CHEMISTRY LETTERS, pp. 671-674, 1973. Published by the Chemical Society of Japan

# THE AZULENE RADICAL ANION PRODUCED BY ONE-ELECTRON TRANSFER FROM TRIMETHYLSILYLSODIUM(1)

Hideki SAKURAI, Hiroshi UMINO, and Akane OKADA
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The esr spectrum of the radical anion of azulene prepared by the reaction with trimethylsilylsodium in hexamethylphosphoramide with all of the expected 108 lines is reported. The minimum interaction between the azulene radical anion and countercation as compared with any previous results was observed.

In a recent communication(2) we reported a new technique of producing radical anions involving one-electron transfer from trimethylsilylsodium.(3) Many advantages of the technique are noted over the older methods of chemical and electrolytic reduction. We report here the extention of the technique to the investigation of the radical anion of azulene.

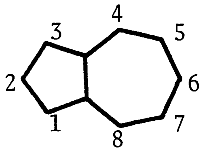
Bernal, Rieger, and Fraenkel prepared first the azulene radical anion electrolytically in N, N-dimethylformamide (DMF) with tetra-n-propylammonium ion.(4) They reported the esr spectrum of 94 lines out of the expected 108 lines. Later, Reddoch(5) observed that the same radical anion prepared in dimethoxyethane (DME) by reduction with lithium showed quite different hyperfine coupling constants from those observed by Bernal et al. However, the esr spectra in DME were more close to that obtained electrolytically in DMF at lower temperature. Reddoch explained the difference by a model involving a rapid chemical equilibrium between two states of the azulene radical anion, namely, between ion pairs and free anions. The ion pairs dissociate to free ions at low temperature. The free ions exist only at -40°C.

One of the advantages of our new method is the formation of the most "free" radical anion as evidenced by the smaller hyperfine coupling constants of both nitrogen of nitrobenzene and ring protons of benzophenone than any recorded values.(2) Accordingly, our prime interest is to observe the most "free" azulene radical anion after testing the applicability of the method to azulene, a representative non-alternant hydrocarbon.

The experimental method is briefly described. About 0.05 mg of sublimed azulene was placed in a Pyrex glass tube constructed with a 6 x 60 mm upper portion and a 1 x 80 mm thin-walled lower portion. Under argon, 0.5 ml of a 0.5 M solution of trimethylsilylsodium in hexamethylphosphoramide (HMPA) was added by means of a hypodermic syringe to azulene. The tube was then sealed off after three freez-thaw cycles on a vacuum line.

Table 1

The hyperfine coupling constants of azulene radical anion at room temperature (Gauss)

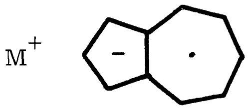


| Proton | Countercation | | |
|---|---|---|---|
| | $Li^+$(DME)[5)] | $\underline{n}$-$Pr_4N^+$(DMF)[4)] | $Na^+$(HMPA) |
| 1, 3 | 0.22 | 0.27 | 0.29 |
| 2 | 3.80 | 3.95 | 3.98 |
| 4, 8 | 6.46 | 6.22 | 6.03 |
| 5, 7 | 1.46 | 1.34 | 1.26 |
| 6 | 9.07 | 8.83 | 8.64 |

The resulting esr spectrum at room temperature was remarkably well resolved as seen in Firure 1.[6)] All of the expected 108 lines can be identified. The coupling constants assessed by a first-order analysis of the spectrum were tested by computer simulation. Table 1 lists the coupling constants together with the previously reported values.

The hyperfine coupling constants in the present study are rather similar to those obtained by electrolysis, but there is a definite tendency of systematic changes in these values. The coupling constants of the five-membered ring protons increase in the series of solvents: DME (with $Li^+$) > DMF (with $\underline{n}$-$Pr_4N^+$) > HMPA (with $Na^+$). However exactly the inverse order of magnitude in the coupling constants of protons of the seven-membered ring can be seen in the Table.

It is well documented that azulene in the ground state has a significant dipole moment of 1.0 D with the five-membered ring at the negative end of the dipole.[7)] Therefore, such a trend can be explained by a model of the azulene radical anion in which the negative charge is localized considerably on the five-membered ring.



The degree of association between the radical anion and the countercation depends on the basicity of the solvent. Thus, the less basic the solvent is, the more the electrostatic interactions increase, particularly with the metal ions of smaller size or higher charge, to favor the ion pair structure relative to the free ions.[8)] It is also expected that in the ion pair the negative charge is localized on the five-membered ring in higher degree than in the free ion. As a result, in less basic solvent the proton coupling constants of the seven-membered ring will

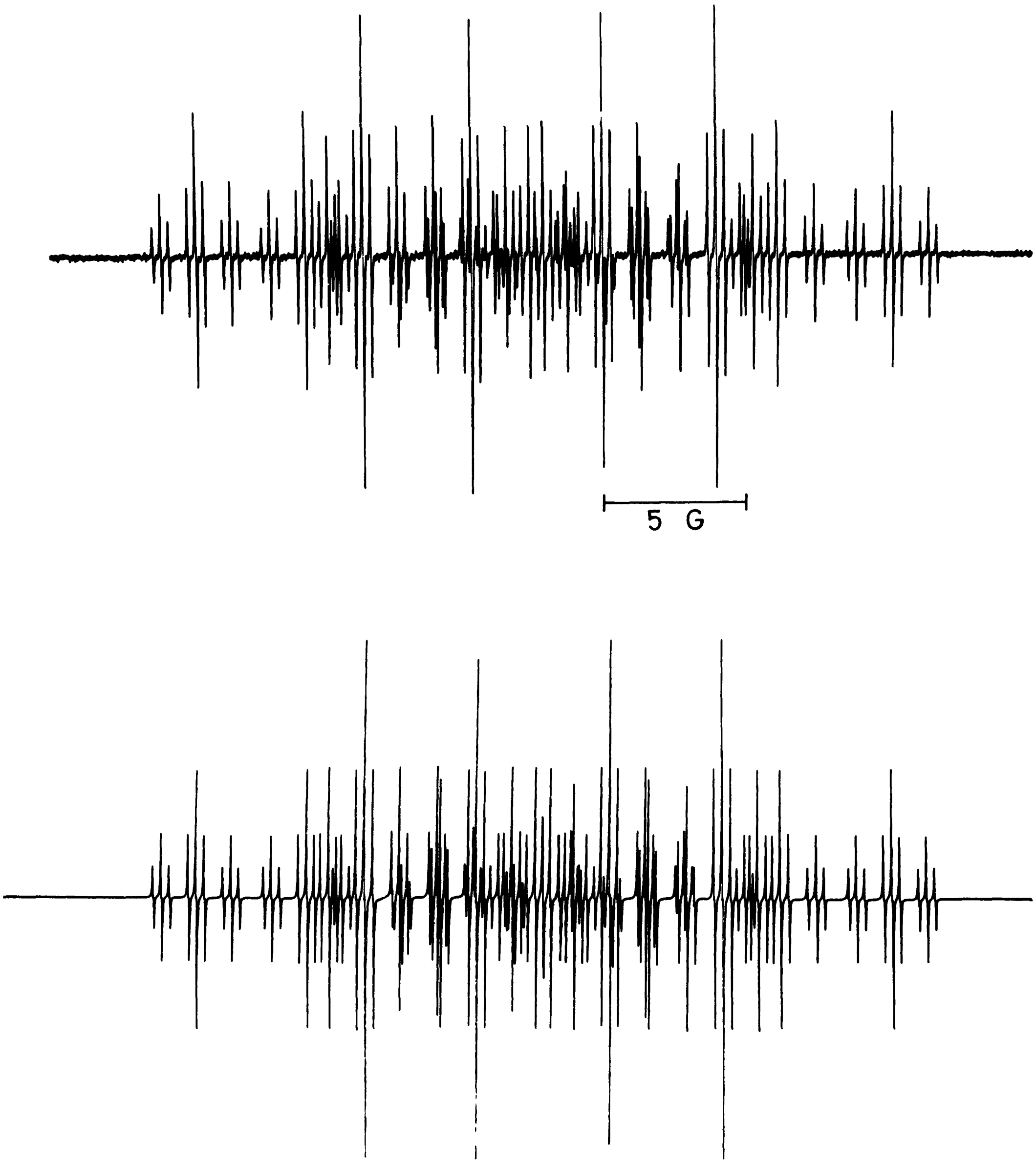


Figure 1. Esr spectra of the radical anion of azulene: upper, experimental; lower, computer simulated using Lorentzian line shapes and a line width of 0.02 G

increase, and at the same time those of the five-membered ring will decrease with increasing contribution of the ion pair. It should be noted in this context that the azulene radical anion in the present study corresponds to the most free ions, because the largest hyperfine coupling constants for protons of the five-membered ring and the smallest ones for the seven-membered ring were observed in this case. Moreover, the maximum separation of each lines of the spectrum than any recorded spectra indicates the minimum interaction between the anion and the countercation.

Undoubtedly a strongly basic nature of HMPA as a solvent is responsible for the situation.[9,10] However, at the same time, a point of advantage of the new method may be noted, as follows. Since trimethylsilylsodium can be used in large excess to substrates, essentially no neutral molecule is left in the system. Further reduction of the radical anion is seemingly very slow. As a result, well-resolved, strong signals such as those in Figure were observed.

In conclusion, the convenient procedure of the new technique using trimethylsilylsodium in HMPA will be very useful tool for the study of radical anions. Related studies are in progress.

ACKNOWLEDGMENT We thank Professor K. Takase and Dr. T. Morita for the sample of azulene. The support of this work by the Ministry of Education of Japan (Grant-in-Aid No.8304 and No.68304) is gratefully acknowledged.

REFERENCES

1) Silyl anions V. For part IV, see ref.2.
2) H. Sakurai, A. Okada, H. Umino, and M. Kira, J. Amer. Chem. Soc., 95, 955 (1973).
3) H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, Tetrahedron Lett., 1511 (1971).
4) I. Bernal, P. H. Rieger, and G. K. Fraenkel, J. Chem. Phys., 37, 1489 (1962).
5) A. H. Reddoch, J. Chem. Phys., 41, 4444 (1964).
6) The esr spectrum was taken with a Varian Associates E-12 spectrometer with a 9.5-GHz microwave bridge and a multipurpose cavity.
7) G. W. Wheland, and D. E. Mann, J. Chem. Phys., 17, 264 (1949).
8) For an excellent review of the problem of relating ion-pair association to hyperfine coupling constants, see N. Hirota in "Radical Ions", E. T. Kaiser, and L. Kevan, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 2.
9) G. R. Stevenson, L. Echegoyan, and L. R. Lizardi, J. Phys. Chem., 76, 1439 (1972).
10) A. Cserhegyi, J. Chaudhuri, E. Fanta, J. Jagur-Grodzinski, and M. Szwarc, J. Amer. Chem. Soc., 89, 7129 (1967).

( Received May 7, 1973 )