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FLUORENONE KETYL ANIONS GENERATED IN HYDROCARBON MEDIA BY PHASE TRANSFER CATALYSIS

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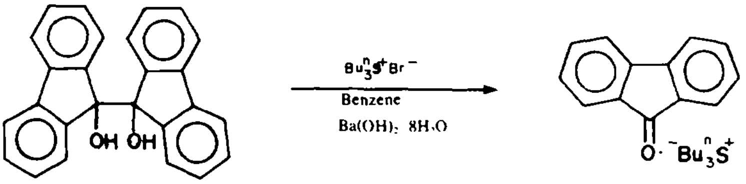
Abstract—Fluorenone ketyl anions with the counterions $\mathrm{Bu}^n_3\mathrm{S}^+$, $\mathrm{Bu}^n_4\mathrm{N}^+$ and $(n-\mathrm{C}_{12}\mathrm{H}_{25})_3(\mathrm{CH}_3)\mathrm{N}^+$ have been generated in benzene by decomposing fluorenopinacol with the relevant alkylammonium or alkylsulphonium base, under phase-transfer catalytic conditions. The recorded ESR spectra in the hydrocarbon medium exhibit a marked cation dependence. The phenomenon is interpreted on the basis of spin density transfer from the anion to the magnetic nuclei of the cation. The implications to the phase transfer catalysis are discussed.

We report an application of the phase-transfer-catalysis principle on the generation of ketyl anions of fluorenone, $\mathrm{FlO}^{\cdot -}$, with complex counterions of the ammonium or sulphonium type. We utilized the known[1] tendency of aromatic pinacols to undergo a facile fragmentation by reacting with basic reagents, e.g. eqn (1), and the effect of bulky cations to solubilize[2] insoluble anions in non-solvating media such as hydrocarbons. This work is interest for the following reasons: (1) It expands the lower limit of the solvent polarity range in which the ESR spectrum of a ketyl anion has been recorded. (2) It may resolve the problem whether or not the unpaired electron interacts with the magnetic nuclei of the complex cation. (3) It utilizes the fluorenone ketyl anion as a "spin label" in order to probe into the ion-pairing situation in this solvent medium, a matter of great importance to the phase transfer catalysis itself.



(1)

To the best of our knowledge, prior to this report, no ESR spectrum of a ketyl anion has been recorded in a hydrocarbon solvent such as benzene. The addition of toluene to a solution of sodium fluorenone ketyl anion in methyltetrahydrofuran has been reported[3] and resulted in the disappearance of the characteristic absorption due to the ketyl. Even poorly cation solvating cosolvents, e.g. triethylamine, when added to solutions of lithium fluorenone ketyl anion caused a marked decrease of the solution paramagnetism.[4] A question then arises—whether or not solubilization of a ketyl anion in a hydrocarbon medium results in a paramagnetic species in solution. Our results (see spectra in Figs. 1-3) indicate that bulky counterions such as $\mathrm{Bu}^n_3\mathrm{S}^+$, $\mathrm{Bu}^n_4\mathrm{N}^+$ and $(n\text{-}\mathrm{C}_{12}\mathrm{H}_{25})_3(\mathrm{CH}_3)\mathrm{N}^+$, do stabilize the paramagnetic fluorenone ketyl anion. The hyperfine splittings corresponding to the spectra in Figs. 1-3, are summarized in the Table. Obviously the spectra exhibit a marked cation dependence. In previous investigations[5,6] tetraalkylammonium counterions have been employed in polar media in order to obtain unperturbed ESR spectra of the anion. Although this may be true for aprotit solvents of high dielectric constant,[7] our results in benzene do not agree with the above mentioned conclusion.

We interpret this perturbation by the cation as arising by spin density transfer from the anion to the magnetic nuclei of the cation, albeit outside the resolving power of the instrument. The reasoning is as follows: Magnetic nuclei of alkali metal counterions do receive a finite spin density from the anion, as manifested by either the alkali metal hyperfine splitting in the ESR[8] or the alkali metal contact shift in the NMR.[9] Moreover, a number of mechanisms for spin density transfer through saturated chains of C atoms are available.[10] Spin density drainage also occurs to the solvent molecules which are in the coordination sphere of the cation.[11,12] The latter effect is evidenced by the observed contact shifts of solvent-molecule protons, which range between *ca* 0.2 to 10.0 ppm.[12,13] These contact shifts correspond[14] to coupling constants in the range 10^{-3}–10^{-1} G; the lower limit occurs most frequently, and this explains why the present day ESR spectrometers do not resolve the perturbation caused by the solvent. Bearing all this in mind, the hypothesis for spin density transfer from the anion to the onium cation seems very probable. In such a case, one could conclude that the anion–cation pair exhibits covalency to a certain extent,[15] namely, that it is of the tight or intimate ion-pair type. It is of interest that the largest splittings (Table) are observed with $Bu^n_3S^+$. The central atom of the onium ion, i.e. S^{32} with natural abundance 95%, is non magnetic. In the case of alkylammoniums where the central atom is ESR active, the splittings are smaller. These observations agree with the hypothesis of spin density transfer from the anion to cation. Furthermore, the differences in the splittings between the two alkylammonium fluorenone ketyls could be taken as evidence for spin density transfer to protons of the alkyl groups.

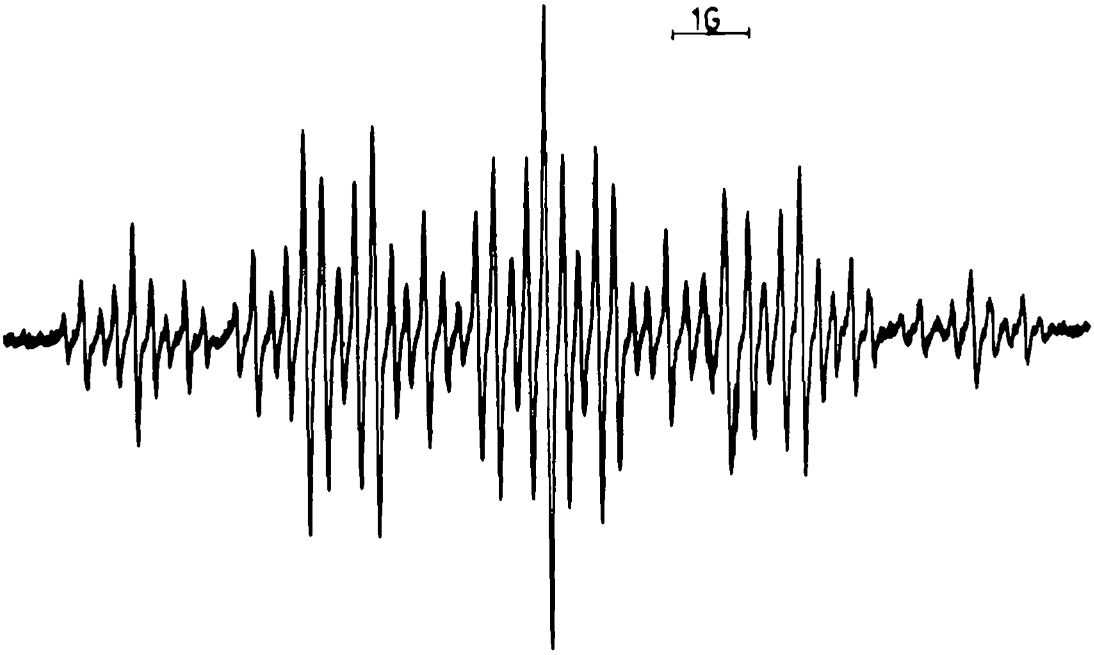


Fig. 1. ESR spectrum of tri-*n*-butysulphonium fluorenone ketyl anion in benzene.

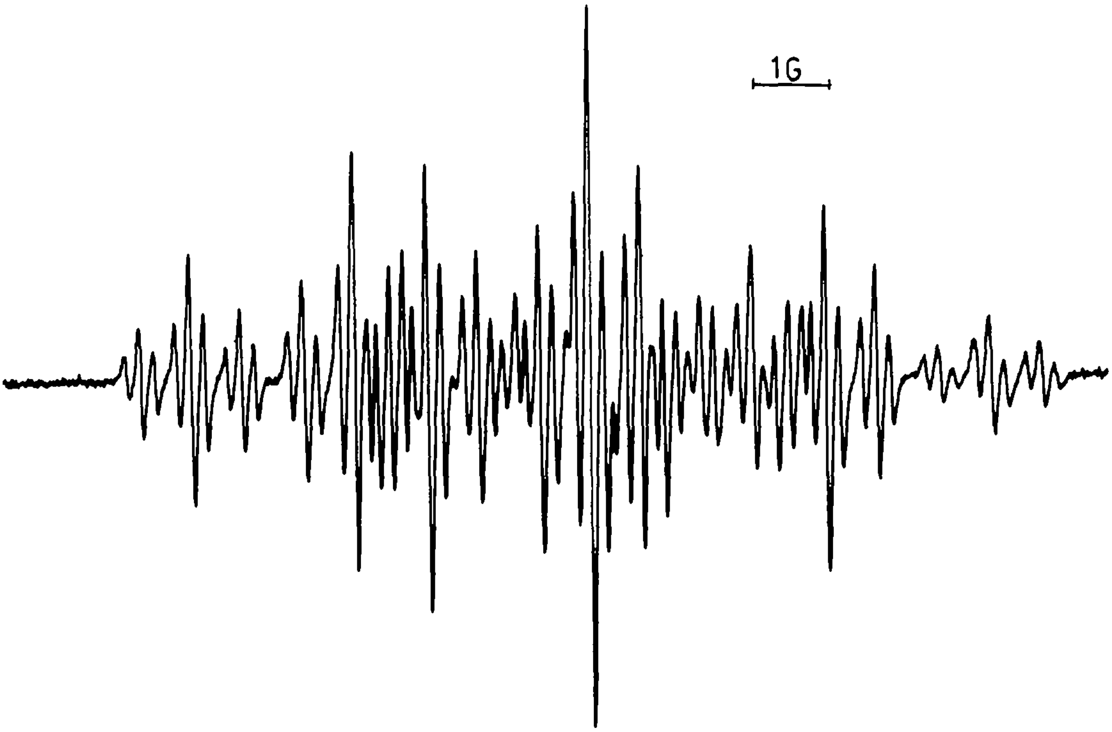


Fig. 2. ESR spectrum of tri-*n*-dodecylmethylammonium fluorenone ketyl anion in benzene.

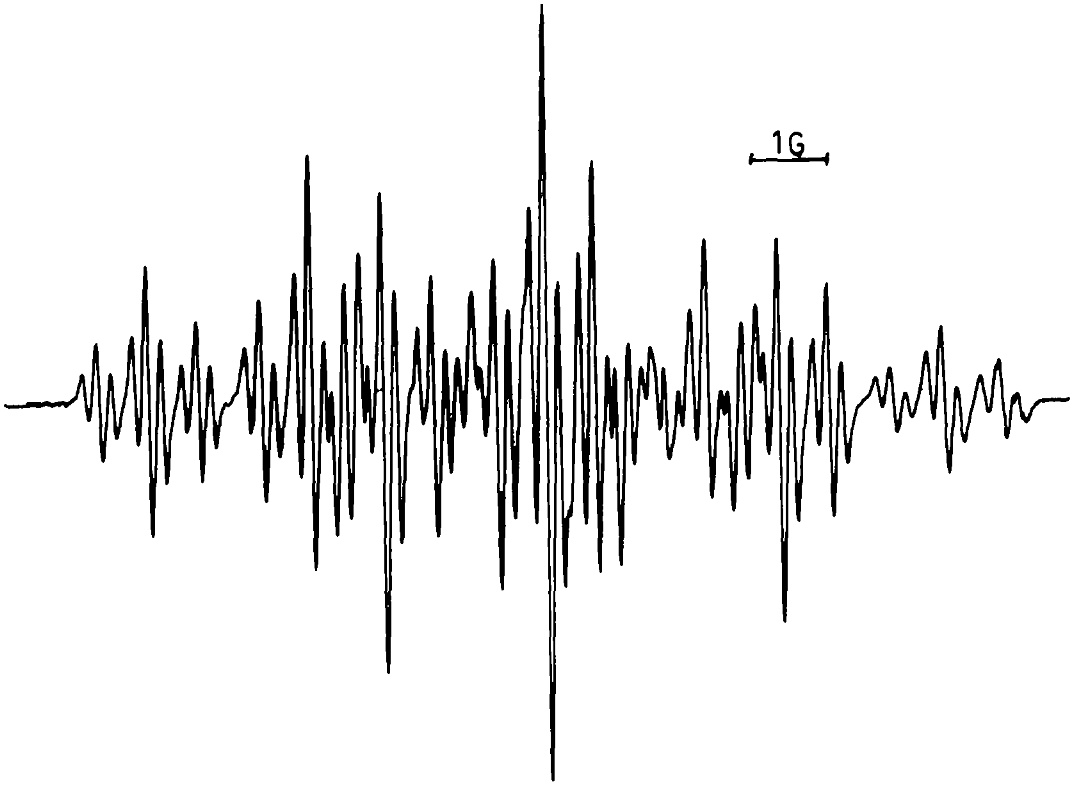


Fig. 3. ESR spectrum of tetra-*n*-butylammonium fluorenone ketyl anion in benzene.

Table 1. Hyperfine splittings in some fluorenone ketyl anions, with alkylammonium or alkylsulphonium counterions (in G) (Solvent: Benzene)

Cation	$H^{1,8}$	$H^{2,7}$	$H^{3,6}$	$H^{4,5}$
$Bu_3^nS^+$	2.28_5	0.25	3.20	0.69
$(n\text{-}C_{12}H_{25})MeN^+$	2.18_5	0.19_5	3.16	0.66
$Bu_4^nN^+$	2.17_5	0.17_5	3.12_5	0.66_5

The conclusion that fluorenone ketyl anion–onium cation pair is of the intimate ion-pair type, despite the high dilution, bears some relevance to the phase transfer catalysis. Specifically, it concerns the question of what is "the dominant nucleophile".[2] Our results suggest that an alkylammonium or alkylsulphonium salt QX reacts as a nucleophile as an ion pair rather than in the form of "naked" ions.[16] The latter conclusion agrees with the suggestion made by Brändström.[2]

EXPERIMENTAL

Electron-spin-resonance spectra were recorded on a Varian E-4 ESR spectrometer, using Fremy's salt for field calibration (a_N = 13G). Fluorenopinacol was prepared by rapid acidification with 6N HCl of a soln of lithium fluorenone ketyl anion in THF. The recrystallized pinacol from benzene melted at 188–190°, lit.[17] m. 190–192°. Tri-*n*-butylsulphonium bromide was prepared from di-*n*-butyl sulphide and butyl bromide in chloroform. Bu_2^nS was synthesized from Na_2S and Bu^nBr by phase transfer catalysis using tetrabutylammonium bromide as catalyst. The latter reagent as well as tri-*n*-dodecylmethylammonium chloride were commercial products. Samples of fluorenone ketyl anions were prepared by standard vacuum line techniques by stirring equivalent amounts of fluorenopinacol and the onium salt in spectroscopic grade benzene, with a large excess of barium hydroxide octahydrate, to make an approximately 10^{-3} M soln of the ketyl anion. The soln of the ketyl was of a brownish colour, resembling potassium fluorenone ketyl anion in THF.

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