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REACTIONS IN SOLUTIONS UNDER PRESSURE

L. VOLUME CHANGE DURING THE SOLVENT SEPARATION OF THE SODIUM NAPHTHALENIDE TIGHT ION PAIR IN TETRAHYDROFURAN *

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Summary

The effect of pressure on the equilibrium constant for the process relating the tight and loose ion pairs of sodium naphthalenide in THF has been measured over a range of 600 bars. From the effect, the volume change has been calculated: the loose pairs occupy 15 cm^3/mol less space. This reinforces our earlier conclusion that the electrostriction effects accompanying ionic processes in non-polar solvents are much larger than in polar media, as implied by the Drude—Nernst equation.

Introduction

It is well known [1] that ionization in solution (unlike homolytic fission) is characterized by a volume decrease: ΔV is negative. This decrease is largely the result of the polarization and attraction of surrounding solvent molecules by the ions (electrostriction). In ionic equilibria, ΔV can be determined from density measurements extrapolated to infinite dilution if stable solutions of the ions and of the neutral species are available; alternatively, it can be calculated from the effect of pressure on the equilibrium constant via the relation $\Delta V = -RT\partial \ln K/\partial p$. Both methods have been used for a number of weak acids in water; ΔV is generally found to be —10 to —15 cm^3/mol, which corresponds to an increase in K by roughly 50% for every thousand atmospheres. The dissociation of some ion pairs in water has also been studied at high pressure; the ΔV values for the $MnSO_4$ and $MgSO_4$ pairs are both about —7 cm^3/mol [2]. Similar considerations govern the volume changes that accompany the partial ionization

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* Dedicated to Professor Herbert C. Brown, in recognition of his contributions to chemistry.

accomplished as the transition state is reached in solvolytic processes; one is then dependent on the effect of pressure on the rate constant and the relation $\Delta V^* = -RT\partial \ln k/\partial p$. For S_N1 hydrolyses, the activation volumes are usually somewhat smaller than the ionization [3] volumes characterizing weak acids since charge separation is incomplete in the transition state.

The electrostriction phenomenon is described to a first approximation by the Drude—Nernst equation $\Delta V = -(q^2/2rD^2)\partial D/\partial p$. Both the q (charge) and r (radius) dependences of ΔV have been confirmed at least qualitatively; little is known, however, about solvent effects (D is the dielectric constant). Solvolysis reactions generally seem to be accelerated more by pressure if they are carried out in solvents such as alcohol or aqueous acetone than in pure water, but less is known of the large pressure effects to be expected for ionization in nonpolar solvents. There have been reports of such large effects of pressure on the solvent separation of the tight fluorene—lithium ion pairs in tetrahydrofuran; however, although the experimental data obtained by two groups have agreed closely, the corresponding volume changes deduced from these data have diverged rather widely [3—5], at least partly because of a large and unanticipated pressure sensitivity of the UV spectra of the two types of ion pairs themselves.

Accordingly, we have sought information by means of another technique, namely ESR. Although this approach turned out to be experimentally much more difficult, the system studied (the sodium-naphthalenide ion pair in tetrahydrofuran) is much more tractable in that the sodium coupling in the loose pair is zero [6], and in that we are not concerned with intensities in the evaluation so that no corrections for the compressibility of the solutions are required.

Experimental

Materials. Naphthalene was purified by recrystallization from ethanol followed by vacuum sublimation. Sodium (J.T. Baker) was melted under high vacuum and loaded into 2 mm glass capillary tubing for storage; pieces of 15 mm length were broken off as needed and introduced into the vacuum line. Tetrahydrofuran (THF; Fisher Scientific) was refluxed over sodium—potassium alloy [7] for 24 h and distilled. A center fraction of the distillate was degassed by means of several freeze-thaw cycles under high vacuum and transferred to a storage bulb containing additional alloy and a few naphthalene crystals. For storage, the THF was vacuum transferred to a smaller bulb again containing some alloy and naphthalene crystals. After the green color had formed, the solution was degassed three more times before use. The mercury was triply distilled. Since it was found still to contain a component able to discolor the radical anion solution, it was introduced into a storage bulb (part I, Fig. 1) which was then evacuated; 2 *M* THF solution of the radical anion was introduced by syringe through the system. The apparatus was then evacuated, the constriction above the bulb was "washed" with THF (by external cooling with a cotton swab soaked with liquid nitrogen), the liquids were frozen and the seal-off was completed. The mercury was usable after 24 h of standing and occasional swirling. The break-off seals were charged with mercury and some of the THF solution, the constrictions were washed, the contents frozen, and the tubes sealed off.

Preparation of radical anion samples. The apparatus for the preparation of radi-

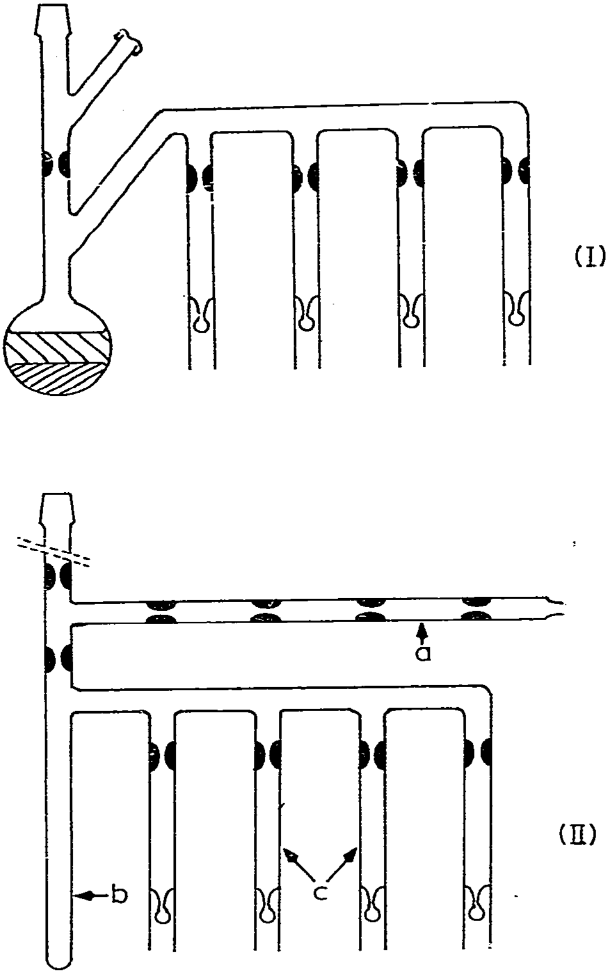

Fig. 1.

cal anion aliquots is shown in Fig. 1, part II. A 15 mm length of sodium in the 2 mm capillary is placed into the end of tube "a", which is then sealed. Approximately 20 mg of purified naphthalene is placed in "b". The assembly is evacuated to about 10^{-6} torr (this vacuum must be maintained throughout); adsorbed gas is driven off by heating with a soft blue flame. The sodium is then gently heated until it melts and flows out of the capillary; this is accompanied by the escape of trapped gas. After further evacuation, the sodium is heated until it vaporizes and condenses as a mirror into the next section. The first section is then sealed off and removed. At this point, THF ($\sim$12 ml) is distilled into "b", degassed once and frozen. Thereafter, the sodium mirror is transferred into successively further sections, each previous one being sealed off in turn, until a bright mirror obtains in the last section of "a". The assembly is then sealed off just below the ground glass joint and removed from the vacuum line. The THF solution is then permitted to thaw, and come into contact with the sodium mirror. Production of the green color of sodium naphthalenide normally commences within a few seconds. The reaction is continued for a half hour; meanwhile, "b" is "washed" so as to consume all of the parent hydrocarbon. No significant amounts of dianion form under our conditions. After appropriate washing, "a" is removed altogether. Aliquots of 3 cc solution are transferred to the break-off seal tubes "c" and frozen there; these tubes are then sealed off in the usual way. The contents are not allowed to thaw until the sealed glass has cooled; the thawing must be done slowly to minimize breakage.

ESR spectra. The ESR sample tubes themselves were made by a process of gathering the glass of 5 mm/0.25 mm Pyrex capillary tube to create a bulge of about 12 mm diameter. This bulge was sliced in half and ground to a flange. The tube is bent to provide a U-trap as shown in Fig. 2, annealed overnight, washed with 5% hydrofluoric acid, rinsed, dried, sealed at the open end, and annealed again. The filling apparatus is prepared by attaching the sample tubes with radi-

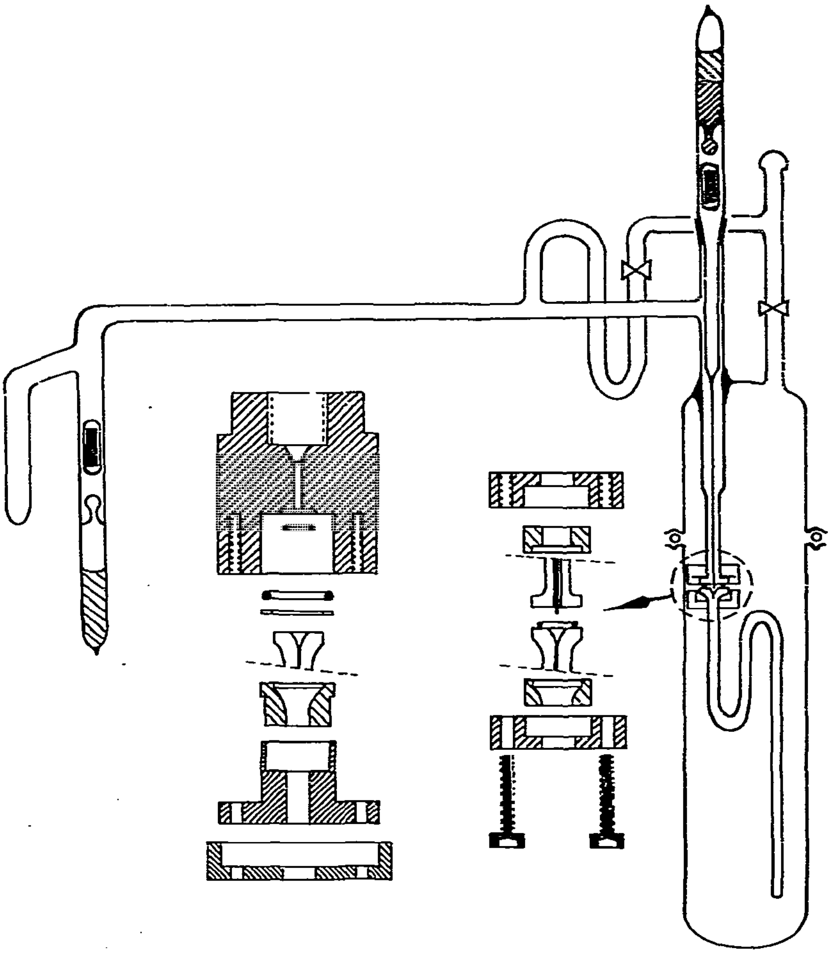

Fig. 2.

cal anion solution and the mercury, as shown in Fig. 2; glass-covered magnets are enclosed and secured with an external spin-bar held in place with a rubber band. All parts of the apparatus should be cleaned by rinses with distilled water and freshly distilled THF before use. Before tightening the screws of the flange assembly, an indium gasket, made by wrapping four turns of 0.010" indium wire around a 6 mm glass tube, is centered on the sample tube flange face, and the two faces are pressed together. The entire apparatus is evacuated overnight; this is necessary because of the several small passages of the apparatus.

To fill the sample tube, both stopcocks to the apparatus are closed, and the latter is removed from the vacuum line. The sodium naphthalenide break-seal is then broken and a few drops of the solution are transferred to the side arm of the filling apparatus. All of the THF is then distilled into this, thus producing a more dilute, pale green solution. This solution is used to wash the interior of the apparatus, and ESR sample tube; this is done by tilting the apparatus, forcing the solution into the ESR sample tube by applying hand heat to the solution. Before the solution reaches the end of the ESR sample tube, the sample is allowed to run out again by turning the apparatus upside down; this washing is done to remove any surface impurities on the wall of the ESR sample tube. The solution is then gathered back into the side arm and diluted again by a factor of ten or so; this solution is used again to wash the ESR sample tube. This operation is repeated once again and then the ESR sample is filled completely. The mercury break-seal is broken and the mercury allowed to seal off the ESR sample tube.

The mercury dropping assembly is removed, the vacuum is released, the apparatus disassembled, and the ESR sample tube is removed. The latter is immediately topped with a drop of white mineral oil. The tube is then fitted with the high pressure coupling flange, inserted in the ESR probe and connected to the high pressure generating equipment, similar to that used previously [3]. The pressure could be kept constant to about 10 psi during a run, and the temperature to a few tenths of a degree.

The spectra are recorded with a Varian E-Line E-12 spectrometer with 100 kHz modulation. Cavity access was bored to 13.4 mm and cavity width expanded with rubber spacers to match. This is done in order to accommodate a dewar vessel of 6 mm I.D. and 13 mm nominal O.D. especially made for the ESR sample tubes. The large mass of Pyrex inserted in the cavity increases its apparent length and decreases the resonant frequency of the cavity below the minimum klystrom frequency, necessitating the insertion of a silver plated stainless steel faceplate with an 0.3 mm rectangular elevation into the cavity to regain tuning range. For temperature control, two nitrogen streams are mixed; one which has been heated to slightly above room temperature and one which has been cooled either in an ice bath, or a dry ice/acetone bath for lower temperatures. Flow control is provided by needle valves. Although equilibration is slow (ca. 15—20 min), the temperature remains stable for extended periods. Temperature is determined and monitored by a copper-constantan thermocouple inserted into the sample dewar to a point just above where its presence perturbs cavity turning. Spectrometer settings need to be determined and optimized for each sample. At each temperature, spectra are first recorded at one atmosphere and then at 2000 psi increments up to 8000 psi, thereafter, at 7000, 5000, and so on back down to atmospheric pressure. The ESR sample tubes can withstand at least

TABLE 1

VOLUME CHANGE FOR THE TIGHT-LOOSE PROCESS

Temperature (°C)	ΔV (cm^3/mol)	Corr. Coeff.
—7.0	—15.4	0.990
—4.0	—15.0	0.983
—2.5	—13.1	0.978
—1.9	—16.4	0.965
+1.0	—13.1	0.961
+3.0	—15.1	0.995

1 kbar, but not for prolonged periods. If the pressure is kept below 8000 psi, the entire *P/T* range recorded below can if desired, be scanned with a single sample.

Analysis. The spectra recorded at one atmosphere agreed with those reported in the literature [6]. The proton hyperfine coupling constants are not noticeably affected by pressure. The sodium splittings were measured from about five pairs of selected lines; agreement was usually within 0.2% (standard deviation). The equilibrium constant for the "tight ⇌ loose" ion-pair equilibrium is determined by the formula $K = a_{\text{tight}}/a_{\text{obs'd}} - 1$($a_{\text{loose}}$ equals zero) [6]. The ln K data did not systematically deviate from a linear pressure dependence in the range studied here, and hence ΔV was simply obtained as the slope.

Results and discussion

Table 1 shows the results compiled over the temperature range of —7 to +3° C. Below that temperature, line broadening under pressure * is such that the splittings could not be determined with sufficient accuracy, and above 3° C, K deviates too far from unity to reveal the pressure dependence very clearly (it ranges from 0.2 at 3° C to 0.3 at —7° C at one atmosphere). The conclusion is that the tight-loose process is accompanied by a volume change of —15 ± 1 cm^3/mol in THF. This result agrees well with that obtained by Szwarc et al. [4,5], for sodium fluorenide in THF (—16 cm^3/mol).

The temperature and pressure ranges available to us were not wide enough to show beyond any doubt that the sodium splittings of the ion-pairs themselves are independent of pressure; however, this is a very reasonable assumption since they are not sensitive to temperature [6], and since the volume change agrees so closely with that for the fluorenide pair.

These results may be compared with some available for the highly polar medium of water. The complete dissociation of monovalent pairs in water has a volume change associated with it estimated to be —1.8 cm^3/mol (one quarter of that of the bivalent pairs of $MnSO_4$ and $MgSO_4$); the mere loosening of a tight pair in THF causes a volume contraction an order of magnitude larger. We conclude that the use of a non-polar medium in charge separation processes indeed greatly magnifies the volume and entropy decreases as qualitatively predicted by the Born and Drude—Nernst equations, a conclusion which may well

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* This was also noted by Schindewolf in his study of the process equilibrating free electrons in ammonia and amide ion [8].

be of interest, among others, to mechanistic chemists concerned with questions of charge separation in transition states [9,10].

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