. Comparison of line widths of the *extreme* low-field and high-field lines is of direct interest in an attempt to determine the sign of the ¹⁷O coupling constant. However, our experimental results do not permit an *unequivocal* quantitative comparison of the widths of the *extreme* lines.

Line widths in Table I are reported for the signals from unlabeled radicals since in general the ¹⁷O structure was observed with high modulation amplitude which artificially broadened the lines. When the labeled and unlabeled lines were observed under identical experimental conditions, however, the lines of the labeled spectrum were always distinctly broader than corresponding lines in the unlabeled spectrum. The line-sharpening effect of added water is clearly indicated, although not quantitatively since the solutions involved did not all contain the same concentration of nitrobenzene. Clearly, none of the reported line widths represents the intrinsic line width of the spectrum of nitrobenzene anion because all the concentrations employed were large enough to introduce significant broadening.

Discussion

It is clear that a detailed understanding of ¹⁷O isotropic coupling constants in terms of π-electron spin densities cannot be achieved by investigation of a single radical anion. Nevertheless measurement of the ¹⁷O coupling constant in the nitrobenzene anion radical is an entirely sensible way to start.

The latter statement is based on two facts. First, the theoretical calculations[5,8] suggest that the oxygen π-electron spin density is not vanishingly small in the nitrobenzene anion radical. Second, and perhaps more important, is the strong solvent dependence of the isotropic ¹⁴N coupling constant, a_N, in nitro aromatic anion radicals as established by Adams and co-workers.[4,6] Parallel examination of the solvent variation of ¹⁷O and ¹⁴N coupling constants would thus appear to be a fruitful endeavor.

Inspection of the data in Table I[18] reveals that the ¹⁷O coupling constant, a_O, increases slightly with addition of water to either DMF or acetonitrile solutions. Thus, while the value of a_N increases by more than 20% during addition of 10% water to DMF, the oxygen coupling constant increases by less than 2%. The latter effect is so small that differences between contiguous values of a_O are smaller than the experimental uncertainty and only when the entire series of measurements is considered does the trend become convincing.

Glarum and Marshall[19] have reported increases in nitrogen coupling constants upon addition of metal cations to solutions of several trinitro radical anions. Kitagawa, Layloff, and Adams[20] observed an increase in a_N when metal cations were introduced into solutions of the anion radical of 4-chloronitrobenzene. Increases in a_N of similar magnitude for the nitrobenzene anion are noted in this study.

It is noteworthy that addition of sodium or potassium ions to solutions of the nitrobenzene anion radical increases both nitrogen and oxygen coupling constants in a way that parallels the behavior on addition of water.

(18) The present values of a_N for 100% DMF and 100% acetonitrile are slightly smaller than the values reported by earlier workers,[4,6] a fact which can be attributed to small variations of residual water content in the pure solvents.

(19) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **41**, 2182 (1964).

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

We therefore presume that the same sort of mechanism is operative, *i.e.*, a metal cation–radical anion complex is formed, the result of which is to redistribute the π-electron spin density in the nitro group.

The additional effect of added water, that of sharpening the lines, has been pointed out previously.[8] A possible explanation of this effect may be found in the recent work of Adams and co-workers[21] who report that the rate constant for electron exchange between nitrobenzene and its anion is reduced by a factor of 100 when 10% water is added to DMF solutions.

Attention was first focused on the solvent dependence of isotropic coupling constants by the work of Piette, Ludwig, and Adams[4] who noted that the nitrogen coupling constants for nitroaromatic anion radicals were 3–4 gauss larger in water than in acetonitrile. Shortly thereafter Gendell, Freed, and Fraenkel[22] treated solvent effects in terms of rapidly exchanging solvent–radical complexes which effect a redistribution of spin densities. They suggested that the nitrogen coupling constant was dependent on the oxygen spin density, $\rho_O{}^\pi$, as well as on the nitrogen spin density, $\rho_N{}^\pi$, in nitroaromatic radicals. Thus relatively small variations in spin densities could cause appreciable changes in coupling constants. They also suggested that oxygen atoms are probably the atoms most directly affected by solvent interactions.

Rieger and Fraenkel[5] subsequently presented a semiempirical correlation of nitrogen coupling constants with oxygen and nitrogen spin densities (eq. 2). Spin

$$a_N = (99.0 \pm 10.2)\rho_N{}^\pi - (71.6 \pm 11.8)\rho_O{}^\pi \quad (2)$$

densities were evaluated from molecular orbital calculations using the Hückel LCAO theory and the approximate configuration interaction treatment suggested by McLachlan.[23] Solvent effects were treated by increasing the oxygen Coulomb integral in the MO calculations to simulate increasing solvation of the nitro group oxygen atoms in more polar solvents. The calculations for nitrobenzene anion radical (Figure 2 in ref. 5) predict an increase of nitrogen spin density and a slight decrease of oxygen spin density over the range of 1.4 to 1.8 in the value of the Coulomb integral parameter δ_O. The spin density at the *para* carbon decreases 7.7% over the same range while spin densities

(21) T. Layloff, T. Miller, H. Fah, A. Horsfield, W. Proctor, and R. N. Adams, *Nature*, 205, 382 (1965).

(22) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2832 (1962).

(23) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

at the *ortho* and *meta* carbons remain essentially unchanged.

These calculations may be compared with the data[6] for the nitrobenzene anion radical in various DMF–water mixtures. Successive addition of water to DMF does result in a 10% decrease in the *para* proton coupling constant and the *ortho* and *meta* coupling constants remain essentially unchanged. The spin density at the *para* carbon in the nitrobenzene anion radical in water approximates the spin density calculated by Rieger and Fraenkel[5] for $\delta_O = 1.8$. If the nitrogen and oxygen spin densities at the same value of δ_O (as estimated from Figure 2, ref. 5) are used together with eq. 2, the calculated nitrogen coupling constant is 17.2 gauss, a value somewhat higher than the experimental value of 13.87 gauss.

If the model of solvent effects described above is correct for the nitrobenzene anion radical, then an expression of the form of eq. 3 is necessary to describe

$$a_O = Q_1\rho_O{}^\pi + Q_2\rho_N{}^\pi \quad (3)$$

a_O. This statement necessarily follows from the observation that $|a_O|$ increases although $\rho_O{}^\pi$ is calculated to *decrease* as the radical environment is made more polar, *i.e.*, by addition of water. No *a priori* restriction on the relative signs of Q_1 and Q_2 is possible.

One further possibility should be examined. Ludwig, Layloff, and Adams[6a] called attention to the possible role of solvation-induced steric effects which could twist the nitro group out of the plane of the benzene ring. Such a distortion is known to result in increased nitrogen coupling constants and is expected to result in an increase of spin density on both the nitrogen and oxygen atoms.[5,8] This mechanism would permit Q_2 in eq. 3 to be set equal to zero.

We regard acquisition of the ^{17}O data presented in this paper as the first step in establishing a relationship between a_O and nitrogen and oxygen spin densities. It would be premature to assert that the functional relationship expressed in eq. 3 is valid or to estimate the relative importance of the two suggested mechanisms of solvent effects. Measurement of a_O in nitroaromatic anion radicals with widely differing nitrogen coupling constants appears to be necessary.