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Effect of Pressure upon the Equilibrium: Tight Ion-Pairs⇌Loose Ion-Pairs

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The effect of pressure (up to ~5000 atm) upon the equilibrium, tight ion-pairs⇌loose ion-pairs, was investigated for sodium and lithium fluorenyl in THF at about 22°C. Pressure shifts the equilibrium towards the loose pairs, ΔV being -24.4 and -15.6 ml for the sodium and lithium salts, respectively. The ΔV values correlate with the relevant ΔS values, thereby indicating that both are reflecting the increase in the number of immobilized solvent molecules arising from the conversion of one pair into the other.

The linear extinction coefficients at λ_{max} of either pair substantially increase with pressure, viz., by about 60 % when the pressure rises from 1 to 4000 atm. Apparently, the absorption curves become sharper at higher pressures, probably because the rotation of a pair and its soft vibrations are hindered.

The spectra of the salts of fluorenyl carbanions have two peaks in the near u.-v. region, one attributed to tight contact ion-pairs, the other assigned to loose pairs with solvent molecules separating the ions.[1] Their relative intensities vary with the nature of cations and solvents, and in each system they are temperature dependent. This dependence permits one to determine ΔH and ΔS for the process, tight pair⇌loose pair. Since the two types of pairs are thermodynamically distinct one may inquire what is the change of volume arising from the conversion of one pair into the other. This information is derived from studies of the pressure dependence of the equilibrium, and the pertinent results are reported here.

EXPERIMENTAL

MATERIALS

Sodium and lithium salts of fluorenyl were prepared on a high vacuum line using standard procedures. A THF solution of sodium α-methyl-styrene tetramer was used to generate the former salt, while butyl lithium was used for making the latter. The methods of purification of the reagents and solvents are well known. The solutions, approximately 10^{-2} M, were stored in evacuated glass ampoules equipped with breakseals.

APPARATUS AND PROCEDURE

The optical cell was made from true-bore quartz tube with two optically flat windows sealed in its lower part close to the centre of the tube. The windows were 2 mm apart and a quartz spacer reduced the optical path to about 0.01 cm. A piston with two O-rings fitted the tube and effected its closure.

The device shown in fig. 1 was used for filling the cell. The cell F was placed in a holder attached to a Teflon rod C. The piston E was lightly screwed into the end of the Teflon rod B. Both rods and a glass tubing A were inserted in a Teflon ground-stopper D, the O-rings (marked by dots) ascertaining the vacuum tightness of the device. The stopper fitted the ground joint of a glass vessel which was attached to a high-vacuum line.

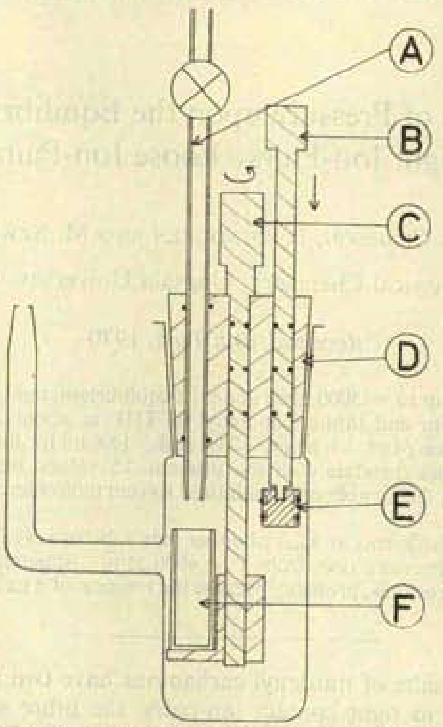

FIG. 1.—The device used for filling the cell in vacuum and closing it with a piston.

The ampoule containing the solution to be investigated was sealed to tube A above the Teflon stopcock marked in fig. 1 by a cross. The unit was evacuated, the Teflon stopcock closed and the break-seal broken. Thereafter, the cell was filled in vacuum by manipulating the stopcock; then it was placed under the piston by turning rod C. The piston was pushed into it by shifting the rod B which was eventually disengaged from the piston by unscrewing. After letting air into the vessel, stopper D was lifted and the filled and closed cell removed. The cell was inserted in the high pressure steel vessel, as described in the preceding paper,[2] and the spectrum investigated under the desired pressure. A Zeiss M4 QIII spectrophotometer, with accuracy better than 0.01 units of O.D., was used.

In a typical run the spectrum of each solution was recorded at normal pressure, then the pressure was gradually increased, the spectrum being recorded at each increment (940, 1920, 2920, 3900 and 4900 atm). The optical densities were corrected for the absorption of the solvent and of glycerol that filled the space between the sapphire windows and the cell. These corrections were determined for all the required wave-lengths and pressures.

A direct check of the reversibility of the process was not feasible because some carbanions are destroyed when the pressure is reduced. This is caused by contact of the solution with the walls of the cell which were wetted by glycerol when the pressure was high. Nevertheless, reversibility was demonstrated by showing that the ratio of optical densities of the two peaks is the same whether the required pressure was attained from below or from above. The pressure gauge was calibrated from compression measurements on water using piezometers of the type described by Andersson.[3] The compressibility of the solvent was determined by the same technique.

RESULTS

Four independently-prepared solutions of sodium and lithium fluorenyl in THF were investigated. Typical spectra of these salts recorded at various pressures are