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STRUCTURE OF THE IONIC SPECIES IN ORGANOSODIUM COMPOUNDS DISSOLVED IN n-ELECTRON DONOR, LOW DIELECTRIC CONSTANT MEDIA*

J.M. ALVARIÑO

Departamento de Química-Física, Facultad de Ciencias, Universidad de Bilbao, Bilbao (Spain)

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Summary

The structure of the carbanion and the solvated sodium ion in n-donor, low dielectric constant solvents are discussed in the light of kinetic and conductometric measurements on the anionic polymerization of styrene. The noteworthy cation solvating ability of 1,2-dimethoxyethane against other ethereal solvents is enhanced.

Introduction

Organo-alkaline solutions, especially in solvents of low dielectric constant, often appear in the form of different kinds of ionic species. This can be proved by direct, absolute methods (spectrometry, conductometry, colligative properties) and manifests itself also in kinetic experiments involving such compounds in the indicated solvents.

In hydrocarbon solvents, it may even result in a total (or almost total) hiding of the ionic character, so leading to the formation of agglomerates. This is easier in the case of aliphatic hydrocarbon solutions of organolithium compounds, probably on account of the rather covalent nature of the carbon—lithium bond [1,2], but it also takes place with other counter-ions and in aromatic solvents [3]. In this case, however, the more ionic character of the carbon—alkali metal bond and the weak cation solvation ability of aromatic solvents (π-electron donors) lead to an enhanced breaking of the agglomerates.

The picture is rather different in n-electron donor solvents, such as ethers. No agglomerate needs to be formed, even if the dielectric constant of the medium does not differ from that of a hydrocarbon solvent, an evident indication of the specific interaction between ionic species and solvent molecule [4].

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* The experimental part of this work was performed at the Institut für physikalische Chemie, Universität Mainz, West Germany.

A nice confirmation of this is provided by the rather different mechanisms of the reaction of polystyrylsodium with styrene (i.e. the propagation step in the anionic polymerization of styrene with sodium as counter-ion) in benzene [3] and dioxane [5], two solvents with about the same dielectric constant. While in benzene, a π-electron donor solvent, most of the species seem to be dimerised ion-pairs, no such agglomerate is detected in dioxane. Instead, only ion-pairs of a tight character ("contact" ion-pairs) are present.

When the donor power and the dielectric constant of the ethereal solvent increase, not only free ions appear, but also loose, "solvent separated" ion-pairs can be directly (e.g. spectrophotometrically [6]) and/or indirectly (e.g. kinetically [7]) detected. The ionic dissociation may thus be assumed to take place from contact ion-pairs to free ions through intermediate solvent-separated ion-pairs [7].

In this paper, some kinetic and conductometric results involving polystyrylsodium in 1,2-dimethoxyethane (DME) are used to prove the good cation solvating ability of DME and the structure of the "living" carbanionic chain end, and to speculate about the structure of the cationic entity which migrates in an electric field formed by the sodium ion and the DME molecules coordinated by it.

Experimental

The flow technique, purification of the reactives, and other experimental details have been described elsewhere [7,8]. In conductometric experiments the flow tube was substituted by a flow conductivity cell [9]. Measurements were analysed according to Fuoss and Kraus [10]. SI units are used throughout.

Results and discussion

Conductometric measurements show the presence of free ions in the system, K_d being the overall measured dissociation constant. Kinetic experiments, on the other hand, also lead to a formal K_d. Figure 1 shows a van 't Hoff plot of the temperature variation of K_d. The fact that the conductometric and kinetic K_d's do not perfectly agree is irrelevant to our present purposes [4]. On the other hand, the curved shape of this plot as well as the S-shaped T^{-1} dependence of the observed propagation rate constant in the absence of free ions [7] is interpreted as being originated by a propagation reaction, proceeding via three different ionic species, according to the scheme:

$$\begin{array}{ccccc} \mathrm{I} & \xrightleftharpoons{K_{cs}} & \mathrm{II} & \xrightleftharpoons{K_d^{\star}} & \mathrm{III} + \mathrm{Na(DME)}_n^+ \\ +\mathrm{M} \downarrow k_{(\pm)c} & & +\mathrm{M} \downarrow k_{(\pm)s} & & +\mathrm{M} \downarrow k_{(-)} \end{array}$$

where M stands for monomer (styrene), I for contact ion-pair, II for solvent-separated ion-pair and III for free carbanion, while $k_{(\pm)c}$, $k_{(\pm)s}$ and $k_{(-)}$ are the individual first order propagation rate constants of I, II and III, respectively, and K_{cs} and $K_d^{\star}$ the constants for the corresponding equilibria. Both constants are formally related to K_d by

$$K_d = K_d^{\star} K_{cs} (1 + K_{cs})^{-1} \qquad (1)$$

The same kinetic scheme applies to other ethereal solvents [11].

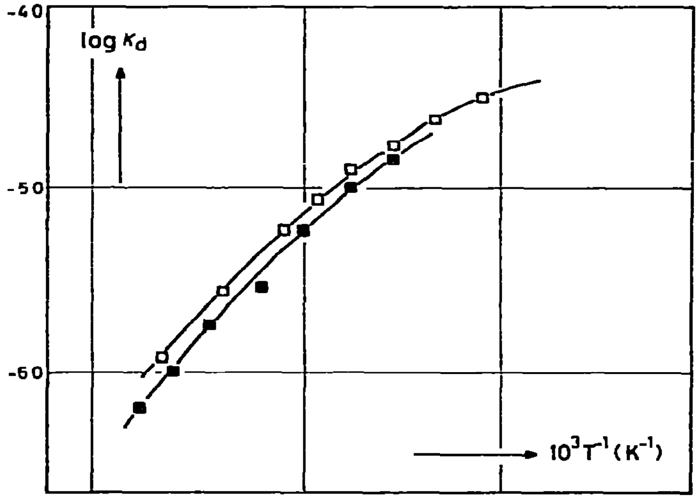

Fig. 1. Temperature-dependence of the overall dissociation constant, K_d, of polystyrylsodium in DME. Open points, conductometric results. Filled points, kinetic results.

From a kinetic analysis, all the rate constants can be derived [7]. We shall focus our attention on $k_{(-)}$, whose temperature dependence in DME [7], tetrahydrofuran (THF) [12] and tetrahydropyran (THP) [13] is plotted in Fig. 2.

The fact that the same straight line connects all points, irrespective of solvent, seems to imply that no free carbanion— solvent molecule interaction exists, i.e. the carbanionic "living" chain ends would indeed be naked ions. This point will be discussed in further detail in a later publication [4]. These conclusions seem, however, to be in an open contradiction with experiments by Ise et al. [14], where the electric field effect on the anionic polymerization of

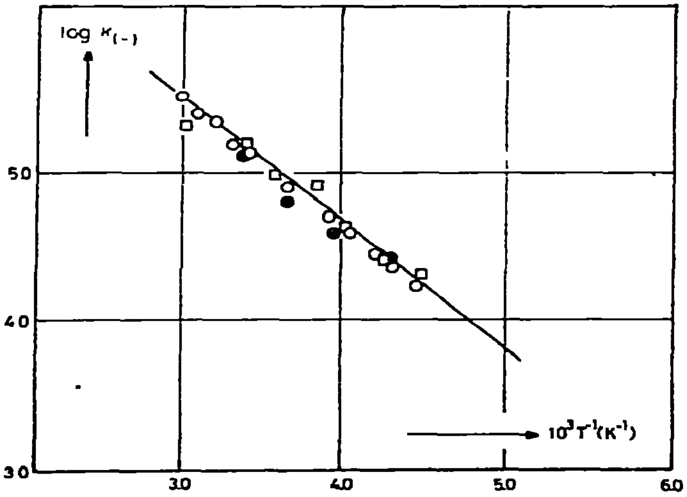

Fig. 2. Arrhenius plot of the carbanion rate constant $k_{(-)}$ in DME (squares), THF (open circles) and THP (filled circles).

TABLE 1

THERMODYNAMIC PARAMETERS FOR THE EQUILIBRIA I ⇌ II AND II ⇌ III IN DIFFERENT SOLVENTS. MEAN VALUES FROM KINETIC AND CONDUCTANCE MEASUREMENTS

Solvent	ΔH_{cs}	$\Delta H_d^{\ddagger}$	ΔS_{cs}	$\Delta S_d^{\ddagger}$
	(kJ mol^{-1})		(J mol^{-1} K^{-1})	
DME	−21.3	−4.6	− 93.6	−108
THF	−27.6	+0.8	−134	− 96
THP	−12.5	+1.2	−117	−113

styrene in ethereal solvents is investigated. They find an increase in the overall propagation rate, which is attributed to a stepwise desolvation of the "free" carbanion. If this is so, then the latter must be solvated in the absence of an electric field and it would be necessary to explain how carbanions solvated by different kinds of ether molecules behave similarly with respect to monomer addition. On the other hand, this would not be unthinkable. One has to be aware of the fact that contact ion-pairs and solvent separated ion-pairs also display, in different ethereal solvents, very similar reactivities [7]. So, why could solvated carbanions not bear the same rate constant in different solvents?

We shall now direct our attention to the equilibria I ⇌ II and II ⇌ III leaving aside any other purely kinetic interpretation. K_d may, indeed, be separated in its contributions K_{cs} and $K_d^{\ddagger}$ according to Böhm and Schulz [15], and eqn. 1. This gives us the thermodynamic parameters which are collected in Table 1, together with results in THF [12] and THP [13].

From Table 1 some facts are evident. We first notice that for every solvent ΔS_{cs} and $\Delta S_d^{\ddagger}$ are both negative, pointing to a loss in configurational entropy on going from I to II, and from II to III. This means that a number of solvent molecules is fixed in the first and again in the second solvation sphere of the cation. The smaller value of $-\Delta S_{cs}$ in DME compared to other solvents has to do with the presence and adequate separation of two O atoms in that molecule, a point which will be discussed in greater detail in a later publication [4].

The fact that $-\Delta H_d^{\ddagger}$ is about five times larger in DME than in THF or THP points also to the more powerful solvating ability of that solvent.

Another point related to the I ⇌ II equilibrium deserves attention. Table 2 shows a comparison of the entropy and enthalpy parameters of that equilibrium,

TABLE 2

THERMODYNAMIC PARAMETERS FOR THE I ⇌ II EQUILIBRIUM IN THF FOR DIFFERENT ORGANOSODIUM COMPOUNDS

Organic moiety	$-\Delta H_{cs}$ (kJ mol^{-1})	$-\Delta S_{cs}$ (kJ mol^{-1} K^{-1})	Method[a]	Ref.
Oligomeric α-methylstyryl	27.2	136	s	16
Polystyryl	27.6	134	k,c	12
Naphthalene	29.9	132	c	17,18
Biphenyl	31.4	125	c	17,18
Fluorenyl	31.8	138	s	6
Anthracene	32.8	137	c	17,18

[a] s, spectroscopy; c, conductivity; k, kinetics.

for a series of carbanionic and radical-carbanionic sodium salts in THF, as determined by direct (spectroscopy, conductivity) or indirect (kinetics) methods. The compounds are listed in order of increasing $-\Delta H_{cs}$. Note that the first two members of the series are carbanion-sodium, while the others are radical carbanion-sodium compounds. The differences are, however, so small that they can scarcely be taken as conclusive of, for example, a weaker solvation of the Na^+ ion in the carbanionic compounds by THF molecules. We arrive rather at the conclusion that, within the limits of error, ΔH_{cs} and ΔS_{cs} are the same, irrespective of the organic moiety of the listed compounds. This proves that the position of the equilibrium is decisively controlled by the Na^+ ion—solvent molecule interaction, i.e. that the entity formed by the sodium ion and its coordinated solvent molecules (first solvation sphere) constitute a kinetic and thermodynamic well-defined entity.

Conductivity studies on $NaBPh_4$ [16] show the hydrodynamic radius (Stokes radius) of the sodium ion in DME to be ≈3.4 Å. This dimension corresponds to the kinetic entity moving in an electric field. It must also correspond to the well-defined entity formed by the cation and its first solvation sphere, i.e. the positive entity of the solvent-separated ion-pair rather than the solvated free cation. The small value of $-\Delta H_d^{*}$ points indeed to a weak fixation of the DME molecules in the second solvation sphere. These molecules would then not be able to keep firmly on the positive entity when an electric field is applied to the system [19].

A careful inspection of molecular models shows that a 3.4 Å radius is compatible with a tetrahedral structure, as indicated in Fig. 3c. Two DME molecules are specifically coordinated by a sodium ion, giving rise to the kinetic entity $[Na(DME)_2^+]$.

Figure 3a represents, in a Newman projection, the *trans* state of the central C—C bond of a DME molecule. This is, on steric and electrostatic energy grounds, the most probable state of that bond, corresponding to the greatest separation of the lone electron pairs of the oxygen atoms. The presence of Na^+ ions from an electrolyte probably causes the solvent molecules which will form the kinetic entity to reorientate themselves. The gain in solvation energy due to the Na^+ ion is sufficient to overcome the energy barrier which separates the *trans* and the *gauche* state in the C—C central bond of the DME molecule. The Na^+ ion thus exerts a similar "atractive" effect to that which permits the crystalline

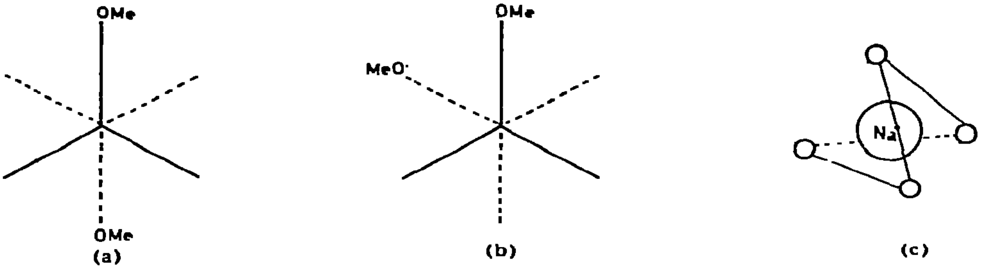

Fig. 3. Most probable conformations of (a) pure DME molecule (C—C central bond in *anti* state); (b) DME molecule specifically coordinated by a Na^+ ion (C—C central bond in *gauche* state, dotted line links imaginarily both O atoms), and (c) kinetic entity $[Na(DME)_2^+]$ (dotted line links imaginarily O atoms from the same DME molecule).

isotactic poly(vinyl alcohol) to be in the fully-extended poly(ethylene) type conformation in spite of the steric hindrance of the hydroxyl groups [20].

We arrive in this way at a compromise between the situation sketched in Fig. 3a and the polarization of the solvent molecule by the powerful electric field generated by the sodium ion. Under these conditions a *gauche* state for the central C—C bond would probably be preferred (see Fig. 3b). Two such molecules would then become coordinated by a cation (Fig. 3c), the four oxygen atoms being then situated on the vertices of a tetrahedron with the sodium ion at the center.

However, the Stokes radii being generally underestimated for ions less than 5 Å, the number of oxygen atoms could be greater than 4. For example, six O atoms could fit in an octahedral arrangement or eight O atoms in a cubic body-centered arrangement around the Na^+ ion, giving rise in this way to kinetic entities consisting of a sodium ion and 3 or 4 DME molecules [21]. With the data at hand one can only make speculations in this connection. Anyway, one has to bear in mind the similar problem of the ionic coordination numbers in water, where a comparable uncertainty exists, different physical methods (ultrasonic waves, compressibility, ionic mobility) leading to different hydration numbers [19].

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