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OCTAFLUORONAPHTHALENE RADICAL CATION

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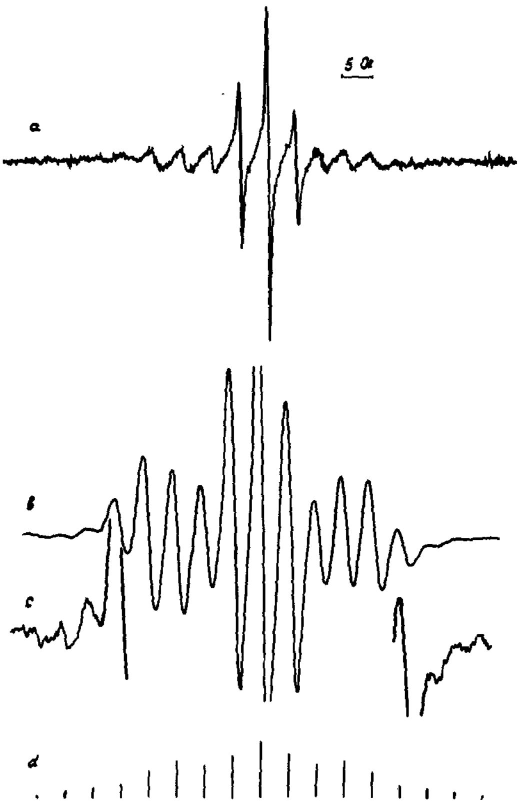
We have demonstrated recently, that polyfluoroaromatics undergo the reaction of electrophilic addition with NO_2^+ cation(1). Now we report the reaction of octafluoronaphthalene with oleum, SO_3 and SbF_5. In all of these octafluoronaphthalene forms intensely green solution producing E.S.R. signals(Fig.1 a,b,c).

Since some aromatic hydrocarbons produce radical cations (RC) by the action of Lewis acids (2), the most plausible interpretation of the E.S.R. spectra we observed seems to be the formation of octafluoronaphthalene RC (ORC). The observed spectra correspond to the theoretical one (Fig.1d) with constants a_F^{α} equal 13.9 and 13.65±0.15 and a_F^{β} 4.7 and 4.6± 0.05 for solutions in SO_3 and SbF_5-$(CH_3O)_2SO_2$ respectively. Since the ratio $a_F^{\alpha}/a_F^{\beta} = 3$, a partial superposition of lines is observed. The side quintuplets are much better resolved in SbF_5-$(CH_3O)_2SO_2$ system compared with SO_3. The observed increase of the linewidth from the centre to the borders of the

FIG. 1



a. E.S.R. spectrum of the solution of $C_{10}F_8$ in SO_3.

b. E.S.R. spectrum of the solution of $C_{10}F_8$ in SbF_5 diluted with $(CH_3O)_2SO_2$.

c. Gain increased to display the outside quintuplets.

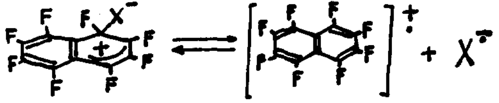
d. E.S.R. spectrum of ORC done on the basis of the experimental data for a_F. If the interval between the two lines is smaller than the line width they are represented as one line.

spectrum and the deviation of the experimental amplitude ratios from those theoretically predicted are perhaps due to the non-zero average anisotropic dipole-dipole interaction.

Schastnev and Zhidomirov have proposed the equation (3) for the fluorine hyperfine coupling constant: $a_F = Q_1 \cdot \rho_C + Q_2 \cdot \rho_F + Q_3 \cdot \sqrt{\rho_C \cdot \rho_F}$, where ρ_C and ρ_F are π-electron spin densities in the C-F fragment; Q_i are unknown constants. This equation can be simplified to a form similar to that of the McConnel relationship (4): $a_F = Q \cdot \rho_C$ /1/
On this basis the a_F-values for a series of radicals with nearly the same values of the ρ_C/ρ_F ratio may be estimated using approximately constant Q-values. Values ρ_C and ρ_F for ORC were computed by the Huckel MO-method using two sets of parameters in the usual representation of coulomb and resonance integrals: $\alpha_F = \alpha_C + h \cdot \beta_{CC}$ and $\beta_{CF} = k \cdot \beta_{CC}$. The first set (h=1.6, k=0.7) was used earlier to calculate the spin density distribution in the C-F fragment of radicals (5) and fluoronitroaromatic radical anions (6), and the latter (h=2, k=1) was applied to the interpretation of ^{19}F chemical shift (7). The calculated spin densities appeared practically the same with the two sets: $\rho_C^\alpha = 0.142$, $\rho_C^\beta = 0.054$, $\rho_F^\alpha = 0.039$, $\rho_F^\beta = 0.015$. The ratio ρ_C/ρ_F was nearly the same (3.6-3.7) for two positions of naphthalene ring. The Q-values equal to~97 and~86 Oe for α- and β-C-F fragments respectively were obtained from the relationship /1/ by using calculated values of ρ_C and the experimental data for a_F. Thus, supposition of ORC formation is confirmed both by the hyperfine structure of the E.S.R. spectrum and by the correspondence of the relation of a_F constants to spin density distribution between two positions in the naphthalene

ring. Fluorinated aromatic RC have not yet been reported. It should be noted that naphthalene produces only the RC of the dimer (8).

The equilibrium between RC and σ-complexes is known for some aromatic hydrocarbons (2). Perfluoroaromatics also seem to be able to produce σ-complexes by the action of electrophilic reagents (1). Hence, it appears probable that there is the following equilibrium in the systems now reported:



, where X = SO_3, SbF_5.

The work in this field is now in progress.

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