pears on mixing aqueous $NaBH_4$ with an acid solution of $Ru(bipy)_3{}^{3+}$; we also find luminescence on reduction of $Ru(bipy)_3{}^{3+}$ by aqueous H· atoms.

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Evidence for Stepwise Solvation of Strontium Carbanion Salts in Ethereal Solvents

Sir:

The structure of ion pairs of alkali salts of carbanions and radical anions in aprotic solvents has been extensively studied in the last few years. The existence of contact or tight ion pairs and solvent-separated or loose ion pairs in these systems is now well documented.[1-3] Only recently has information on the structure of alkaline earth carbanions become available.[4,5]

In a previous communication we reported on the structure of fluorenylbarium and its crown ether complex in a few aprotic solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME).[4] It was shown that this salt in THF over the temperature range 25 to −70° exists essentially as a tight ion pair. We now want to report evidence for a distinct stepwise solvation of the fluorenylstrontium ion pair in THF in the temperature range 20 to −100°. This process involves the formation of an asymmetrically solvated ion pair in which one of the fluorenyl moieties is separated from the strontium ion followed by the separation of the second fluorenyl unit to give a symmetrically solvated ion pair.

$$Fl^-M^{2+}Fl^- \rightleftarrows Fl^-||M^{2+}Fl^- \rightleftarrows Fl^-||M^{2+}||Fl^-$$

The strontium salt was prepared in THF over a strontium mirror in the presence of a stoichiometric quantity of 1,1-diphenylethylene in an all-glass apparatus under high vacuum (10^{-6} mm) conditions. The visible spectrum of the recrystallized salt has maxima at 343, 435, and 458 nm and indicates a contact ion pair (Figure 1). On lowering the temperature the small shoulder at 372 nm, identifiable with separated ion pairs, increases rapidly in intensity. At −22° the two bands at 343 and 372 nm are approximately equal in intensity but at lower temperatures a large absorption band at 343 nm persists (Figure 1).[6] This behavior contrasts sharply with that of the alkali salts such as fluorenylsodium in this solvent where the transition from contact ion pairs to separated ion pairs is essentially complete at −70° and the contact ion pair absorption has disappeared.[1] The latter process is relatively straightforward

$$Na^+Fl^- \overset{R}{\rightleftarrows} Na^+||Fl^- \qquad \Delta H = -7.6\ \text{kcal}$$

and the log R *vs.* $1/T$ plot is essentially straight over the entire temperature range (R = [separated ion pairs]/[contact ion pairs]). In the present case, however, the log R *vs.* $1/T$ plot is strongly curved (Figure 2).[7] Apparently the process is strongly exothermic ($\Delta H \simeq -12$ kcal), until approximately 50% of the contact ion pairs have been converted into separated ion pairs. The apparent enthalpy of the solvation process then decreases to a much lower value ($\Delta H \simeq -0.5$ kcal) and increases again at lower temperatures.

These observations suggest that the process is not represented by a simple one-step solvation process

$$Fl^-Sr^{2+}Fl^- \overset{K_3}{\rightleftarrows} Fl^-||Sr^{2+}||Fl^-$$

but possibly by a two-step process in which the fluorenyl ions become successively separated from the Sr^{2+} ion. The first step is expected to be highly exothermic, the second step much less so.

$$Fl^-Sr^{2+}Fl^- \overset{K_1}{\rightleftarrows} Fl^-||Sr^{2+}Fl^- \overset{K_2}{\rightleftarrows} Fl^-||Sr^{2+}||Fl^-$$

From this scheme it can be seen that the ratio of [separated ion pairs] to [contact ion pairs] is given as shown in eq 1.

$$R = (1 + 2K_2)/(1 + 2/K_1) \tag{1}$$

Taking the logarithm and differentiating with respect to $1/T$ gives the apparent enthalpy of the process, contact ion pairs ⇆ separated ion pairs (eq 2). From

$$\Delta H = (2/(2 + K_1))\Delta H_1 + (2K_2/(1 + 2K_2))\Delta H_2 \tag{2}$$

(2) it follows that at high temperature, where K_1 and $K_2 \ll 1, \Delta H \simeq \Delta H_1$.

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[6] Complete reversibility of the spectral phenomena and very low conductance of the solution assure that we are again dealing with ion-pair equilibria.

[7] The ratio R can as before (see ref 1) be evaluated using spectra of carbanion solutions existing as contact ion pairs or as separated ion pairs over the entire temperature range. In this case data on fluorenylbarium in THF and fluorenyllithium in DME were used to describe the behavior of contact and separated ion pairs. R was calculated on the assumption that the spectra of the two "types" of separated ion pairs, *e.g.*, of $||Fl^-$ in $Fl^-Sr||Fl^-$ and in $Fl^-||Sr||Fl^-$, are identical. Extinction coefficients (ϵ) of contact and separated ion pairs are taken as 10,100 and 14,000, respectively, at 25°. The change of extinction coefficient with temperature expressed as $-d(\epsilon_{T°}/\epsilon_{20°})/dT$ was determined as 4.0×10^{-3} and 6.0×10^{-3} for contact and separated ion pairs, respectively. The contribution of separated ion pairs at 343 nm defined as $OD_{343}/OD_{max\ 372}$ and the contribution of the contact ion pairs at 373 nm ($OD_{372}/OD_{max\ 343}$) were determined as a function of temperature. At −76°, for instance, these values were 0.26 and 0.27, respectively. Using these data one calculates that the increase of OD of the contact ion pair at 343 nm on lowering the temperature is only apparent. For instance, the corrected absorption of the contact ion pair at −76° is only about 0.60.

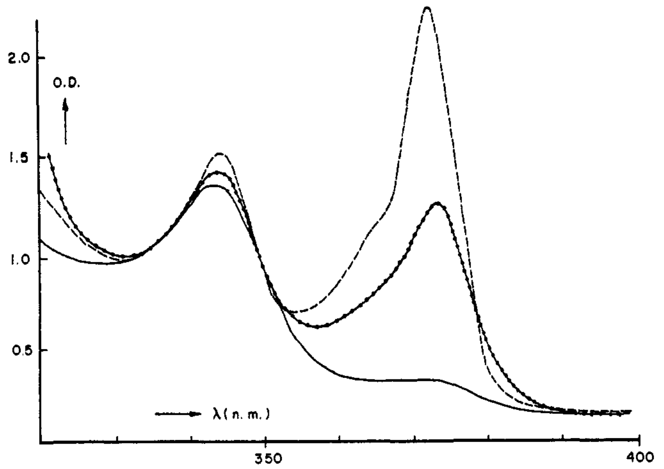

Figure 1. Temperature dependence of the near-uv spectrum of fluorenylstrontium ($Sr^{2+}Fl_2^-$) in THF: (——) 24.5°; (-·-·-·-) −15.4°; (- - -) −76.1°.

As the temperature decreases, K_1 increases rapidly ($\Delta H = -12.3 \pm 2$ kcal mol^{-1}), and K_2 increases much more slowly. One expects, therefore, the apparent enthalpy to decrease sharply due to the factor $2/(2 + K_1)$. The second term, $(2K_2/(1 + 2K_2))\Delta H_2$, however, is expected to increase slowly. If the second term is small in the temperature region where the first term vanishes, the apparent enthalpy is expected to approach zero before it rises again to its low-temperature limit, where $\Delta H = \Delta H_2$. Inspection of Figure 2 indicates that the system qualitatively conforms to the predicted behavior.

A more quantitative correlation can be obtained by reasonable estimates of K_1 and K_2 at any one temperature. One can then calculate K_1 and K_2 at all temperatures provided that ΔH_1 and ΔH_2 are known. ΔH_1 is known (see above) and K_1 can be calculated under the reasonable assumption that at high temperatures the 372-nm absorption band is due to $Fl^-||Sr^{2+}Fl^-$.[8] K_2 can now be calculated in the region where $K_1 \gg 1$ (−70 to −100°, Table I), since there $R = 1 + 2K_2$ and ΔH_2 can then easily be evaluated in the usual manner. Table I lists the extrapolated K_1 and K_2 values for a number of temperatures. R can now be calculated at all temperatures and the calculated log R *vs.* $1/T$ plot is shown in Figure 2. It can be seen that the experimental plot is well simulated by a two-step process. Enthalpy and entropy values for the two processes are calculated to be: $\Delta H_1 = -12.3 \pm 2$ kcal mol^{-1}, $\Delta S_1 = -47 \pm 7$ cal deg^{-1} mol^{-1}; $\Delta H_2 = -2.8 \pm 1$ kcal mol^{-1}, $\Delta S_2 = -17 \pm 5$ cal mol^{-1}.

Table I. Values of R, K_1, and K_2 at a Number of Temperatures[a]

$1/T \times 10^3$	T, °C	R	K_1	$K_2 \times 10^2$
3.44	+18.0	0.103	0.18	2.1
3.77	−8.4	0.489	1.26	3.3
3.99	−22.1	0.950	5.50	4.6
4.45	−48.0	1.37	87.4	8.7
4.92	−70.0	1.49	1,700	17
5.85	−102.0	2.66	526,000	74

[a] Total carbanion concentration = 6.5×10^{-4} M.

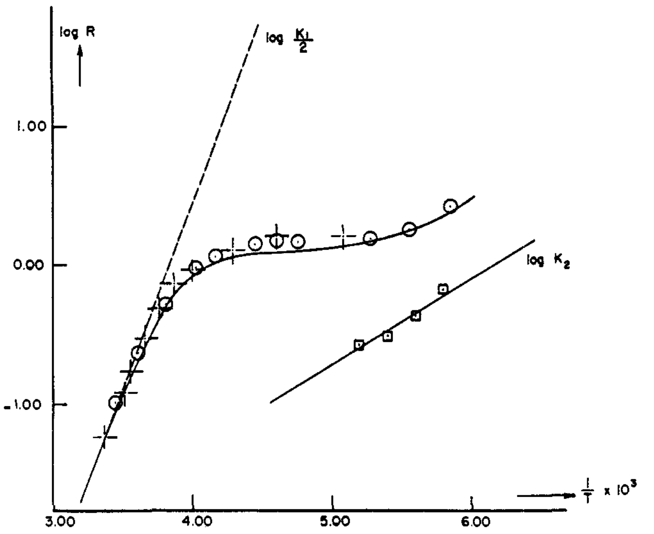

Figure 2. The ratio of [separated ion pairs] to [contact ion pairs] as a function of temperature: R = [separated ion pairs]/[contact ion pairs]; (⊙–┼–) refer to runs on different samples; (——) calculated log R *vs.* $1/T$ curve; (- - -) calculated values of the log of the equilibrium constant of the first solvation step K_1 *vs.* $1/T$; (⊡) calculated values of the log of the equilibrium constant of the second solvation step K_2 at the four lowest temperatures.

Results on other systems such as fluorenylbarium–trimethylene oxide suggest that this surprisingly specific two-stage solvation process may be quite general in solutions of this type.

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[8] Since at high temperatures K_1 and $K_2 \ll 1$, it follows from (1) that $R = K_1/2$.

Stable Carbocations. CXXXVI.[1] Intramolecular 1,2-Hydrogen Shifts in Difluoro- and Dimethylbenzenium Ions

Sir:

Protonation of isomeric difluorobenzenes and xylenes in superacids has been studied.[2,3] However, there was no report on the temperature-dependent behavior of these ions. Furthermore, *o*-difluorobenzene was not protonated in FSO_3H-SbF_5 solution at low temperature.[2] Using the improved $HF-SbF_5-SO_2ClF$ superacid system we presently wish to report the results of temperature-dependent nmr (^1H and ^{19}F) studies of

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