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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 $\lambda_{\max}$ 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^{-3} 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.

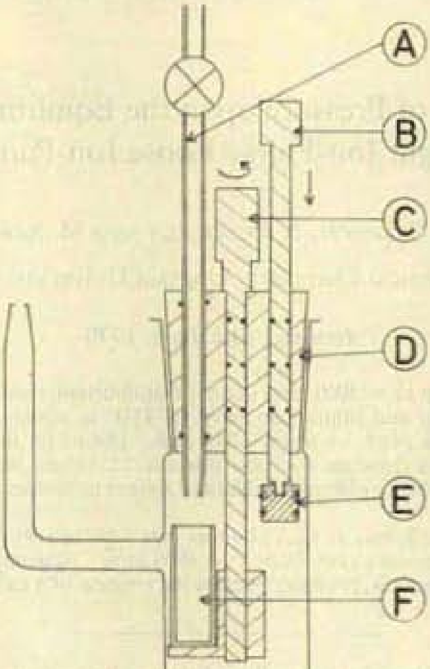

FIG. 1.—The device used for filling the cell in vacuum and closing it with a piston.

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

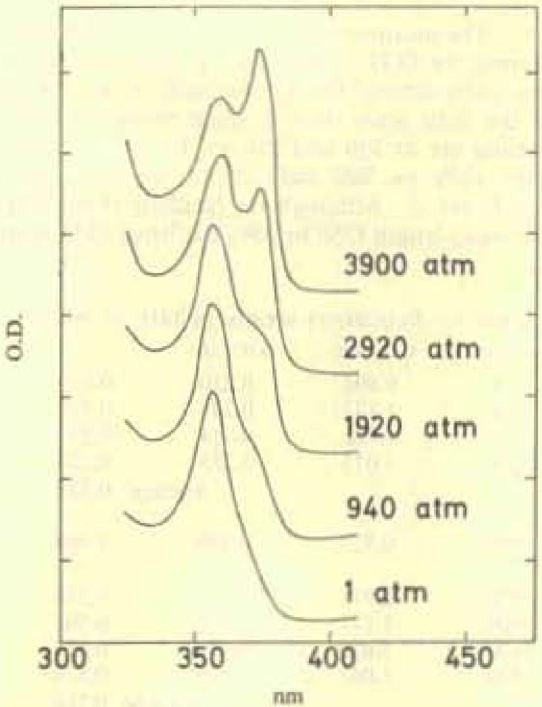

FIG. 2.—The spectra of sodium fluorenyl in THF at ~22°C at various pressures. The absorption curves are progressively shifted upwards to avoid overlapping.

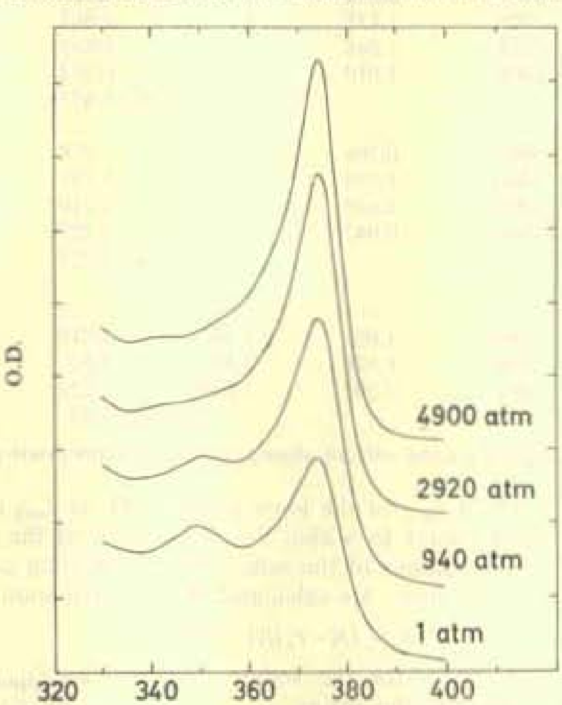

FIG. 3.—The spectra of lithium fluorenyl in THF at ~22°C at various pressures. The absorption curves are progressively shifted upwards to avoid overlapping.

shown in fig. 2 and 3. The maxima of absorption were carefully determined in each experiment by measuring the O.D. in the vicinity of each peak at 1.0 nm intervals. The λ_{max} of the loose pairs derived from either salt are at 374 nm at all pressures, whereas the λ_{max} of the tight pairs show a slight pressure dependence. At 1 atm their absorption maxima are at 356 and 350 nm for the sodium and lithium salts, respectively, but they shift to 360 and 353 nm at 4900 atm. The results are summarized in tables 1 and 2. Although the heading of the third column of each table refers to a fixed wave-length (356 or 350) the listed O.D. were measured at the appropriate maxima.

TABLE 1.—FLUORENYL SODIUM IN THF AT ~22°C

expt.	pressure atm	O.D. (356)	O.D. (374)	*R*	*K*
1	1	0.895	0.220	0.246	—
2	1	1.133	0.246	0.233	—
3	1	1.762	0.414	0.235	—
4	1	1.073	0.255	0.238	—
			average	0.238	
1	940	0.922	0.340	0.369	0.15
1	1920	0.911	0.525	0.576	0.42
2	1920	1.177	0.661	0.562	0.40
3	1920	1.639	0.920	0.561	0.40
4	1920	1.061	0.609	0.574	0.42
			average	0.568	0.41
1	2920	0.836	0.743	0.889	0.94
2	2920	1.131	0.974	0.862	0.89
3	2920	1.548	1.340	0.865	0.90
4	2920	1.010	0.893	0.884	0.93
			average	0.875	0.915
1	3900	0.768	0.982	1.278	1.88
2	3900	1.074	1.279	1.191	1.63
3	3900	1.445	1.748	1.210	1.68
4	3900	0.943	1.157	1.227	1.73
			average	1.227	1.73
1	—	—	—	—	—
2	4900	1.028	1.563	1.519	2.73
3	4900	1.378	2.10	1.52	2.74
4	4900	0.893	1.358	1.521	2.74
			average	1.52	2.74

O.D. corrected for the solvent absorption at the appropriate pressure.

The ratios R (O.D. at λ_{max} of the loose pairs)/(O.D. at λ_{max} of the tight pairs) at each pressure are constant to within 2-3 %, in spite of the substantial variations in the total concentrations of the salts. The equilibrium constants K of the process, tight pairs$\rightleftharpoons$loose pairs, are calculated from the equation,

$$K = (R-r_1)/(1-r_2R),$$

where $r_1 = \varepsilon_{374,\text{tight}}/\varepsilon_{356,\text{tight}}$ for the sodium salt and $\varepsilon_{374,\text{tight}}/\varepsilon_{350,\text{tight}}$ for the lithium salt, and r_2 denotes the ratios $\varepsilon_{356,\text{loose}}/\varepsilon_{374,\text{loose}}$ or $\varepsilon_{350,\text{loose}}/\varepsilon_{374,\text{loose}}$ of the respective salts.

The equation giving K is based on the following assumptions. (i) The extinction coefficients of the two types of pairs at their respective maxima are equal at all pressures. (ii) The shape of the absorption curve of the loose pairs is independent of pressure and of the nature of cation (whether Li^+ or Na^+). (iii) The absorption curves of the tight pairs derived from the lithium or sodium salts are identical in shape but one is displaced with respect to the other by 6 nm. Moreover, their shape is again assumed not to be affected by pressure. It follows then that r_1 and r_2 are also independent of pressure. A critical examination of these assumptions is given in the appendix.

TABLE 2.—FLUORENYL LITHIUM IN THF AT ~22°C

expt.	pressure atm	O.D. (350)	O.D. (374)	R	K
1	1	0.658	0.988	1.502	2.7
2	1	0.833	1.281	1.538	2.8
3	1	0.818	1.243	1.520	2.7
4	1	0.290	0.431	1.486	2.6
			average	1.509	2.7
1	940	0.617	1.225	1.985	4.9
2	940	0.812	1.679	2.068	5.5
3	940	0.785	1.574	2.005	5.0
4	940	0.288	0.571	1.983	4.9
			average	2.010	5.1
1	1920	0.598	1.423	2.380	8.7
2	1920	0.813	1.986	2.443	9.6
3	1920	0.770	1.886	2.450	9.8
4	1920	0.269	0.638	2.372	8.6
			average	2.406	9.2
1	2920	0.595	1.575	2.647	14.2
2	2920	0.801	2.19	2.734	17.3
3	2920	0.751	2.08	2.770	18.9
4	2920	0.265	0.715	2.698	15.8
			average	2.712	16.5
1	3900	0.578	1.646	2.848	23
2	3900	0.794	2.35	2.960	35
3	3900	0.734	2.19	2.984	38
4	3900	0.261	0.765	2.961	31
			average	2.938	32
3	4900	0.719	2.28	3.17	—
4	4900	0.258	0.793	3.07	—

O.D. corrected for the solvent absorption at the appropriate pressure.

The absorption curve of the sodium salt at 1 atm is assumed to represent the spectrum of the pure tight-pairs. From it we determined r_1 to be 0.24 for the sodium salt and 0.10 for the lithium salt (the latter is given by O.D.$_{380}$/O.D.$_{356}$). The validity of these results was confirmed by determining the spectrum of sodium fluorenyl in a flat quartz cell (optical path ~0.01 cm) attached to the storage ampoule. For example, O.D.$_{374}$/O.D.$_{356}$ = 0.242 in the flat cell while the average of 4 experiments performed in the pressure vessel led to the ratio 0.238 (see table 1). It is assumed that the lithium salt at 4900 atm forms only loose pairs. From its absorption curve (see fig. 3) r_2 is calculated to be 0.35 and 0.31 for the sodium and lithium salts, respectively.

The plots of log K against P are shown in fig. 4. Their initial slopes give ΔV of -24.4 ml/mol for the sodium salt and -15.6 ml/mol for lithium fluorenyl.

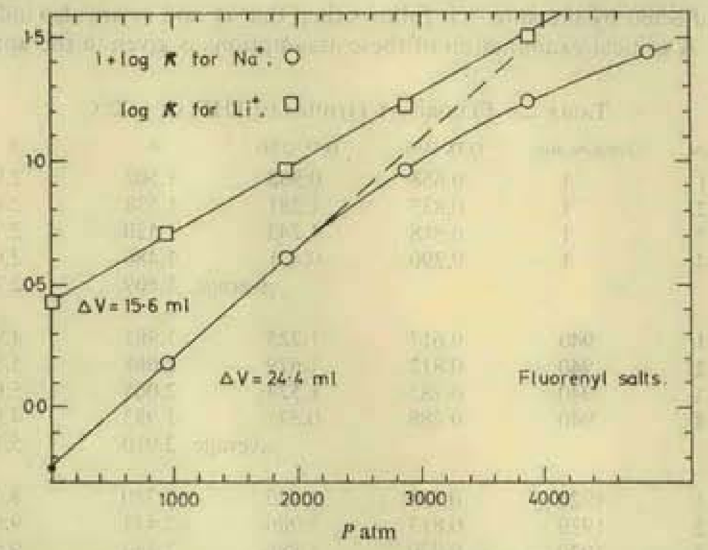

FIG. 4.—Plots of log K against pressure for lithium and sodium fluorenyls in THF at ~22°C. K is the equilibrium constant of the conversion of a tight ion-pair into a loose one.

DISCUSSION

We have established that the conversion of tight ion-pairs into loose ones decreases the volume of the system. This result resembles the phenomenon of electrostriction viz., as a tight pair is transformed into a loose one more solvent molecules are bound to it and this accounts for the observed contraction of volume.

The magnitude of ΔV is related to the number of solvent molecules which become attached to the loose pair during its formation. The solvent molecules are mainly clustered around the cation and our results indicate that the formation of the loose sodium salt binds more THF molecules ($\Delta V = -24.4$ ml/mol) than the formation of the lithium pair ($\Delta V = -15.6$ ml/mol). Apparently, the degree of solvation of the *tight* lithium pair is greater than that of the sodium one, and consequently the further gain in solvation arising from the formation of the loose pairs is larger for the latter than the former. Judging from their mobility [4] the free Na^+ and Li^+ cations are equally bulky in THF.

Freezing of solvent molecules around loose ion-pairs accounts also for the decrease in the entropy of the system accompanying the process; tight ion-pairs→loose ion-pairs. The relevant ΔS were -33 and -22 cal/mol K for sodium and lithium fluorenyls, respectively, in THF.[1, 5] The correlation of ΔS with ΔV is remarkable—both increase by about 50 % as sodium is substituted for lithium. Assuming that the binding of 1 mol of solvent decreases its (mainly translational) entropy by ~11 cal/mol K, we conclude that the compression arising from packing of 1 mol of THF into the solvation shells of the loose pairs contracts the volume of the system by about 8 ml, i.e., by ~10 % of its molar volume. Our data, given in table 3, show that the volume of THF decreases by about 10 % at 2000 atm.

Inspection of fig. 4 reveals that the plot of log *K* against *P* for sodium fluorenyl in THF is curved; ΔV is, therefore, a function of pressure, slightly decreasing with its increase. The observed curvature seems to be real, although the deviations from linearity are within the experimental uncertainties. The decrease of ΔV with pressure might be expected—the compression of solvent molecules around the ions being less significant, as the bulk of the liquid is compressed. The curvature could not be observed for the lithium salt because the relevant *K* could not be accurately determined at higher pressures.

TABLE 3.—COMPRESSION OF THF AT ~22°C

P atm	% volume compression	relative O.D. ($\lambda_{\max}$ tight)+ O.D. ($\lambda_{\max}$ loose) corrected for the compression
1	0.0	1.00
940	6.2	1.11
1920	10.1	1.20
2920	12.8	1.34
3900	15.1	1.47
4900	extr. ~17.4	~1.58

Finally, we note the substantial increase of the linear extinction coefficients of the ion-pairs at higher pressures. The data collected in table 3 show that the sum of the optical densities at both $\lambda_{\max}$ increases by about 60 % (after being corrected for the volume contraction) as the pressure rises from 1 to about 5000 atm. The partial destruction of fluorenyl carbanions by glycerol, which leaked at higher pressures into the cell, makes the determination of the pressure dependence of the O.D. difficult. We believe that the leakage was negligible in expt. 2 given in table 1, and, at lower pressures, in expt. 2 and 3 given in table 2. Apparently, the absorption curves become sharper at higher pressure, presumably because the rotation and the soft vibrations of the pairs are impeded by the compression of the solvent.

APPENDIX

The equilibrium constants *K* are calculated from the experimentally determined *R* in conjunction with the auxiliary constants r_1 and r_2. Fortunately, the numerical values of *K* are not greatly affected by the values of r_1 and r_2 if *R* is substantially greater than r_1 and smaller than $1/r_2$. The most reliable values of *K* are obtained in this range of *R*, e.g., in the experiments involving sodium fluorenyl (see table 1).

Under conditions when both types of pairs co-exist, the r_1 and r_2 values cannot be obtained directly. Our choice may be criticised, e.g., one may argue that r_1 and r_2 decrease with pressure because the absorption curves become sharper. However, at increasing pressure the absorption peaks come closer together and this should increase the r_1 and r_2 values. It seems, therefore, that the assumption of constant, pressure-independent r_1 and r_2 may be valid.

Unfortunately, previous workers did not give their procedure to determine r_1 and r_2 and their temperature dependence. In a private communication [6] they confirmed our claims, i.e., at 25°C and 1 atm pressure both ion-pairs have the same extinction coefficients, $r_1 = 0.24$ for the sodium salt and 0.11 (compared with our 0.10) for the lithium salt. They found, however, that on lowering the temperature $\varepsilon_{\text{loose}}/\varepsilon_{\text{tight}}$ increases and r_1 and r_2 decrease, the latter diminishing more than the former. These conclusions were obtained from studies of the caesium salt in THF (only tight pairs are present in such a solution) and the lithium salt in DME (only loose pairs appear in the latter system). It is assumed then that the numerical results apply to the investigated systems—a plausible but not necessarily a correct procedure.

In spite of these difficulties, extrapolation to 1 atm gives a value of K for sodium fluorenyl at ~25°C which is identical with that obtained by extrapolation to 25°C, of the previously reported data [1] pertaining to lower temperatures (i.e., $K_{25^\circ,\ 1\mathrm{atm}} \sim 0.058$). Some discrepancy is found, however, for the lithium salt (our $K = 2.7$, reported 4.6).

The equation for K is modified if $\varepsilon_{\mathrm{loose}}/\varepsilon_{\mathrm{tight}} \neq 1$. Denoting this ratio by γ we find

$$K = (R - r_1)/(\gamma - Rr_2).$$

It is possible that our r_2 is too small, because it was determined from the spectrum of lithium fluorenyl recorded at the highest pressure. This may account for our low value of K for the lithium salt at 1 atm. At higher pressures the error is probably partly compensated by γ being larger than 1.

Finally, we have checked that any reasonable changes of r_1 and r_2 have negligible effect upon the final values of ΔV for the sodium salt, although the results obtained for the lithium salt are less certain.

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