Title

THE ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS OP SEVERAL 1,3-DIENES

Authors

Levy, Donald H.
Myers, Rollie J.

Publication Date

1965-09-01

UCRL-16410

University of California

Ernest O. Lawrence Radiation Laboratory

THE ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS OF SEVERAL 1, 3-DIENES

UCRL-16410

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California
AEC Contract W-7405-eng-48

THE ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS OF SEVERAL 1,3-DIENES

Donald H. Levy and Rollie J. Myers

September 1965

THE ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS OF SEVERAL 1,3-DIENES

Donald H. Levy* and Rollie J. Myers

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

September 1965

ABSTRACT

The ESR Spectra of the radical anions of 2,3-dimethyl 1,3-butadiene, 1,3-cyclohexadiene and isoprene have been examined in liquid amonia. The proton hyperfine interaction can be readily assigned except for the case of isoprene where there is a small discrepancy between our assignment and the observed spectrum. In the case of 2,3-dimethyl 1,3-butadiene two distinct CH_2 coupling constants are observed as might be possible for the radical anion in either a cis or trans conformation, Hückel theory with the inclusion of hyperconjugation are in good agreement with the observed proton coupling constants.

INTRODUCTION

The technique developed for the electrolytic generation of radical anions in liquid ammonia[1,2] can be used for a variety of conjugated hydrocarbons. In this paper, we use this method for the electron spin resonance spectra of three 1,3-dienes. If the molecular symmetry is fairly high as it is for 2,3-dimethyl 1,3-butadiene and for 1,3-cyclohexadiene a complete assignment of the proton coupling constants is a very easy task. In the case of isoprene [CH_2 CCH_3 CH CH_2] we find that the increase in the number of possible coupling constants makes our assignment less certain and only a tentative assignment is given.

For all of these radicals some of the proton hyperfine interaction can be considered as arising through hyperconjugation with the pi-system of the diene.[3] The equations developed by Levy[4,5] have been used to include hyperconjugation in a Hückel calculation for the proton coupling constants and to help confirm the assignments of the experimental spectra.

EXPERIMENTAL METHOD

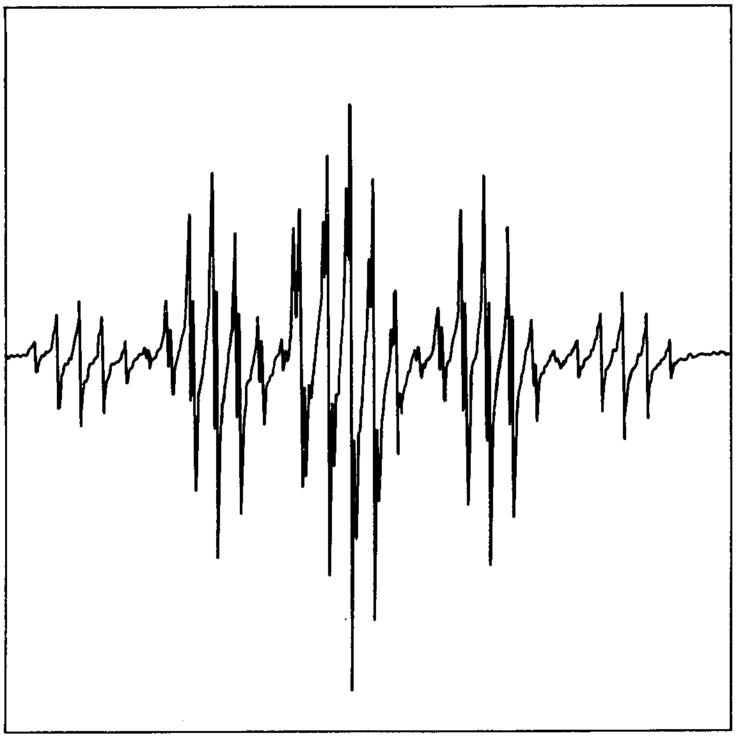
The apparatus is the same as previously described.[1] In most cases the electrolyte is provided by using a saturated solution of tetramethylammonium iodide but for isoprene the spectra were run using a saturated solution of tetraethylammonium iodide. Wide variations were observed in the voltage necessary for the best spectrum and some of these details are given in the next section. The best spectrum is probably a compromise between removal of the parent molecule to reduce exchange broadening, the lifetime of the radical anion and any further reduction to other species. In most cases a good spectrum could be obtained without the appearance of the solvated electron line in the spectrum. Further experimental details can be found elsewhere.[4]

The chemicals used were of the best available commercial grade and in some cases they were also purified further. Several samples of isoprene were used and both purification and mass spectrographic analysis were made in an effort to either eliminate or establish the apparent source of the extra lines observed for this compound.

EXPERIMENTAL RESULTS

The radical anion of 2,3-dimethyl 1,3-butadiene was prepared from a 0.01 M solution of the parent hydrocarbon dissolved in liquid ammonia. At low voltages (e.g. 10 volts) the spectrum consisted of five septets of rather wide lines. As the voltage was raised (e.g. 30 volts) the lines narrowed and the lines of the inner septets were further split to give the spectrum shown in Fig. 1. If the voltage was raised even further (e.g. 100 volts) the line width remained roughly constant but the spectrum became considerably weaker. If the voltage was at this point reduced to the intermediate level the spectrum would grow very rapidly and then decay to the level it originally had when the voltage was at an intermediate (e.g. 30 volt) level. We interpret this behavior as evidence for the formation of a relatively stable diamagnetic dianion which is in equilibrium with the electron and the radical anion.

A spectrum consisting of five septets could be readily assigned to the splittings caused by four equivalent methylene protons and six equivalent methyl protons. However, the additional small splittings of the inner septets can only be accounted for by assuming a slight inequivalence of the methylene protons which produces two sets of two



MU-32839

Fig. 1

equivalent protons. On that basis the spectrum can be completely assigned with the coupling constants given in Table I.

The usual treatments for hyperfine coupling constants predict a single pi-sigma interaction parameter for any given carbon and consequently imply that all protons attached to a given carbon should have the same coupling constant even if they are geometrically unequivalent. This conclusion is generally true and only one other case of unequivalent protons attached to the same carbon has been reported. Fessendon and Schuler[5] have noted that the two methylene proton coupling constants in the allyl radical differ by 0.10 gauss. In order to explain this phenomenon an extension of the usual treatments of sigma-pi interaction is necessary.

The radical anion of 1,3-cyclohexadiene was prepared from a 3-millimolar solution of cyclohexadiene in liquid ammonia. In this case the optimum signal-to-noise ratio was produced with a rather high electrolysis voltage (ca. 60 volts). The resulting spectrum with the signal of the solvated electron superimposed is shown in Fig. 2. The outermost triplet indicates that one of the coupling constants is given by the spacing of the lines in the triplet and a reasonable value for a second coupling constant would be the distance between the first and fourth lines. The third coupling constant is determined from the total width of the spectrum. The coupling constants derived from this assignment are also given in Table I.

The radical anion of isoprene was prepared from a 0.01 M solution of the parent molecule in liquid ammonia. The best spectrum shown in Fig. 3 was produced at rather high electrolysis voltages (ca. 80 volts). At these voltages a large electron line is superimposed upon the isoprene

Table I. Observed and Calculated Proton Coupling Constants

Molecule	Position[a]	Coupling Constant[b]	
		obs.	cal.[c]
2,3-dimethyl butadiene	CH_2	7.241 ± .003 7.033 ± .003	7.27
	CH_3	1.200 ± .002	3.61
Cyclohexadiene[d]	1-CH	1.996 ± .009	2.61
	2-CH	8.212 ± .011	6.75
	3-CH_2	11.114 ± .012	14.30
Isoprene[e]	1-CH_2	7.91 ± .03	7.46
	2-CH_3	3.42 ± .03	3.73
	3-CH	3.10 ± .03	2.78
	4-CH_2	6.50 ± .03	7.33

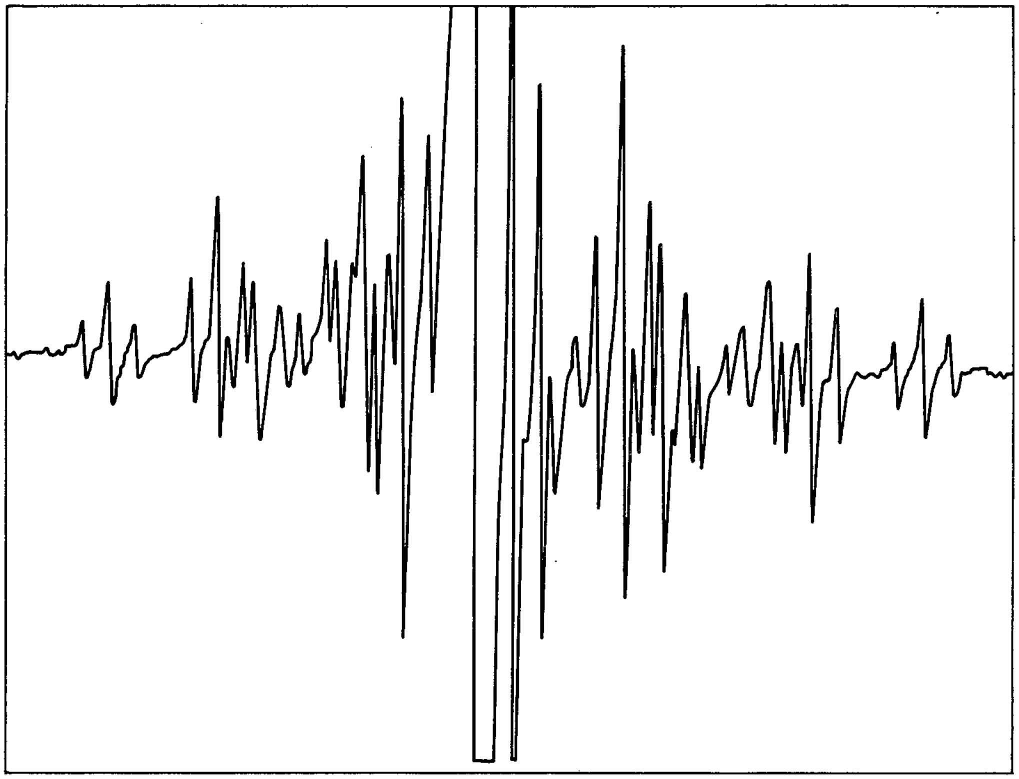
(a) Position numbers given first when necessary -- see (d) and (e).

(b) Absolute magnitudes in gauss.

(c) Assuming Q = 20.82 for the in-plane CH and CH_2 groups (see Ref. 1). For the out-of-plane CH_2 and CH_3 groups see Ref. 4,5, for the method of including hyperconjugation.

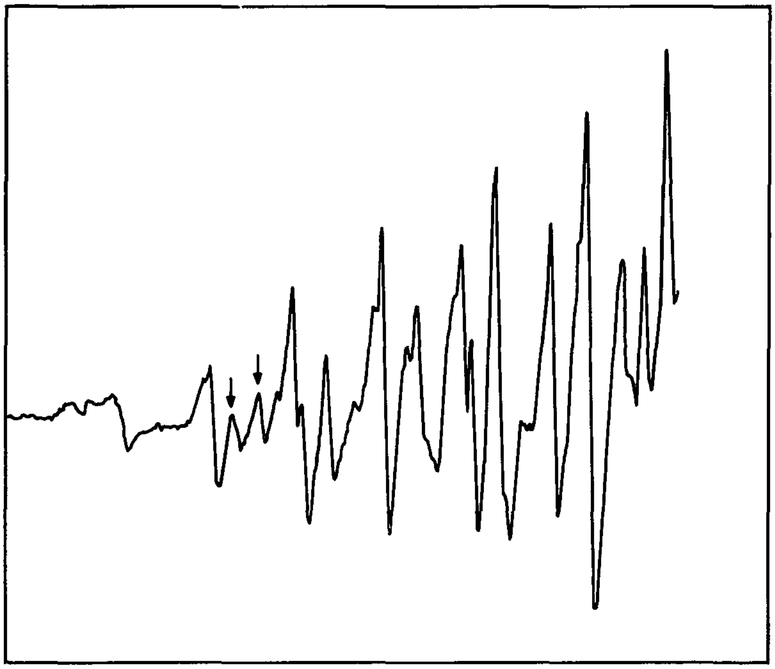
(d) Ring numbered in order starting with the two equivalent adjacent CH groups.

(e) Numbered in order starting with the CH_2 group next to the CH_3 group.



MU-33563

Fig. 2



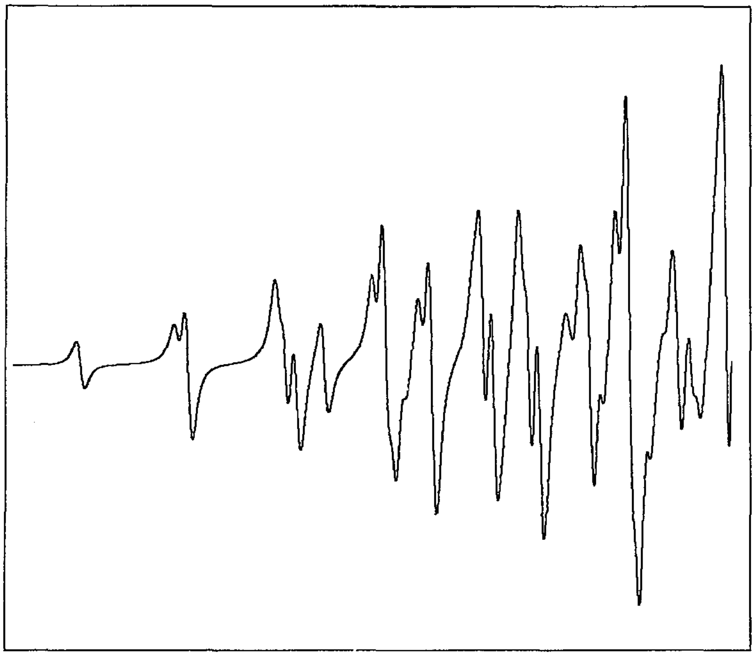
MU-35077

Fig. 3

spectrum. By lowering the electrolysis voltage the electron line could be eliminated but this did not change the details of the radical anion spectrum other than to weaken it.

Unfortunately in this case the assignment of the spectrum is not a trivial matter. Assuming that the protons on any given methyl or methylene group are equivalent or almost equivalent the spectrum should be able to be assigned with four coupling constants. After considerable effort to assign the spectrum by the usual intuitive method an attempt was made at a systematic approach to the problem. To begin with, it is clear from the spin Hamiltonian that in general every distinct coupling constant in any given radical is represented by the distance between the outermost line in the spectrum and one of the interior lines. This gives a large number of possible assignments which can be tested with the constraint imposed by total width = $\sum_n I_n | A_n |$. Most of the combinations are ruled out because they do not satisfy this constraint. Of the 10^5 possible assignments only 208 satisfied this constraint within experimental error. The complete spectrum predicted by each of these was calculated but none of them agreed with the experimental spectrum.

The cause of the difficulty is lines 4 and 5 indicated by arrows in Fig. 3. If the existance of these lines is ignored a very good assignment can be made for the rest of the spectrum with the coupling constants listed in Table I. The theoretical spectrum based on these coupling constants is shown in Fig. 4 and may be seen to be in excellent agreement with the rest of the experimental spectrum. This excellent fit and the fact that the assignment agrees so well with the predictions of molecular orbital theory have led us to the conclusion that lines four and five are anomalous, perhaps caused by impurities, and that the assignment given in Table I is probably correct.



MU-35056

Fig. 4

DISCUSSION

In the case of 2,3-dimethyl 1,3-butadiene, the most interesting observation is the two CH_2 coupling constants. For this molecule it seems very likely that it is held rather firmly in a transconfirmation as a result of the steric effect of the two methyl groups. Previously for 1,3-butadiene,[1] we only observed a single CH_2 coupling constant under conditions of slightly poorer resolution. From the experimental spectrum, however, we are able to say that any two CH_2 coupling constants in 1,3-butadiene must differ by less than 0.1 gauss. The difference in these two cases is either due to a lower cis-trans barrier in butadiene giving a greater vibrational averaging or possibly to a clear difference in the source of the different proton hyperfine interaction for two protons bonded to the same carbon.

If d-orbitals are included in a Hückel type of treatment it is then possible to have two protons bonded to the same carbon atom with different coupling constants through a spin polarization mechanism. Sovers and Kauzman[7] have made an effort to include d-orbitals in a Hückel treatment for butadiene. On the basis of their molecular orbitals coefficients and Q values for d-orbitals near 20 gauss it is possible to predict two CH_2 coupling constants in butadiene which should differ by about 0.05 gauss. It is not clear at this time if such a treatment could explain the larger difference observed for 2,3-dimethyl butadiene but calculations are being done in this direction.

In Table I a number of calculated coupling constants are given. These values were determined utilizing Hückel molecular orbitals without overlap with the hyperconjugation parameters of Coulson and Crawford.[8] The exact method of including these parameters is discussed elsewhere[4,5] but the agreement shown in Table I is a reasonable confirmation of both the method and our assignments.

The large CH_2 coupling constant observed for cyclohexadiene is to be expected[9] and the calculated value is very satisfactory in this case. The similarity of the CH and CH_3 coupling constants in isoprene is the kind of agreement that led some workers[9] to assume a spin polarization mechanism for methyl or methylene groups with Q values both near 20. The smaller CH_3 coupling constants in 2,3-dimethyl butadiene is a good test of hyperconjugation vs spin polarization for methyl group coupling constants, although the cation/anion ratios used by Bolton et al[3] is a far more sensitive one. While the calculated methyl coupling constant given in Table I is in only fair agreement with the observed one, Levy[4,5] has found that generally good agreement can be obtained for a number of radicals if hyperconjugation is included in the usual Hückel treatment.

Acknowledgement

This work was supported by the United States Atomic Energy Commission.

FOOTNOTES AND REFERENCES

* Present address: Department of Theoretical Chemistry, Cambridge University, Cambridge, England.

1. D. H. Levy and R. J. Myers, J. Chem. Phys. 41, 1062 (1964).
2. D. H. Levy and R. J. Myers, J. Chem. Phys. (accepted for publication).
3. J. R. Bolton, A. Carrington and A. D. McLachlan, Mol. Phys. 5, 31 (1962); J. P. Colpa and E. De Boer, Mol. Phys. 7, 333 (1964).
4. D. H. Levy, "The Electron Spin Resonance Spectra of Radical Anions in Liquid Ammonia", Ph. D. Thesis, University of California, Berkeley, California (1965). Also available as Lawrence Radiation Laboratory Report UCRL - 11864.
5. D. H. Levy, to be published.
6. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39, 2147 (1963).
7. O. Sovers and Kauzmann, J. Chem. Phys. 38, 813 (1963); O. Sovers, Thesis, Princeton University, Princeton, New Jersey (1961).
8. C. A. Coulson and V. A. Crawford, J. Chem. Soc. 1953, 2052.
9. See Ref. 6 for example for cyclohexadienyl radical.

FIGURE CAPTIONS

Fig. 1. The observed spectrum for the radical anion of 2,3-dimethyl 1,3-butadiene.

Fig. 2. The observed spectrum for the radical anion of 1,3-cyclohexadiene. The strong signal near the center of the spectrum is due to the "solvated electron".

Fig. 3. The observed spectrum for the radical anion of isoprene. The two arrows mark the lines which are not assigned. Only the half of the spectrum free from the "solvated electron" is shown (see Fig. 2, for example).

Fig. 4. A theroetical spectrum for isoprene based upon the coupling constants given in Table I. The pair of lines marked by arrows in Fig. 3 are not assigned although these lines appear clearly in both halves of the experimental spectrum.