3. *Meßergebnis*

Bei einer Absorption von 10% des Primärlichts durch die dotierte Schicht werden 90% der Fluoreszenzintensität der reinen Schicht beobachtet, entsprechend z. B. bei 20% Absorption noch 80%. Die Messung zeigt also (nach Abzug des in der dotierten Schicht absorbierten Anregungslichts) mit und ohne K_2 dieselbe Fluoreszenzausbeute. Es liegt Fall (2) oder (5) vor.

Aus den Diffusionsmessungen dieser Arbeit ist bekannt, daß Excitonen von einer Schicht in die andere wandern können. Singulett-Excitonen zerfallen also an der Oberfläche von Naphthalinschichten strahlungslos.

Die Meßgenauigkeit von 4% ist ausreichend, da der Diffusionsstrom durch die vordere Oberfläche 21% der erzeugten Excitonen entspricht. Dieser Diffusionsstrom läßt sich aus der Diffusionsgleichung mit der bekannten Diffusionslänge berechnen.

Die Arbeit wurde mit Mitteln der Deutschen Forschungsgemeinschaft durchgeführt.

Electron Spin Resonance of Fluorinated Benzophenone Anion Radicals

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(Z. Naturforsch. **23 a**, 1339—1342 [1968]; received 20 June 1968)

Electron spin resonance spectra have been observed for anion radicals derived from 4-fluorobenzophenone, 2-fluorobenzophenone, 4,4′-difluorobenzophenone, 3,3′-difluorobenzophenone and decafluorobenzophenone. All radicals have been generated by electrolytic means in dimethoxyethane-acetonitrile mixtures. In the case of the mono- and difluorinated species, interpretation of the spectra as arising from the corresponding anion radicals is possible. In the case of decafluorobenzophenone, the anion radical cannot be the species giving rise to the spectrum.

I. Introduction

Several fluorine containing radicals have been investigated by ESR techniques, but their number is still quite limited, and as yet not sufficient reliable data on such radicals exist to permit a satisfactory evaluation of C-F-spin-polarization parameters.

In an attempt to obtain spin polarization parameters applicable to a larger number of aromatic anion radicals we have prepared a large number of fluorine containing species.

We wish to report here the results obtained for the anion radicals of 4,4′-difluorobenzophenone, 3,3′-difluorobenzophenone, 4-fluorobenzophenone, 2-fluorobenzophenone, and the anomalous behavior of decafluorobenzophenone under polarographic conditions.

II. Experimental

2-Fluoro- and 4-fluorobenzophenone were obtained from Fluka AG/Switzerland, 3,3′-difluorobenzophenone from Pierce Chemical Co./USA and 4,4′-difluoro- and decafluorobenzophenone from Aldrich Chemical Co./USA. All substances were used without further purification. The solvents employed were acetonitrile, dimethylformamide, dimethylsulfoxide and dimethoxyethane. As supporting electrolyte we used tetra-n-propylammonium perchlorate, prepared according to Geske and Maki's procedure [1].

The radicals were generated in a vacuum electrolytic cell and reductions carried out at a platinum wire cathode. The solutions were generally 10^{-3} M in the substance being investigated, and 10^{-1} to $5 \cdot 10^{-2}$ M in supporting electrolyte. The spectra were recorded with a Varian V-4500 spectrometer using 100 kHz first, and in some cases 400 Hz second modulation, for recording of second derivative spectra. The field from a 6″ magnet was monitored with an AEG magnetometer.

III. Results and Discussion

4,4′-Difluorobenzophenone : 4,4′-difluorobenzophenone in a 75%/25% mixture of dimethoxyethane and acetonitrile yielded, upon reduction, a faintly blue solution which gave rise to the EPR spectrum shown in Fig. 1. The spectrum consists of 45 of the theoretically possible 75 lines. The spectrum can easily and without ambiguity be analyzed in terms of three coupling constants: $4\,a_1 = 2.74$ and $4\,a_2 = 0.96$ gauss from two sets of four equivalent protons, and $a_{\mathrm{F}} = 7.50$ gauss. There is no uncertainty in assigning the 7.50 gauss splitting as arising from the fluorine nuclei. From work on the benzophenone anion radical [2] and from experimental knowledge of

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[1] D. H. Geske and A. H. Maki, J. Amer. Chem. Soc. **82**, 2671 [1960].

[2] P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **37**, 2811 [1962].

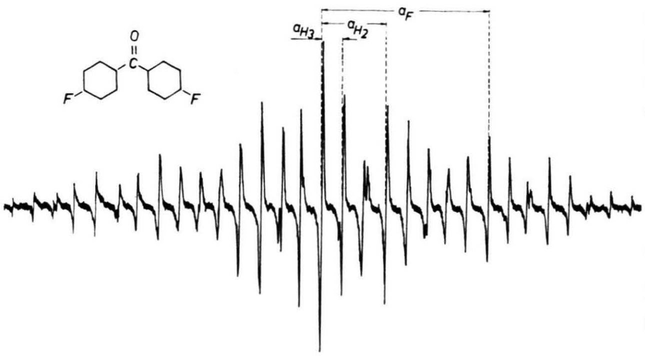

Fig. 1. ESR Spectrum of 4,4′-Difluorobenzophenone Anion.

spin density distribution in anion radicals having strongly electron-withdrawing substituents we ascribe the smaller splitting of 0.96 gauss to the meta protons, the coupling constant of 2.74 gauss to the ortho protons. The proton coupling constants in the fluorinated and unfluorinated systems are thus of comparable magnitude. This is in agreement with the finding that fluorine substitution does not modify other splittings in the radical to an appreciable extent. The ratio of fluorine splitting to proton splitting in corresponding positions of substituted and unsubstituted benzophenone anions of 7.50/3.50 = 2.14, also falls within the range of ratios commonly found experimentally, and presents no anomalous behavior.

4-Fluorobenzophenone: When we reduced 4-fluorobenzophenone in the 75%/25% dimethoxyethane-acetonitrile mixture, we obtained a faintly blue solution exhibiting the hyperfine pattern shown in Fig. 2. In this spectrum the second derivative is presented, as the first derivative spectrum, showing 60 lines only, indicated from line shapes that a second derivative spectrum might produce considerable additional information. The second derivative spectrum does in fact allow us to discern 78 lines of the theoretically possible 324. Towards the wings of the spectrum a group of lines in the intensity ratio of 1 : 4 : 6 : 4 : 1 is visible so that at least 4 protons must be equal to within the linewidth. The spectrum may be very well reproduced with the following five coupling constants:

$$4\,a_1 = 0.87\text{ G},\quad 2\,a_2 = 2.52\text{ G},\quad 2\,a_3 = 2.61\text{ G},$$
$$a_4 = 3.63\text{ G},\quad\text{and}\quad a_5 = 6.73\text{ G}.$$

The decrease in intensity to the left of the spectrum is due to decreasing radical concentration as a result of the long recording time.

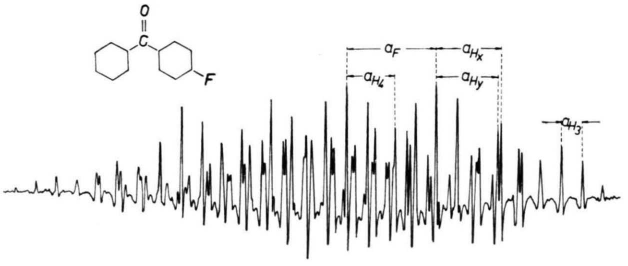

Fig. 2. ESR Spectrum of 4-Fluorobenzophenone Anion.

The splitting of 6.73 gauss from a single spin 1/2 nucleus is with reasonable certainty to be attributed to the fluorine substituent. The ratio of a_F to a_H is in this case smaller, namely 1.92, is still, however, to be considered normal. The splitting of 3.63 gauss due to a single spin 1/2 nucleus must on the basis of symmetry considerations be due to the splitting from the proton in the para position of the non-fluorine substituted phenyl ring. Furthermore, the value compares very favorably with the value of 3.50 gauss found by RIEGER and FRAENKEL[2] for the para position proton splitting. It appears as if the presence of a fluorine substituent in one phenyl ring affects the spin density distribution of the second phenyl ring very negligibly. To preserve consistency in the assignment amongst the various benzophenones, the splitting of 0.87 gauss is assigned to the meta protons. The two remaining coupling constants must be due to the ortho position protons. Employing the idea that fluorine substitution is more likely to alter the spin density distribution in the ring containing the fluorine substituent, the coupling of 2.61 gauss is ascribed to the ortho protons in the fluorine containing phenyl ring, the coupling of 2.51 gauss to the ortho nuclei in the unsubstituted ring. This value is furthermore in excellent agreement with the benzophenone value of 2.52 gauss, but it is emphasized that this assignment is to be considered tentative and could well be reversed.

3,3′-Difluorobenzophenone: Reduction of a 3,3′-difluorobenophenone solution at the first halfwave potential yields a blue solution showing the EPR spectrum reproduced in Fig. 3. It consists of 93 of the 243 possible lines. It is unambiguously analyzed in terms of the following set of coupling constants:

$$2\,a_1 = 3.29\text{ G},\quad 2\,a_2 = 2.62\text{ G},\quad 2\,a_3 = 2.16\text{ G},$$
$$2\,a_4 = 1.65\text{ G},\quad\text{and}\quad 2\,a_5 = 0.68\text{ G}.$$

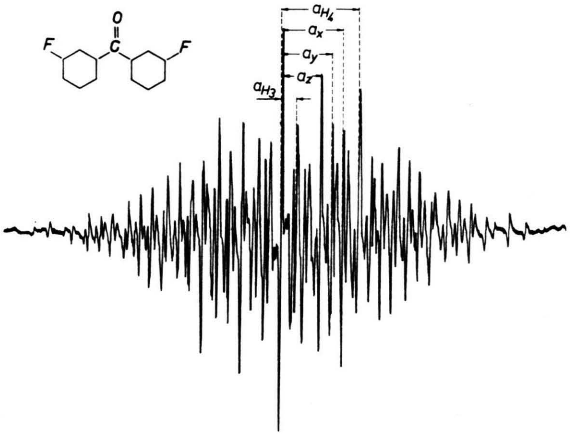

Fig. 3. ESR Spectrum of 3,3′-Difluorobenzophenone Anion.

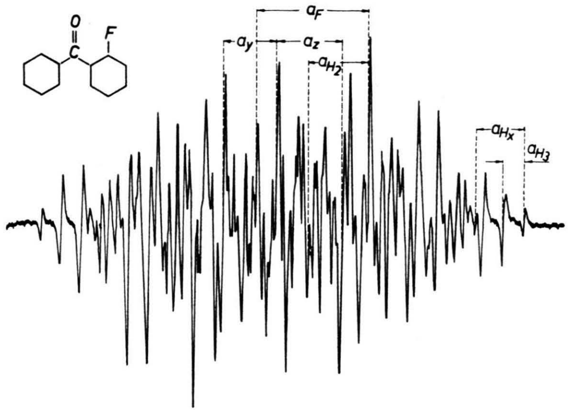

Fig. 4. ESR Spectrum of 2-Fluorobenzophenone Anion.

As in the case of the other benzophenones it appears reasonable to assign the smallest splitting to the meta position protons, as the fluorine splitting, though also from nuclei in the 3 and 3′ positions, would, to be consistent with other fluorine data, be expected to be in the range 1.5 to 2 gauss. From similar considerations we assign the largest splitting of 3.29 gauss to the protons in the para positions of the phenyl rings. The remaining 3 coupling constants cannot be asigned to specific positions.

2-Fluorobenzophenone: For 2-fluorobenzophenone a blue solution as for the other benzophenones results upon reduction. This solution exhibits the hyperfine pattern shown in Fig. 4. Due to the low symmetry of the molecule a large number of lines is theoretically possible, namely 576. As, however, near the wings of the spectrum a 1 : 4 : 6 : 4 : 1 quintuplet structure is visible, at least 4 nuclei must be equivalent. The intensity ratio of this quintuplet structure is not exactly 1 : 4 : 6 : 4 : 1, and linewidths do vary slightly from line to line. This is undoubtedly due to the fact that the coupling constants for the four spin 1/2 nuclei are not exactly equivalent. The spectrum may reasonably be interpreted in terms of the following coupling constants:

$$4\,a_1 = 0.82\text{ G},\quad a_2 = 4.63\text{ G},\quad a_3 = 1.92\text{ G},$$
$$a_4 = 2.22\text{ G},\quad a_5 = 2.54\text{ G},\quad \text{and}\quad 2\,a_6 = 2.48\text{ G}.$$

The first four of these coupling constants are given to ±0.01 G, in the latter two the error, because of lack of resolution, may be as large as ±0.05 G.

The assignment of the coupling of 0.82 gauss, arising from interaction with four equivalent nuclei, to the protons in the meta positions is consistent with the other results and can be quite safely assumed. Although four coupling constants due to a single spin 1/2 nucleus are obtained from the EPR spectrum, only the asignment of the largest coupling of 4.63 gauss to the fluorine interaction can be made with reasonable certainty. The ratio of a_{F} to a_{H} of 1.84 is of the correct magnitude. The splitting of 2.48 gauss can be assigned to the ortho protons in the phenyl ring not containing the fluorine substituent on the basis of symmetry considerations. The assignment of the other three coupling constants remains ambiguous.

Decafluorobenzophenone: When a 10^{-4} M solution of this substance is reduced in an acetonitrile-dimethoxyethane mixture containing less than 50% acetonitrile, a very faint and shortlived blue color is observed changing rapidly to red, this red solution exhibiting the hyperfine pattern shown in Fig. 5. If higher percentages of acetonitrile or pure acetonitrile were employed, no EPR signal could be detected. From the negative ion of decafluorobenzophenone we would theoretically expect 75 lines from two sets of 4 equivalent fluorine atoms and one set

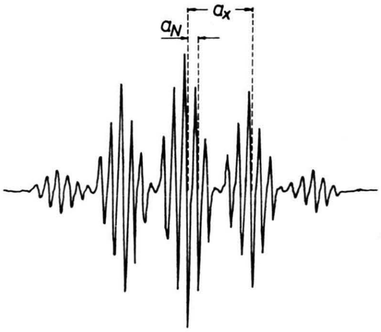

Fig. 5. ESR Spectrum of Radical Derived from Decafluoro benzophenone.

of 2 equivalent fluorines. The spectrum, however, consists of 25 lines only, composed of 5 groups of lines in the ratio 1 : 4 : 6 : 4 : 1, and each group composed of five equidistant lines, in the intensity ratio of 1 : 2 : 3 : 2 : 1. Linewidths are 250 mG, and the spectrum is perfectly reproduced with the coupling constants

$2\,a_1(I=1)=0.64$ G and $4\,a_2(I=1/2)=4.05$ G.

The spectrum is at complete variance with the expected hyperfine pattern, especially the apparent presence of spin $I=1$ nuclei is unexpected, and points towards a species different from the decafluorobenzophenone anion radical.

Because of this anomalous spectrum other solvents were tried. In dimethylsulfoxide and in dimethylformamide a faintly blue color of short duration was observed, no EPR signal could, however, be detected.

Great care was taken to exclude possible impurity effects. Chromatographic purification, melting point, and elementary analysis, as well as intensity of the spectrum from a solution of accurately known concentration, indicate absence of an impurity to account for the spectrum. Tatlow [3] has indicated that nucleophilic attack at the ortho and para position can readily occur in highly fluorinated systems such as this, and in a very recent paper Brown and Williams [4] postulated nucleophilic substitution of OCH_3 groups during the photolysis of decafluorobenzophenone in basic ethanol. When these authors photolyzed the above mixture, a spectrum unambiguously interpretable in terms of hyperfine interaction with two sets of four equivalent spin 1/2 nuclei, with coupling constants 4.60 and 1.14 gauss, was obtained. These authors did likewise not obtain an EPR signal during electrolysis of decafluorobenzophenone in acetonitrile and dimethylformamide, although, as in the present case, a blue coloration of the solution was observed. Possibly a nucleophilic substitution of CN groups occurs in the present system, in which case the presence of two equivalent spin $I=1$ nuclei, quite likely in the para positions, is possible. Substitution in the para positions would be preferred to ortho substitution, because of the higher spin density in the former positions and because of steric reasons. The coupling constants of 0.64 gauss is small, however not unfeasable for the nitrogen splitting from CN groups in the para positions. The splitting of 4.05 gauss from four equivalent spin 1/2 nuclei could then be attributed to hyperfine interaction with the four ortho fluorines, this value being in reasonable agreement with the expected value and also the coupling of 4.60 gauss found for the ortho fluorine nuclei in the postulated 4,4′-dimethoxyoctafluorobenzophenone anion radical [4]. These workers do also find a further, although somewhat small, value of 1.14 gauss for the splitting resulting from hyperfine interaction with four meta fluorines in the above radical. No such splitting can be observed in the spectrum of the paramagnetic species in our investigation. If present, the splitting would have to be considerably smaller than the linewidth of 250 mG, an unreasonable supposition. The species giving rise to the EPR spectrum can, however, not be identified with reasonable certainty as the anion of 4,4′-dicyanooctafluorobenzophenone, mainly because of the lack of an observable splitting from four aditional equivalent spin 1/2 nuclei.

We have observed other anomalous spectra from highly fluorinated species, i. e. spectra which cannot result from simple one electron reduction products of the systems being investigated. Further work needs to be done on this type of system.

IV. Conclusions

Polarographic reduction of four mono- and difluorinated benzophenones yields the corresponding anion radicals through addition of one electron, giving EPR spectra which allow a reasonable assignment coupling constants to be made. In certain cases assignment of coupling constants is determined by symmetry considerations, in others by comparison with related system and consistency considerations. Other coupling constants remain completely ambiguous. For decafluorobenzophenone, as for other highly fluorinated species, simple one electron reduction does not take place, rather introduction of nitrogen, very likely in the form of CN groups, occurs upon polarographic reduction in solvent mixtures containing acetonitrile. The paramagnetic species could not be identified with certainty.

Acknowledgement

We wish to express our thanks to Professor K. H. Hausser for his continued interest during the course of this work.

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[3] J. C. Tatlow, Endeavour **22**, 89 [1963].

[4] J. K. Brown and W. G. Williams, Trans. Faraday Soc. **64**, 298 [1968].