Lawrence Berkeley National Laboratory

Recent Work

Title

THE ELECTRON SPIN RESONANCE SPECTRUM OF THE RADICAL-ANION OF 1,3-BUTADIENE
IN LIQUID AMMONIA

Permalink

<https://escholarship.org/uc/item/2k5226gn>

Authors

Levy, Donald H.
Myers, Rollie J.

Publication Date

1964-04-01

University of California
Ernest O. Lawrence
Radiation Laboratory

THE ELECTRON SPIN RESONANCE SPECTRUM OF
THE RADICAL-ANION OF 1,3-BUTADIENE IN LIQUID AMMONIA

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Rept. sub. for pub. in
Chemical Physics.

UCRL-11211

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

THE ELECTRON SPIN RESONANCE SPECTRUM OF THE
RADICAL-ANION OF 1,3-BUTADIENE IN LIQUID AMMONIA

Donald H. Levy and Rollie J. Myers

April, 1964

The Electron Spin Resonance Spectrum of the
Radical-Anion of 1,3-Butadiene in Liquid Ammonia

Donald H. Levy and Rollie J. Myers

Inorganic Materials Research Division of the
Lawrence Radiation Laboratory and Department
of Chemistry, University of California
Berkeley, California 94720

April, 1964

Abstract

The electron spin resonance spectrum of the radical-anion of 1,3-butadiene has been observed by means of continuous electrolysis in liquid ammonia. The proton coupling constants were observed to be $A(\text{CH}) = 2.791 \pm 0.007$ oe and $A(\text{CH}_2) = 7.617 \pm 0.005$ oe. These values give a $Q(\text{av.}) = 20.82 \pm 0.02$ oe. The source of this low Q value is discussed together with theoretical spin densities. Simple Hückel theory predicts a spin density ratio of 2.615 which can be compared with the observed coupling constant ratio of 2.729 ± 0.007 . The predictions of Parr and Mulliken's SCF theory are much less satisfactory and give a low spin density ratio. Electrolysis in liquid ammonia appears to be an excellent method for the generation of radical-anions.

Introduction

The molecule 1,3-butadiene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$) has been considered¹ as a model system for pi-electron molecular orbital calculations. Since the hyperfine spectra of hydrocarbon radicals can be so conveniently related to the pi-electron spin density,² it would seem that the electron spin resonance spectrum of the radical-anion of butadiene is particularly significant. A large number of radical-anions have been prepared by reducing the parent hydrocarbon with alkali metals. In the case of butadiene, it does not appear that this technique could be successfully used since it is well known that butadiene is readily polymerized by contact with alkali metals.

The electrolytic reduction technique developed by Geski and Maki³ has many advantages. Since it is possible to do electrolysis directly in the cavity of an electron spin resonance spectrometer, a radical with a lifetime of a second or less can still be observed. For butadiene we decided to develop an electrolytic reduction technique in which the radical-anions could be produced by homogeneous solution reactions rather than heterogeneous electrode reactions.³ The well known "solvated electron" which can be found in liquid ammonia should represent an excellent homogeneous reducing agent. In addition, the high dielectric constant, low freezing point and excellent solvent properties should make liquid ammonia a very satisfactory solvent for electron spin resonance work.

The application of simple Hückel theory to 1,3-butadiene⁴ indicates that it should have about the same reduction potential as does naphthalene.

Since the radical-anion of naphthalene can be very easily produced by sodium reduction one would think that the "solvated electrons" in liquid ammonia should be sufficient for the reduction of butadiene. This was found to be the case, but the half-life of the radical-anion under favorable circumstances was only a few seconds so that continuous electrolytic reduction was necessary.

Experimental

In the electrolytic method it is necessary to have a supporting electrolyte so that satisfactory current flow can be produced. If a solution of NaI in liquid ammonia is electrolyzed between platinum electrodes, iodine is produced at the anode and "solvated electrons" are produced at the cathode. The nature of the "solvated electrons" is still under investigation⁵ but it is sufficient to say here that the potential of the cathode is largely independent of the cation if various alkali metal salts are used.

A smaller amount of ion association with the radical-anions might be expected if bulky cations are present in the supporting electrolyte. Several workers have investigated the electrolysis of solutions of tetra-alkylammonium salts and Forbes and Norton⁶ found that the cathode potential is independent of the alkyl groups. They postulated the production of "solvated electrons" at the cathode. Laitinen and Nyman⁷ confirmed this conclusion from polarographic studies. Both Doyle and Levy⁸ have investigated the electron spin resonance of electrolyzed solutions of tetramethylammonium iodide in ammonia, and these spectra are similar to that of sodium in liquid ammonia. It has been our

observation that the tetraalkylammonium iodides are better supporting electrolytes for our purposes than is NaI. Since tetramethylammonium iodide is only sparingly soluble in liquid ammonia ($2 \times 10^{-3} \text{ M}$ at -78°C) a saturated solution of this salt is often utilized.

The cell which we used for the liquid ammonia reductions is shown in Figure 1. The platinum wire cathode is sealed to the lower tube by a pressed quartz-to-platinum seal and it is made vacuum tight with a small amount of epoxy resin cement.⁹ The anode is contained in the inner tube and it consists of a platinum foil and wire welded to a tungsten wire. There is a hole in the inner tube above the normal ammonia level to facilitate cleaning and to equalize the pressure inside of the cell. A fritted glass disk separates the anode and cathode reactions of the cell. The upper end of the lower tube is slightly raised to prevent solids from falling into the bottom of the lower tube. When filled to the proper level the cell contains about 10 ml of liquid ammonia.

The cell is placed in the unsilvered quartz dewar, also shown in Figure 1, and mounted in the microwave cavity. Cold N_2 gas is passed through the dewar to maintain the cell between the freezing and boiling points of liquid ammonia. The electron spin resonance spectra were taken with a conventional bridge x-band spectrometer utilizing 100 kcs. field modulation and both 6" and 12" electromagnets. Eastman white label tetramethylammonium iodide was recrystallized from an ethanol-water mixture and dried over P_2O_5 . Excess electrolyte was placed in the cell which was then thoroughly evacuated and the ammonia¹⁰ and butadiene¹¹ were distilled over. The contents of the cell were mixed

before electrolysis. Care had to be taken to prevent any solid ammonia from cracking the lower tube.

The optimum electrolysis voltage varied with the concentration of the butadiene in the ammonia. It was usually observed that the signal-to-noise ratio would improve with increasing electrolysis current, but at too high a current the line associated with the "solvated electron" would appear and then the radical-anion spectrum often seemed weaker. If the butadiene was initially 5×10^{-3} M, then an optimum signal was obtained when about 25 v. was applied between the two electrodes.

Experimental Results

An experimental electron spin resonance spectrum as obtained for butadiene radical-anion is shown in Figure 2. The spectrum is seen to consist of five groups of three lines each. If the two protons attached to the end carbon atoms are equivalent then only two proton coupling constants could be expected. Since the coupling constant $A_1 (= A_4)$ is greater than $A_2 (= A_3)$ then one would expect five sets of triplets as is experimentally observed.

The spectrum was measured several times over a range of microwave power and field modulations and the coupling constants in Table I were obtained. The difference in field between lines 1 and 2 were the same as between lines 14 and 15 thus showing that second order terms in the spin Hamiltonian could be neglected. The field difference between the points of maximum slope of the center line at -78°C is 0.3 oe. A theoretical spectrum¹² is shown in Figure 3 assuming the coupling constants in Table I and Lorentzian line shapes all of equal width. The agreement between the observed and calculated spectrum is excellent.

The line width of the spectrum was not found to vary with temperature within our experimental accuracy between -78 and -68°C. The lifetime of the radical-anion was determined by measuring the decay of the signal after the removal of the electrolysis current. At -78°C the decay was found to follow first-order kinetics with a half-life of 2 sec. Since the signal-to-noise ratio could depend greatly upon the experimental conditions the half-life probably does depend upon the temperature and solute. We have no indication that the observed line width is due to electron exchange with neutral butadiene, but it is possible that solute concentration or other factors may be the primary source of line width. Magnetic field inhomogeneity was not a source of line width.

Discussion

The observed values of the proton coupling constants can be related to theoretical spin densities if the Q values² are known. Recent evidence¹³ indicates that the Q for every carbon position must be calculated taking into account a variation of Q with charge density. In our case since we know the proton coupling constant for every carbon atom an average Q value can be exactly determined. Thus by symmetry, we know that $\rho_1 + \rho_2 = 0.5$ and so $Q(\text{av.}) = 2(A_1 + A_2) = 20.82 \text{ oe.}$

This value of Q is particularly small and it seems to confirm the equation of Colpa and Bolton¹³ where Q in radical-anions should decrease with the charge density. If one also considers the values of $Q(\text{C}_8\text{H}_8^-) = 25.67^{14}$ and $Q(\text{C}_6\text{H}_6^-) = 22.50^{15}$ there appears to be a nearly linear decrease of Q with charge density. Colpa and Bolton's equation is

$$A(\text{H}_i) = -Q\rho(\text{C}_i) = -(Q_0 + K\epsilon) \rho(\text{C}_i)$$

where ϵ is the excess charge density. The three radical-anion Q values indicate that K should be close to 40 and $Q_0 \sim 30.0$ oe. while Colpa and Bolton obtained $K = 17$ and $Q_0 = 31.2$ oe. from other data. It is quite possible that changes in the hybridization of the C-H orbitals are partly responsible for these low values of Q . The trend with charge density is moderately close to that expected from Colpa and Bolton's equation, but a rather large K value must be assumed.

Giacometti et al.¹⁶ have included terms for nearest neighbors and obtained satisfactory agreement for the radical-ions considered by Colpa and Bolton and for $C_6H_6^-$. In the later case agreement was only obtained if overlap was included in the usual Hückel treatment. If we apply the equations recommended by Giacometti et al. to the Hückel orbitals⁴ for butadiene radical-anion the predicted proton coupling constants are $A_1 = 9.8$ oe. and $A_2 = 3.8$ oe. These values are essentially unchanged by the inclusion of overlap as recommended by Giacometti et al. These coupling constants are both about 25% larger than the observed ones and it does not seem that this treatment has any advantage over that of Colpa and Bolton even if overlap is included.

If we neglect the variation of Q with charge density, a direct comparison of the experimental value of A_1/A_2 with theoretical values of ρ_1/ρ_2 can be made. In Table II such a comparison is given for a series of one-electron molecular orbital wave functions. It can be seen that simple Hückel theory gives a most satisfactory agreement.

The inclusion of d-orbitals by Sovers and Kauzman¹⁷ is an interesting extension of Hückel theory. The d-orbital value in Table II is the sum of p- and d- electron spin densities. Since the Q values

would not be expected to be identical for these two kinds of orbitals, the spin density ratio shown in Table II is of only qualitative significance. The two SCF values fall far short of the mark and a considerable improvement must be made in this theory to approach Hückel theory for spin density calculations.

Some interesting valence bond structures can be drawn for our radical-anion as follows:

Structures Ia and Ib are those of a substituted allyl radical and simple valence bond arguments² would predict that $\rho_1/\rho_2 = 2$. Since structures of the type II do not place the odd electron at all on the middle carbon atoms, the inclusion of these structures can only increase ρ_1/ρ_2 . Since simple resonance considerations would give a greater importance to the structures of type I, one would predict that $\rho_1/\rho_2 \geq 2$ and it should not be too far above the lower limit. The valence bond structures also predict that the negative charge should be even more concentrated on the end carbon atoms than is the spin.

The simple Hückel theory of Table II can also be modified for the fact that the radical-anion should have two β values.⁴ Since the bond between the middle carbon atoms should be the longer one it should also have the smaller resonance integral β . The result of this difference would be to increase the calculated value of ρ_1/ρ_2 over that given in Table II. This modification could probably compensate for a correction

based upon the variation of Q with charge density where we expect that $Q_1 < Q_2$. We shall not attempt any such compensation, for there does not seem to be any really satisfactory equation for the variation of Q with charge density in our molecule. At this time, it does not seem proper to try to improve the agreement in Table II by introducing any adjustable parameter.

On the experimental side, we do not know the source of the observed line width. In all of its confirmations the CH_2 hydrogens of butadiene fall into two non-equivalent sets.¹⁸ It is possible for an unresolved splitting of the CH_2 coupling constants to contribute a line width to some of the hyperfine components. Since we observe all of the components in butadiene to have the same line width other effects must be dominant. It seems likely that electron exchange either with the solvent alone or through the solute is the major factor in the line width of this radical-anion in liquid ammonia.

Acknowledgment - This work was supported by a grant from the United States Atomic Energy Commission.

References and Footnotes

1. R. G. Parr and R. S. Mulliken, J. Chem. Phys. 18, 1338 (1950);
C. Sandorfy, Electronic Spectra and Quantum Chemistry, Prentice-Hall, Englewood Cliffs, N.J. (1964).
2. H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107 (1958).
3. D. H. Geski and A. H. Maki, J. Am. Chem. Soc. 82, 2671 (1960).
4. A. Steitwieser, Molecular Orbital Theory, John Wiley and Sons, Inc., N.Y. (1961).
5. E. Becker, R. H. Lindquist and B. J. Alder, J. Chem. Phys. 25, 971 (1956); M. Gold, W. L. Jolly and K. S. Pitzer, J. Am. Chem. Soc. 84, 2264 (1962).
6. G. S. Forbes and C. E. Norton, J. Am. Chem. Soc. 48, 2278 (1926).
7. H. A. Laitinen and C. J. Nyman, J. Am. Chem. Soc. 70, 3002 (1948).
8. Unpublished experiments by L. R. Doyle and D. H. Levy.
9. Armstrong Products Co. C-3 resin. Some care must be taken in the selection and application of these cements since many types are paramagnetic even after curing.
10. 99.99% pure, available from the Matheson Co., P.O. Box 65, Newark, Calif.
11. 99.69% pure, available from the Matheson Co. as Phillips Petroleum Co., Research Grade.
12. Done on an I.B.M. 7094 computer and a California Computer Co. digital x-y plotter. We would like to thank Professor A. Maki and Dr. E. Stone for their EPR III Spectrum Simulator Fortran program which we adapted for the x-y plotter.

(References and Footnotes continued)

13. J. P. Colpa and J. R. Bolton, Mol. Physics 6, 273 (1963).
14. H. L. Strauss, T. J. Katz and G. K. Fraenkel, J. Am. Chem. Soc. 85, 2360 (1963).
15. T. R. Tuttle and S. I. Weissman, J. Am. Chem. Soc. 80, 5342 (1958).
16. G. Giacometti, P. L. Nardio and M. V. Pavan, Theoret. Chim. Acta (Berl) 1, 404 (1963).
17. O. Sovers and W. Kauzmann, J. Chem. Phys. 38, 813 (1963); O. Sovers, Thesis, Princeton Univ. (1961).
18. In the case of dimethylbutadiene we have been able to measure a difference of 0.21 oe for the two CH_2 coupling constants.

FIGURE CAPTIONS

Figure 1. Cell and Dewar for Electrolysis in Liquid Ammonia. The dewar was constructed entirely of quartz and it holds the cell in the cavity of the spectrometer.

Figure 2. The Spectrum of Butadiene Radical-Anion in Liquid Ammonia at -78°C . This spectrum is the derivative of the absorption plotted against the magnetic field.

Figure 3. The Theoretical Spectrum. The output of a digital x-y plotter with the coupling constants in Table I and equal width lines of Lorentzian shape.

MU-33781

Fig. 1.

MU-32841

Fig. 2.

MUB-2276

Fig. 3.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.