Tetrahedron Letters No.10, pp. 797-800, 1969. Pergamon Press. Printed in Great Britain.

ESR SPECTRA OF SOME RADICAL CATIONS OF FLUORINATED HYDROCARBONS

P.H.H.Fischer and H.Zimmermann

Max-Planck-Institut, Jahnstrasse, Heidelberg, Germany

(Received in Germany 11 January 1969; received in UK for publication 27 January 1969)

During the course of our investigation of fluorine hyperfine interaction in aromatic systems we have been able to prepare radical cations from several mono- and difluorinated hydrocarbons employing $SbCl_5$ and CH_2Cl_2 as oxidizing/solvent system. With the exception of two notes on the radical cation of octofluoronaphthlene[1,2] this is to our knowledge the first report on ESR spectra of radical cations of fluorinated aromatic systems.

ESR spectra were obtained from solutions of 1-fluoro-naphthalene, 2-fluoro-naphthalene, 1,5-difluoro-naphthalene, 4-fluoro-biphenyl, 4,4'-difluoro-biphenyl, 3,3'-difluoro-diphenyl, 2-fluoro-fluorene, and 6-fluoro-chrysene, while 2-fluoro-biphenyl, 2,2'-difluoro-biphenyl, octafluoro-biphenyl, decafluoro-biphenyl, and octafluoro-naphthalene did not give paramagnetic species under the present conditions. Samples were prepared as follows: One drop of $SbCl_5$ was added to a 10^{-3}M solution of hydrocarbon dissolved in oxygenfree CH_2Cl_2 at the temperature of dry ice/acetone and allowed to react. In most cases the colored solutions, stable up to room temperature, gave ESR spectra, representative examples of which are shown in Fig.1. In cases where no signal could be obtained, a vacuum transfer apparatus very similar to that employed by Lewis and Singer[3] was used, and controlled concentrations of $SbCl_5$ added to the hydrocarbon solutions. In contrast to the non-fluorinated hydrocarbons, this procedure gave no improved results. Keeping and measuring the samples at temperatures down to -90° C also did not improve resolution of the spectra or stability of the paramagnetic species. Addition of oxygen always caused drastic color change and disappearance of the ESR signal. ESR spectra were measured with a conventional Varian V-4500 spectrometer, using 100 KHz field modulation.

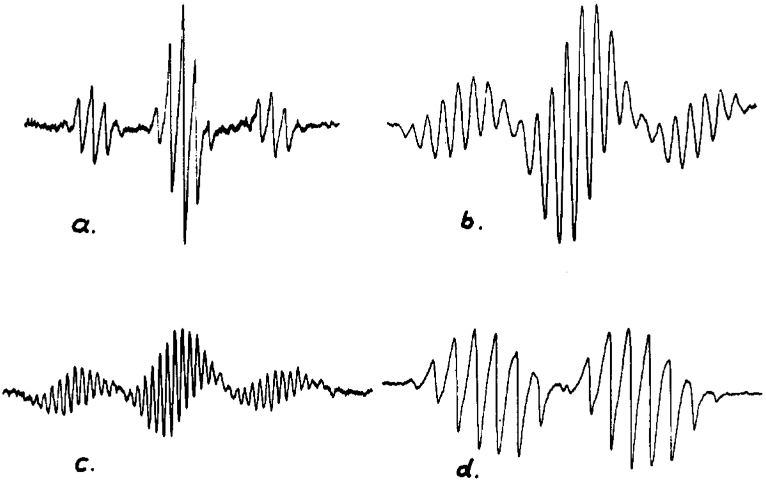

Fig.1. ESR spectra obtained from solutions of a) 4,4'-difluoro-biphenyl, b) 1,5-difluoro-naphthalene, c) 1-fluoro-naphthalene, and d) 4-fluoro-biphenyl in $CH_2Cl_2/SbCl_5$.

The spectrum of the radical cation of 4-fluoro-biphenyl (deep green) can be analyzed in terms of the coupling constants a_1=18.59 gauss, a_2=7.33 gauss, a_3(2x)=2.62 gauss, and a_4(2x)=2.49 gauss. With these couplings line positions are adequately reproduced although intensity anomalies remain, very likely due to nearly overlapping lines. The large coupling of 18.59 gauss is without doubt due to the fluorine nucleus, while the coupling of 7.33 gauss is assigned to the para proton and the couplings of 2.62 gauss and 2.49 gauss are from the 2 sets of ortho protons. An assignment to specific rings is not possible. Whereas the value of 7.33 gauss is somewhat larger than the value of 5.31 gauss[4)] observed in the radical anion, the values of 2.62 and 2.49 gauss compare well with the value of 2.66 gauss in biphenyl$^-$. As the linewidth in the present spectrum is ~0.9 gauss we do not expect to see splitting from the meta protons, which is 0.41 gauss in the negative ion. 4,4'-difluoro-biphenyl (deep blue) gave a 15 line spectrum with coupling constants $a_1(2x)=19.28$ gauss and $a_2(4x)=2.73$ gauss. The large coupling is due to 2 equivalent fluorine nuclei, and the coupling of 2.73 gauss is due to the 4 equivalent ortho protons. This value compares well with the 2.66 gauss found for these nuclei in biphenyl$^-$. The meta proton splitting is again lost in the linewidth of 0.8-0.9 gauss. 1,5-difluoro-naphthalene (deep green) yielded a spectrum of 23 resolved lines at room temperature, but shows signs of further splitting at temperatures below -50° C. The spectrum can be reproduced with the coupling constants $a_1(2x)=16.98$ gauss, $a_2(2x)=4.12$ gauss, and $a_3(4x)=1.98$ gauss. The large splitting is assigned to the 2 equivalent fluorines. The values of 4.12 gauss, due to the 2 remaining α-protons, and the value of 1.98 gauss from 4 nearly equivalent β-protons are comparable with the values observed for the negative ions. In the spectrum obtained from 1-fluoro-naphthalene (deep red) up to 41 lines may be discerned but a complete analysis is not unambiguously possible. There can be no doubt, however, that the spectrum is divided into 3 groups of lines in the intensity ratio 1:2:1. This splitting results from 2 equivalent spin 1/2 nuclei, and the size of the coupling constant of 12.67 gauss, which can only be due to fluorine, seems to indicate that we are dealing with a dimeric, not a monomeric species. Lewis and Singer[3)] have found that naphthalene when treated in CH_2Cl_2 with $SbCl_5$ yields a purple solution, the ESR spectrum of which can be unambiguously assigned to the radical cation of a naphthalene dimer. 2-fluoro-naphthalene also yielded a deep red solution, but only one broad line, with roughly 3o lines indicated, could be discerned. An analysis was quite impossible and no conclusion as to the presence of possible dimeric or monomeric species could be drawn. Similarly, 3,3'-difluoro-biphenyl yielded an orange solution, giving a single broad line only. A green solution of 2-fluoro-fluorene gave a spectrum consisting of 2 groups of 6 lines each. The groups are in the exact intensity ratio 1:1, and the splitting of 18.41 gauss makes an assignment to the single fluorine substituent likely. The six lines in each group are the result of a complex overlapping of lines and a further analysis was not possible. 6-fluoro-chrysene yielded a deep red solution, the ESR spectrum of which consisted of 3 groups of lines of intensity ratio 1:2:1 and a splitting constant 7.85 gauss. Although much further structure was present, an analysis was not possible. Again it seems likely that it is the dimeric cation radical which is giving rise to the spectrum.

Summing up we note that 6-fluoro-chrysene, 1-fluoro-naphthalene, 2-fluoro-naphthalene, and 3,3'-difluoro-biphenyl yield deep red solutions and the spectra of the first two compounds may with reasonable certainty be assigned to dimeric species. Lack of solution does not permit this for the case of the latter two. In contrast, all other compounds yielded deep green or blue solutions and their spectra can be interpreted in terms of monomeric species. Further work is in progress.

---

1) N.M.Bazhin, N.E.Akhmetova,L.V.Orlova, V.D.Shteingarts, L.N.Shchegolova, and G.G.Yakobson, Tetrahedron Let. 42, 4449 (1968)

2) C.Thomson and W.J.McCulloch, Tetrahedron Let.56,5899 (1968)

3) I.L.Lewis and L.S.Singer, J.Chem.Phys.43,2712 (1965)

4) H.Nishiguchi, Y.Nakai, N.Nakanura, K.Ishizu, Y.Deguchi, and H.Tokoki, J.Chem.Phys.40,241 (1961)