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CARBON ACIDITY. 60. EFFECT OF TEMPERATURE ON ION PAIR ACIDITIES OF PENTAFLUOROBENZENE. NATURE OF PENTAFLUOROPHENYLCESIUM AND -LITHIUM ION PAIRS IN CYCLOHEXYLAMINE.[1]

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Abstract

The ion pair equilibrium between 9-t-butylfluorene and pentafluorobenzene in cyclohexylamine has almost zero entropy for their cesium salts but a relatively high entropy change, 21.5 e.u., for their lithium salts. Both pentafluorophenylcesium and -lithium exist primarily as contact ion pairs in cyclohexylamine.

The brilliant pioneering studies of Hogen-Esch and Smid (2) have established that carbanion alkali metal pairs in solution may range from tight or contact ion pairs to loose or solvent-separated pairs. In general, solvent-separated ion pairs are favored for small cations (Li^+) and coordinating solvents (THF). These studies were generally based on visible spectra of delocalized carbanion systems. Application of these techniques to cyclohexylamine (CHA) solution showed that 9-alkyl-fluorenylcesiums form contact ion pairs at normal temperatures whereas the corresponding lithium salts form loose ion pairs (3, 4). In the present paper we report the temperature effects on equilibria involving cesium and lithium salt of pentafluorophenyl anion, PFB^-, a localized carbanion that does not have a visible absorption spectrum, by using an indicator of known ion pair character.

The general approach was to measure equilibrium (1) in which M^+ is Li^+ or Cs^+ and R^- is the 9-t-butylfluorenyl anion.

$$R^-M^+ + C_6F_5H \rightleftharpoons RH + C_6F_5^-M^+ \qquad (1)$$

Pentafluorobenzene (PFB) and 9-t-butylfluorene (9-t-BF) have been shown previously to have comparable acidities towards cesium cyclohexylamide (CsCHA) (5). The experimental approach was similar to that used in our previous studies (6, 7) of carbanion equilibria between a colored indicator and an invisible substrate except that more extensive use was made of a Vacuum Atmospheres recirculating glove box. Pentafluorobenzene was weighed in specially constructed microampoules or was handled with a calibrated syringe. A known amount was added to a known weight of 9-t-BF in CHA which had been partially converted to its Li or Cs salt by addition of LiCHA or CsCHA, respectively. The reaction mixture was maintained in a thermostated cell and the spectrum of the indicator salt was measured before and after addition of the PFB. 9-t-BF is not generally an ideal indicator because its carbanion equilibria are frequently relatively slow to establish; however, other indicators tried, such as 2,7-di-t-butylfluorene, gave rapid side reactions and were totally unsuitable. These side reactions appear to involve reaction with PFB or the tetrafluorodehydrobenzene produced by elimination of fluoride ion from PFB^-. With 9-t-BF, eq. 1 is established rapidly as judged from the initial decrease in indicator spectrum on addition of the PFB but the subsequent side reactions are sufficiently slow that extrapolation to zero time was feasible. Apparently the very steric hindrance features contributed by the 9-t-Bu group that slow carbanion equilibria with some hydrocarbons also slow the side reactions of addition to PFB or its benzyne. The Cs system at 0° showed first order kinetics in decomposition to another species and gave a clear isosbestic point. At higher temperatures the decompositions were more complex but the initial extrapolations back to zero time were still satisfactory and gave consistent results for the concentrations of all four species at equilibrium. Concentrations at equilibrium were in the following ranges: 9-t-BF, 1-5 x 10^{-3}M; 9-t-BF-M^+, 1-4 x 10^{-3}M; PFB, 2-4 x 10^{-2}M; PFB^- M^+, 1-7 x 10^{-4}M. The results are summarized in Table 1. The derived least squares enthalpy and entropy are shown together with the standard deviations.

The near-isoentropic nature of the cesium equilibrium shows that PFB^-Cs^+ exists as expected as a contact ion pair in CHA. Because the phenyl anion is a localized carbanion we expect also that the Coulombic interaction in this ion pair is greater than for a fluorenylcesium; that is, part of the relatively high acidity of PFB comes from this greater ion pair stabilization and its relative gas base acidity is expected to be substantially lower.

The lithium ion pair equilibrium, in contrast, has a high positive entropy that suggests that pentafluorophenyllithium also exists in CHA primarily as a contact ion pair. Fluorenyllithiums are known to be separated pairs in CHA (3), and the reduced solvation of the contact pair corresponds to liberation of solvent molecules and an increased entropy. Indeed, the entropy difference between the Li and Cs systems is close in magnitude to that found for the following equilibrium in CHA (3):

$$\underset{\text{solvent-separated}}{F\ell^- \| Li^+} \rightleftharpoons \underset{\text{contact}}{F\ell^- Li^+} \qquad \Delta S° = 25.6 \text{ e.u.}$$

We anticipate that all aryl anions more basic than PFB^- will also form contact lithium ion pairs in CHA.

TABLE I. Temperature Effects on Equilibrium 1 for Cesium and Lithium Ion Pairs of Pentafluorobenzene and 9-t-Butylfluorene

Temp. °C	-ΔpK	ΔH° Kcal. mol^{-1}	ΔS° e.u.
	Cs Salt		
25	1.71, 1.64, 1.79	1.0±0.9	-4.5±3.1
11	1.75, 1.63, 1.79		
0	1.78, 1.87, 1.69		
	Li Salt		
25	1.65, 1.51, 1.52	8.5±1.1	21.5±3.9
11	1.97, 1.99, 1.68, 1.84		
0	2.29, 2.04, 2.18, 2.08, 2.08		

One interesting corollary is that PFB is less acidic relative to its lithium solvent separated conjugate base. A solvated Li^+ is effectively larger than Cs^+ and the solvent-separated $PFB^- \| Li^+$ should have less ion pair Coulombic stabilization corresponding to a higher pK relative to delocalized indicators (8, 11). Conversion to the contact ion pair is favored for the localized carbanion and the entropy gain associated with released solvent restores the pK to a value close to that for the cesium equilibrium.

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