53. Aromatic Radical Anions in Neat Aromatic Hydrocarbons as Solvents. Direct Evidence of Through Space Spin-Density Transfer to the Ligand of the Counter Ion

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Summary

Contact ion pairs of aromatic radical anions, with a crown ether complex of potassium as cation in a neat aromatic hydrocarbon, can be obtained by reducing the aromatic hydrocarbon in which a small amount of crown ether is dissolved. The unpaired electron stays attached to one aromatic molecule during a time interval which is long on the ESR. time scale. The radicals are stabilized by ion-pair formation in the low polarity solvent. As a consequence of this stabilization, radicals of compounds with low electron affinities, *e.g.* mesitylene, can be prepared. Mesitylene, *m*-xylene, and toluene show additional hyperfine splitting in the ESR. spectra of their anion radical pairs of the order of 18 μT. The proton ENDOR. spectra have signals at the corresponding frequencies, indicating a hyperfine coupling with protons of the crown ether ligand. Using mixtures of two aromatic compounds, their relative electron affinities can be determined by studying the temperature dependence of the radical concentrations.

Introduction. - One method of generating radical anions of aromatic molecules (Ar) is the reduction of such compounds by alkali metals (M) in dilute solutions, using suitable solvents like dimethoxyethane (DME) or tetrahydrofurane (THF) (1) [1]:

$$\mathrm{Ar}+\mathrm{M} \xrightarrow[\text{THF}]{\text{DME or}} \mathrm{Ar}^{\overline{\cdot}}+\mathrm{M}^{+}. \qquad (1)$$

On the other hand, no reaction occurs when neat liquid aromatic compounds are refluxed over alkali metals. It is obviously the lack of solvation, mainly that of the metal cation, which makes reaction (1) energetically unfavourable. If, however, the cation is complexed by a suitable ligand (*e.g.* a crown ether) L, the formation of the radical ion can take place [2] [3]. However, in the neat solvent, the radical thus formed can only exist as a tight ion pair in contact with the complex cation. The reaction can then be formulated using the thermodynamic cycle (2)[2]):

$$\begin{tikzcd}
\mathrm{Ar}^{-}(\mathrm{d})+\mathrm{M}^{+}(\mathrm{d})+\mathrm{L}(\mathrm{d}) \arrow[r, "\mathrm{II}"] & \mathrm{Ar}^{-}(\mathrm{d})+\mathrm{ML}^{+}(\mathrm{d}) \arrow[d, "\mathrm{III}"] \\
\mathrm{Ar}(\mathrm{l})+\mathrm{M}(\mathrm{s})+\mathrm{L}(\mathrm{d}) \arrow[u, "\mathrm{I}"'] \arrow[r, "\Delta G^{\circ}"] & \mathrm{Ar}^{-}\mathrm{ML}^{+}(\mathrm{d})
\end{tikzcd} \qquad (2)$$

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[2]) (s) = solid, (l) = liquid, (d) = dissolved.

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The $\Delta G°$ values for steps II and III will contribute favourably to the $\Delta G°$ of the overall reaction, whereas $\Delta G_{\mathrm{I}}^{\circ}$ will generally be positive. The feasibility of the reaction will depend on the sign of $\Delta G° = \Delta G_{\mathrm{I}}^{\circ} + \Delta G_{\mathrm{II}}^{\circ} + \Delta G_{\mathrm{III}}^{\circ}$. While quantitative estimations of the various contributions are difficult, it is certain that $\Delta G_{\mathrm{III}}^{\circ}$ is large and negative, since the formation of the ion pair takes place in a medium of low dielectric constant, therefore yielding almost the full formation energy for an ion pair in the vacuum.

In the present paper, a series of aromatic compounds is examined to study the formation of such tight ion pairs, and the ESR., and in some cases the ENDOR. spectra are reported.

Results and discussion. - An ESR. spectrum is observed [2] if neat liquid mesitylene, containing 18-crown-6 in low concentration ($\sim 10^{-2}$M or less), is brought into contact with a potassium mirror. This spectrum has been interpreted as being due to direct contact of the radical anion of mesitylene with the complex cation $[K(18\text{-crown-}6)]^+$. The conclusion that it is a contact ion pair was drawn from the fact that a hyperfine coupling of 18 μT was observed, which could be attributed to 6 equivalent protons, believed to be located on the 18-crown-6 ligand. Since 6 protons and two ^{39}K nuclei give rise to almost the same hyperfine pattern, it was not possible to distinguish unambiguously between a mesitylene radical showing additional hyperfine interaction with either 6 protons or two ^{39}K nuclei [6]. The ENDOR. spectrum *(Fig. 1)* proves that the assignment of the 18 μT hyperfine coupling to protons is correct. The model for the ion pair proposed in [2], therefore, seems correct. The hyperfine coupling of the 6 equivalent protons can be interpreted

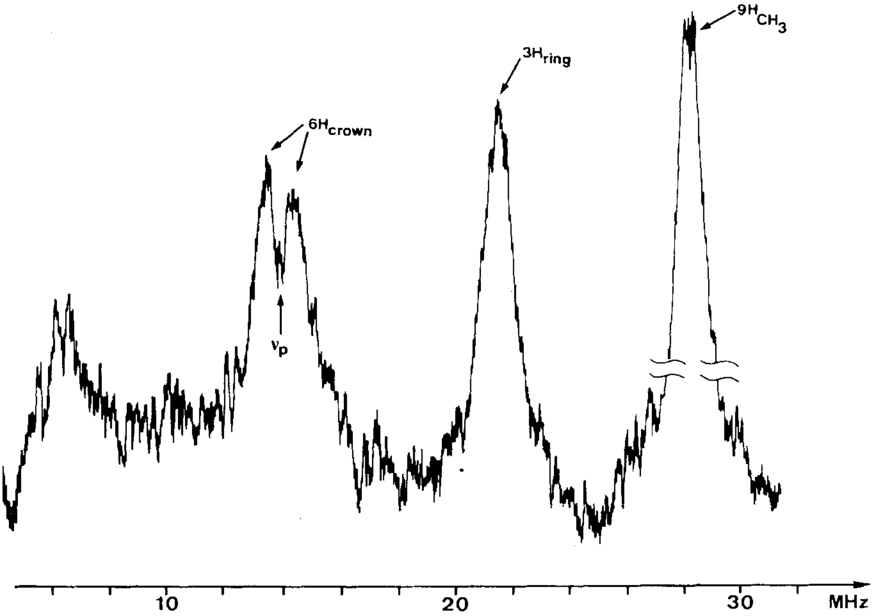

Fig. 1. *ENDOR. spectrum of the radical ion pair mesitylene/K(18-crown-6)* (T = −55°)

as a spin polarization *through space,* and it is interesting to note that its value is of the same order of magnitude as the splitting usually observed for γ-protons [7].

Another, more indirect, proof of the direct coupling of the electron spin to protons in the counter ion can be obtained using derivatives of 18-crown-6. Dicyclohexyl-18-crown-6, separated into its isomers, *cis-syn-cis* (*csc*) and *cis-anti-cis* (*cac*) [5], was used as a complexing agent for K^+, with the *csc* isomer, the coupling constants of the mesitylene protons are almost identical to those of 18-crown-6, but no additional hyperfine structure (hfs.) could be resolved.

With the *cac* isomer, the coupling constants of the mesitylene protons are again the same, and a poorly resolved coupling of the order of 15 µT can be seen. With both isomers, the line width is greater than with the unsubstituted 18-crown-6. This behaviour is to be expected on grounds of our model, since only the unsubstituted 18-crown-6 matches the mesitylene radical in symmetry. It can be assumed that in the latter case a conformation of trigonal symmetry is strongly stabilized in the ion pair. This is not possible for the dicyclohexyl-18-crown-6, and therefore the protons in the counter ion interacting with the electron spin are no longer equivalent, leading to a mere broadening of the ESR. lines.

From the aromatic hydrocarbons with one methyl group less than mesitylene, *i.e.* the xylenes, radical anions can be obtained in the neat liquid with 18-crown-6 as complexing agent for K^+. For all three isomers (*o*-, *m*-, *p*-), the coupling constants of the protons of the radical anion are very similar to the values reported [8]. In the case of *m*-xylene, an additional hfs. is well resolved *(Fig. 2);* it can again be assigned to the protons of the 18-crown-6 ligand. The coupling constant is 18 µT, and the best fit between simulated and measured spectrum is obtained assuming 6 equivalent protons. *o*-Xylene shows no resolved additional hfs., and *p*-xylene one which is barely resolved. These findings support the model of an ion pair where the conformation of the cationic complex is largely determined by the symmetry of the anion. It seems that only molecules allowing the 18-crown-6 to have an approximate

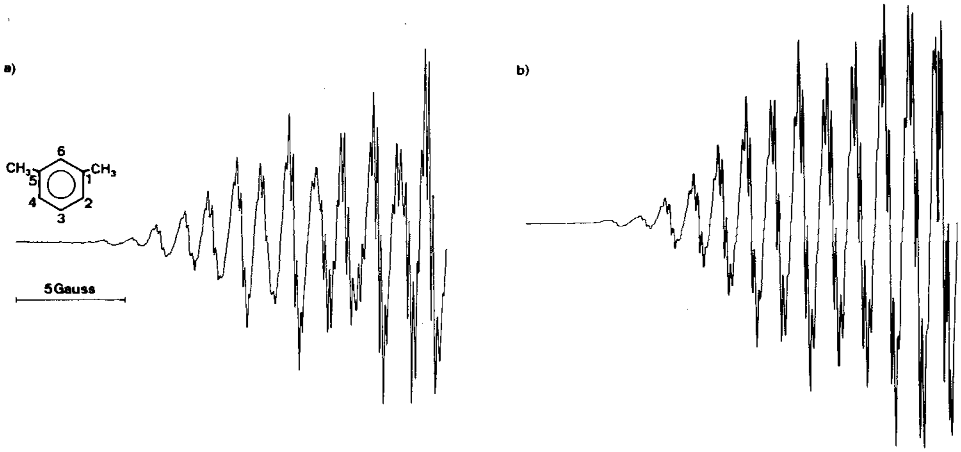

Fig. 2. *ESR. spectrum of the radical ion pair* m-*xylene/K(18-crown-6).* a) observed b) simulated. $a_3 = 780$, $a_6 = 635$, $a_{CH_3} = 242$, $a_2 = 130$, $a_{crown} = 18$. The coupling constants are given in µT.

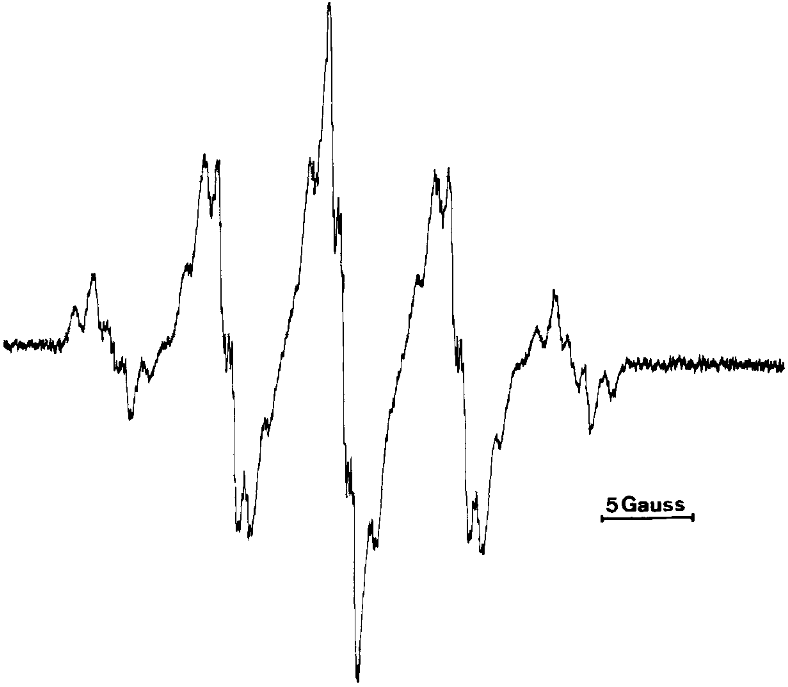

Fig. 3. *ESR. spectrum of toluene/K(18-crown-6)* (T = −60°)

threefold symmetry axis give the hfs. from the counter ion. This hypothesis is corroborated by the observation that toluene also shows an additional hyperfine splitting. The ESR. spectrum of the toluene$^{\overline{\cdot}}$/K(18-crown-6)$^+$ ion pair is shown in *Figure 3*, and its ENDOR. spectrum in *Figure 4*. Probably, there are again 6 protons interacting.

Owing to its three methyl substituents, mesitylene has an extremely low electron affinity. The radical anion can therefore be obtained by the method described in the present paper, utilizing the strongly stabilizing effect of the ion pairing (step III, (2)), but not by the usual method (1). The electron remains localized on one mesitylene molecule for a time which is long on the ESR. time scale, despite the fact that the radical is surrounded by neutral mesitylene molecules. The electron can, however, be easily transferred to any other aromatic molecule having a higher electron affinity than mesitylene itself. Mesitylene can therefore be used as a *general solvent* for preparing contact ion pairs of radical anions with complexed alkali metal cations.

Radical anions of the following aromatic compounds (Ar) were generated in mesitylene using dilute (~10^{-2} M) and equimolar solutions of Ar and of 18-crown-6: benzene, toluene, the three isomers of xylene, biphenyl, pyrene, perylene and coronene. Coupling constants were in all cases very similar to the values reported for the radical anions prepared in other solvents. In the case of each of the xylenes and toluene, both radicals, namely Ar$^{\overline{\cdot}}$ *and* mesitylene$^{\overline{\cdot}}$, were present simultaneously.

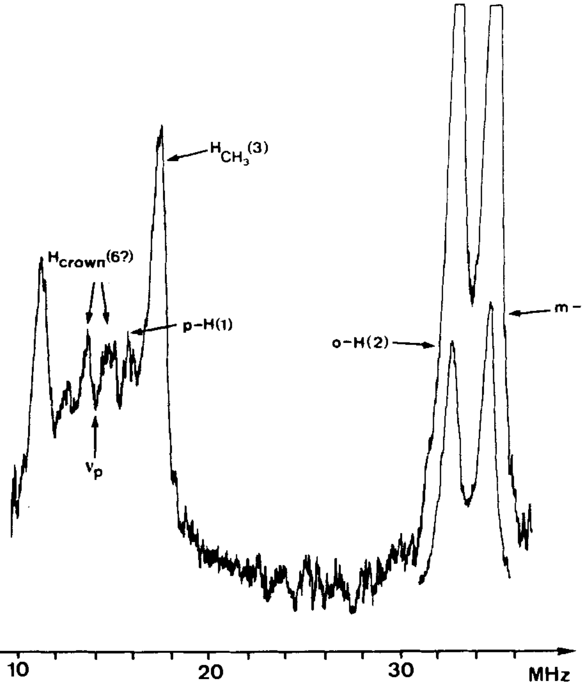

Fig. 4. *ENDOR. spectrum of toluene/K(18-crown-6)* (T = −100°)

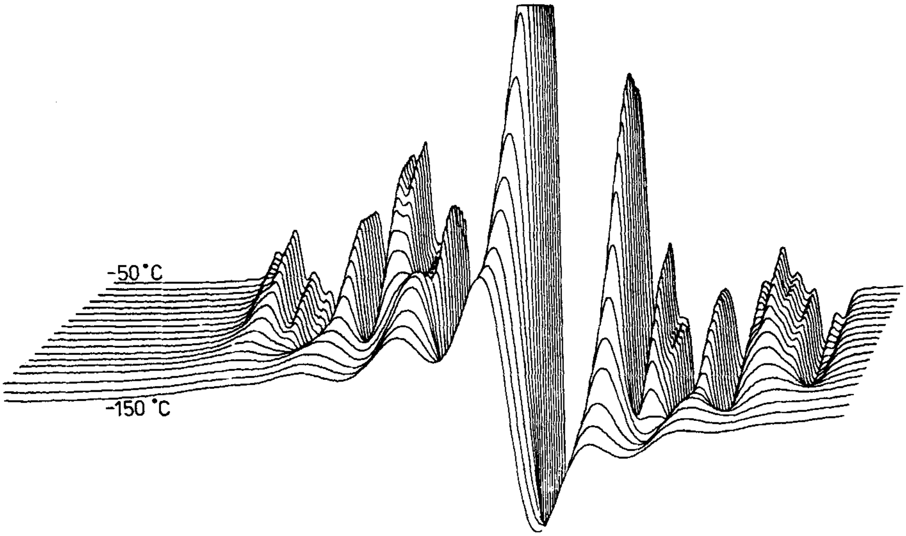

Fig. 5. *ESR. spectrum of the radical ions present in a 1:10 mixture of benzene/toluene containing K(18-crown-6)$^+$ as counter ion at different temperatures.* Temperatures change by 5 to 10 degrees from −150° 'front' to −50° 'back'.

This method can generally be applied for estimating relative electron affinities by using a liquid mixture of two aromatic hydrocarbons Ar and Ar′ as a solvent. Depending on the molar ratio of Ar to Ar′, the equilibrium (3) can be shifted to a

$$\mathrm{Ar/K(18\text{-}crown\text{-}6)+Ar'} \rightleftharpoons \mathrm{Ar'/K(18\text{-}crown\text{-}6)+Ar} \qquad (3)$$

position in which both ion pairs Ar/K(18-crown-6) and Ar′/K(18-crown-6) are observable. In this way, the electron affinities of a series of aromatic hydrocarbons could be compared.

Temperature variation can also be used to displace equilibrium (3). A series of ESR. spectra of a solution containing benzene/toluene in a molar ratio 1:10 is shown in *Figure 5*. At low temperatures, the solution contains only the benzene/K(18-crown-6) ion pair, whereas, at higher temperatures, mainly toluene/K(18-crown-6) is present. This observation corresponds to a positive $\Delta H°$ for reaction (4):

$$\mathrm{C_6H_6(18\text{-}crown\text{-}6)K + C_7H_8 \longrightarrow C_7H_8(18\text{-}crown\text{-}6)K + C_6H_6} \qquad (4)$$

as can be expected from the lower electron affinity of toluene, compared with that of benzene.

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Experimental Part

All preparations have been carried out using well-established vacuum line technique. The commercially available (*Fluka* puriss.) liquid aromatic compounds were dried over potassium and distilled before use. Coronene (*Fluka* purum) was recrystallized twice from benzene, the other solid aromatic compounds were used as received (*Fluka* puriss.). 18-Crown-6 was obtained from *Fluka*. The pure isomers of dicyclohexyl-18-crown-6 were synthesized according to published procedures [4] [5].

ESR. spectra were recorded on a *Varian* E-9 or an E-4 ESR.-spectrometer at X-band frequencies. ENDOR. spectra were measured on a *Varian* spectrometer of the Institute of Physical Chemistry of the University of Basel³).

REFERENCES

[1] *F. Gerson*, «Hochauflösende ESR.-Spektroskopie», Verlag Chemie 1967.
[2] *G. V. Nelson & A. v. Zelewsky*, J. Amer. chem. Soc. *97*, 6279 (1975).
[3] *B. Kaempf, S. Raynal, A. Collet, F. Schué, S. Boileau & J.M. Lehn*, Angew. Chemie *86*, 670 (1974).
[4] *C.J. Pedersen*, J. Amer. chem. Soc. *89*, 7017 (1967).
[5] *R.M. Izatt, B.L. Haymore & J.S. Bradshaw*, Inorg. Chemistry *14*, 3132 (1975).
[6] *M. Symons*, personal communication.
[7] *K. Scheffler & H.B. Stegmann*, «Elektronenspinresonanz», Springer Verlag Berlin, Heidelberg, New York 1970, p. 178.
[8] *J.R. Bolton*, J. chem. Physics *41*, 2455 (1964).

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3) We thank Prof. F. Gerson for permission to use this instrument.