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Abstract

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Equilibria in the Reactions of Sodium and Lithium with Diphenyl and Naphthalene in Electron-Donor Solvents

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The present work considers equilibria in the reactions of alkali metals (Me) with solutions of aromatic hydrocarbons (Ar). These equilibria are interrelated, since they all depend strongly on the conditions of solvation of the metal cation (Me^+) by the electron-donor solvent Sl ($Me + Sl \rightleftarrows Me^+_{Sl}$). In the literature there are almost no thermodynamic data on the equilibria of formation of anion-radicals ([1]) (a.r., $Ar^{\cdot -}$):

$$Ar + Me \rightleftarrows Ar^{\cdot -} + Me^+, \tag{1}$$

and, in order to fill this gap, we measured the equilibrium constants (K) of the reactions of diphenyl (Dph) and naphthalene (Nph) with Na in a number of solvents. The energy balance of reaction (1) is expressed by an equation ([2,3]) into which enter, with a minus sign, the heats of sublimation ($-L$) and the ionization potential ($-I$) of the metal, and with the opposite sign—the electron affinity of the hydrocarbon molecule (ε), the heats of solvation of the ions (S_{Me^+} and S_{Ar^-}, with $S_{Me^+} \gg S_{Ar^-}$) and the energy of Coulomb interaction (Q).

The state of equilibrium (1) is very sensitive to the structure of the solvent molecules, which determines the probability of formation and the strength of the coordination bond between the electron-donor atom (or atoms) of the solvent and the ion Me^+. At the same time, along with the electron-donor properties of the solvent (its strength as a base), an important role is played by a steric factor ([4]), for example, the ratio of the geometric parameters of the Me^+ ion and the Sl molecules, shielding of electron-donor atoms in the latter, etc.

The formation of a more stable bond of solvent molecules with the Me^+ ion corresponds to a greater solvation energy, while the ordering of molecules that occurs in this process is accompanied by a greater loss of entropy. Therefore the change in the free energy of the reaction ($\Delta F = \Delta H - T\Delta S$) is characterized by the presence of a compensation effect ([5]).

Solvation of ions lowers their mobility and the degree of association ($Ar^-_{Sl} + Me^+_{Sl} \rightleftarrows Ar^-_{Sl} \cdot Me^+_{Sl}$). If the influence of the latter effect on the specific electrical conductivity (χ) predominates, then there should be a correspondence

between the value of χ and the values of the thermodynamic parameters of reaction (1) in the same solvents with similar dielectric constants (DC), which is what we found in measurements of the electrical conductivity of NaNph solutions.

Along with the equilibrium of formation of a.r., an equilibrium of their disproportionation is possible, in which dianions (d.a., Ar^{2-}) arise:

$$2Ar^{\cdot-} \rightleftarrows Ar^{2-} + Ar. \qquad (2)$$

It is assumed ([6]) that equilibrium (2) shifts to the right if association of the d.a. with two cations
($Ar^{2-}_{Sl} + 2Me^{+}_{Sl} \rightleftarrows Ar^{2-}_{Sl} \cdot 2Me^{+}_{Sl}$) compensates the energetically unfavorable stretching of two electrons in the d.a. Indeed, such a shift of the equilibrium is observed upon decreasing (to known limits) the solvating ability of the solvent with respect to Me^{+}, which promotes the formation of more stable ionic aggre-

solvates. In solvents with different solvating ability, changing the metal is reflected differently in ion association, since the latter depends on the strength of the interionic interaction and on the solvation energy, which are functions of the cation radius. An increase in the radius should shift equilibrium (2) to the right in well-solvating solvents and to the left in those solvents where the solvate shell does not prevent close approach of the radical anion with two cations. In discussing the likelihood of reaction (2), one must also keep in mind the value of ε and the spatial configuration of the radical anion. The influence of the solvent and metal on radical-anion formation is illustrated below using naphthalene reactions as an example.

1. Enthalpy and entropy of the sodium diphenyl formation reaction

Methods for carrying out the reactions and spectrophotometric measurements improved in comparison with (7) were used. With each solvent, 3-4 series of experiments were performed, with equilibrium approached from both sides. $K_T = D_T/(D - D_T)$, where D_T is the optical density of the solution at $\lambda =$ 625 m and T° K ($\pm 0.1^{\circ}$), and D is the optical density corresponding to complete conversion into the radical anion of the given concentration of Dph with a large excess of Na taken in the form of a mirror. The accuracy of determining K_T is 5-10%. The measurements were performed in the temperature interval from T_1 to T_2° K. The enthalpy and entropy of reaction (1) in each of the solvents were calculated by the least-squares method from the equation

$$\ln K_T = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}.$$

Table 1 gives the average values of $K_{273^{\circ}}$, ΔH, ΔS, and their average deviations for six solvents. In the case of DEE* the dependence of $\ln K$ on $1/T$ is different

in different temperature intervals, apparently owing to a change in the character of solvation of the cation. Therefore two values of ΔH and ΔS are given. The data for the other solvents are located in different parts of Table 1, depending on the temperature region in which the measurements were carried out.

Table 1

Thermodynamic parameters of the Na Dph formation reaction

Solvent	T_1	T_2	K_{273°	ΔH, kcal/mol	ΔS, e.u./mol	$\Delta\nu_{OD}$, cm^{-1}
$CH_3OCH_2CH_2OC_2H_5$ (MEE)	273	318	7.2 ± 0.8	-17.4 ± 0.5	-60 ± 2	95
$CH_3OCH(CH_3)CH_2OCH_3$ (1,2-DMP)	273	318	4.6 ± 0.2	-16.5 ± 0.7	-58 ± 3	96
Tetrahydrofuran (THF)	263	318	1.4 ± 0.1	-11.2 ± 0.5	-40 ± 2	115
$C_2H_5OCH_2CH_2OC_2H_5$ (DEE)	258	293	0.2 ± 0.05	-9.6 ± 0.4	-38 ± 2	98
$C_2H_5OCH_2CH_2OC_2H_5$ (DEE)	248	258	–	-22 ± 1	-86 ± 4	–
$CH_3OCH_2CH_2OCH_3$ (1,3-DMP)	228	273	0.04 ± 0.005	-15.5 ± 0.3	-63 ± 1	100
Tetrapropylporphyrin (TPP)	258	263	0.06 ± 0.005	-6.8 ± 0.2	-31 ± 1	112

The equilibrium of the reaction in 1,2-dimethoxyethane (DME) is completely shifted toward formation of the radical anion even at 50°C, i.e., $K_{DME} \gg K_{MEE}$. $\Delta\nu_{OD}$ is the frequency shift of the OD bond in the infrared spectrum of CH_3OD (8) as a result of formation of a hydrogen bridge with the ether oxygen. The value of $\Delta\nu_{OD}$ gives an idea of the strength of the solvent as a base. K, ΔH, and ΔS depend on the solvent, which indicates a large contribution of the heat of solvation S_{Na^+} to the energetics of the NaDph formation reaction and agrees with the above considerations concerning the cause of the compensation effect.

Judging from the values of $\Delta\nu_{OD}$, the change in solvation upon replacement in the DME molecule (for which $\Delta\nu_{OD} = 193$ cm^{-1}) of CH_3 groups by C_2H_5 cannot be attributed to a difference in solvent basicity. Rather, the indicated effect is caused by shielding of one (or both) oxygen atoms by freely rotating C_2H_5 groups. The conclusion about free rotation around all

* For abbreviations here and below, see Tables 1 and 2.

The presence of C–C and C–O bonds in ethylene glycol ethers follows from the agreement of the dipole moments calculated under this condition with those

determined experimentally ($\mu = 1.69 \pm 0.03$ D), together with E. N. Guryanova and I. P. Goldstein. The important role of the steric factor in the solvation of the Na^+ ion is also indicated by the changes in the values of ΔH and ΔS accompanying lengthening of the methylene bridge (on going from DME to 1,3-DMP) and introduction of CH_2 groups into the bridge (on going from DEM to 1,2-DMP). For the solvents compared, $\Delta\nu_{OD}$ values are very close.

2. Dependence of the equilibrium concentration of diphenyl anion-radicals on the counterion

The development of a method ([9]) for obtaining a metallic Li mirror enabled us to compare the concentrations of Dph anion-radicals in reactions with Li and with Na ([4]) (Table 2). The concentration corresponding to complete conversion of Ar to $Ar^{\cdot -}$ was taken as 100. Although the heat of sublimation and the ionization potential of Li are greater than for Na, the concentration of anion-radicals in the reaction with Li is usually higher (cf. ([3,10])). This is explained by the higher heat of solvation of Li^+ than of Na^+ and by an increase in the Coulomb term in the equation for the energy balance of the reaction with Li. The nonuniform dependence of the anion-radical concentration on Me in THF (Li > Na > K) and in DEE (K ≥ Li > Na) is a consequence of the specific interaction between the solvent and Me^+. If the counterions are Li^+ and Na^+, then the series of solvents arranged according to the magnitude of the equilibrium concentration of anion-radicals are not the same:

for Li^+: DME = THF = 1,3-DMP > TGP > DEE > DOL > DO
for Na^+: DME > THF > DEE ≥ TGP = DOL > 1,3-DMP ≥ DO

The sequence of solvents established by us for solvation of Na^+ is the same as that determined on the basis of changes in the values of E_T—the electron-transition energy for the principal absorption band in the absorption spectrum of sodium benzophenone ([11]) (see the last column of Table 2).

Table 2

Comparison of the solvating ability of solvents

Solvent	Li^+	Na^+	E_T, kcal/mol	Solvent	Li^+	Na^+	E_T, kcal/mol
DG[1]	100	100[7]	40.5	DOL[2]	10^6	10	–
DME	100	100[7]	40.9	1,3-DMP	100	6	–
THF	100	44	42.2	DO[3]	0	4	44.3
DEE	45	15	–	DE[4]	0	1	45.1
TGP	80	10	–	DMM[5]	0	0	45.3

[1] $CH_3OCH_2CH_2OCH_2CH_2OCH_3$. [2] 1,3-dioxolane. [3] 1,4-dioxane. [4] $(C_2H_5)_2O$.

[5] CH_3OCH_3. [6] Rapid decomposition occurs. [7] In a mixture with heptane (1:1 by volume), DG: 89; DME: 22.

3. Enthalpy and entropy of the reaction of sodium naphthalenide formation

Four series of measurements were carried out in DEE at temperatures from 273 to 318 K at λ 365 and 810 mμ.

	K_{273°	ΔH, kcal/mol	ΔS, e.u./mol
Sodium naphthalenide	10.0 ± 1.3	-12 ± 0.5	-40 ± 2
Sodium diphenyl	0.2 ± 0.05	-9.6 ± 0.3	-38 ± 2

Probably, the larger value of ΔH in the reaction of NaNph formation is explained by the higher electron affinity of Nph ([12]) and by the larger magnitude of the Coulomb term in the equation for the energy balance of the reaction. The latter can be concluded on the basis of measurements of the specific electrical conductivity of 0.002 M solutions of NaNph and NaDph in DME ($\chi = 1.6 \cdot 10^{-5}$ and $2.1 \cdot 10^{-5}$ ohm^{-1}·cm^{-1}). The values of ΔS for both reactions are practically the same, in agreement with the view that the anion-radical is solvated to a lesser degree than Me^+.

4. Association of ions in solutions of sodium naphthalene

The electrical conductivity was measured in a cell with smooth Pt electrodes. In Table 3, together with χ, the values of the viscosity (η, centipoises) and the DP of the solvents are given, as well as the values of the electrical conductivity corrected for viscosity ($\chi\eta$). From a comparison of the values of $\chi\eta$ it follows that the degree of ion association in NaNph solutions decreases in the same sequence (DEE > MEE > THF > DME > DG), which corresponds to an increase in the solvating power of the solvents with respect to the Na^+ ion (see Table 2). Data ([15,16]), obtained on the basis of measurements of the EPR spectra of NaNph solutions, indicate that, in agreement with our results, the degree of ion association decreases in the series TGP > THF > DME.

Table 3

Electrical conductivity of NaNph solutions
(0.004 mol/l)

	DG	DME	THF	MEE	DEE
$\chi_{25}10^6$	22	30	3.5	3	0.4
$\eta_{25}10^3$	9.9	4.2	4.7	5.1	6.0
$\chi\eta 10^9$	218	126	16.4	15.3	2.4

	DG	DME	THF	MEE	DEE
DP	5.8	5.5[1]	6.0[2]	–	5.1

[1] 6.8 ([14]). [2] 7.3 ([14]).

5. Equilibrium of formation of naphthalene dianions

In the numerous solvents studied by us ([4]), the reaction of Nph with Na always gave green solutions. The same solutions are obtained in the reaction of Nph with Li in DME or THF. If, however, the reaction is carried out in DEE or DO, the green color appears only at the first moment and then rapidly changes to red; moreover, the appearance of intense absorption in the region of 535 mμ is observed. When an excess of Nph is added to such a solution, decanted from a Li mirror, the 535 mμ peak disappears and the absorption at 365 and 810 mμ increases sharply. In ([17]) it was noted that, in the medium of DE and DMM, it is possible to add two Li atoms to Nph; the solution is colored red. Since in DME and THF the Me^+ ions are solvated considerably better than in DEE, DO, DE, and DMM (Table 2), we conclude that dianions are formed more readily in solvents with not too high a solvating power. The same conclusion was drawn in ([6]), where the concentration of the dianion of tetraphenylethylene increased in the sequence: DG < DME < THF < DO, DE. A comparison of our results with literature data ([6,18,19]) shows that the relationship between the equilibrium constant (2) and the radius of the counterion depends on the conditions of its solvation. In weakly solvating solvents the sequence is usually Li > Na (reaction of Nph in DEE, stilbene ([19]) in DE and 2-MeTHF), whereas for the reaction of tetraphenylethylene in THF ([18]) it was found: Cs > K > Na > Li.

Thus, the results of our work are in good agreement with the considerations set forth above concerning the role of cation solvation in equilibrium reactions of alkali metals with hydrocarbons.

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CITED LITERATURE

1. S. P. Solodovnikov, Dissertation, INEOS, 1962.

2. M. Szwarc, Makromol. Chem., **35**, 132 (1960).

3. A. A. Arest-Yakubovich, A. R. Tantmakher, S. S. Medvedev, Vysokomolek. soed., **3**, 1003 (1961).

4. A. I. Shatenshtein, E. S. Petrov et al., DAN, **151**, 353 (1963).

5. W. B. Person, J. Am. Chem. Soc., **84**, 536 (1962).

6. J. F. Garst et al., J. Am. Chem. Soc., **86**, 8257 (1964).

7. E. S. Petrov, E. A. Yakovleva, A. I. Shatenshtein, ZhOKh, **33**, 107 (1963).

8. I. M. Ginzburg, E. S. Petrov, A. I. Shatenshtein, ZhOKh, **34**, 2294 (1964).

9. E. S. Petrov, M. I. Belousova, A. I. Shatenshtein, ZhOKh, **34**, 2465 (1964).

10. E. A. Yakovleva, E. S. Petrov et al., DAN, **133**, 645 (1960).

11. J. F. Carst et al., J. Am. Chem. Soc., **86**, 412 (1964).

12. G. Briegleb, Angew. Chem., **76**, 326 (1964).

13. J. L. Down et al., J. Chem. Soc., **1959**, 3767.

14. G. Wittig, S. Stahnecker, Ann., **605**, 69 (1957).

15. R. L. Ward, S. J. Weissman, J. Am. Chem. Soc., **79**, 2086 (1957).

16. N. M. Atherton, S. J. Weissman, J. Am. Chem. Soc., **83**, 1330 (1961).

17. A. N. Pudovik, A. A. Muratova, Uch. Zap. Kazansk. univ., **113**, No. 8, 7 (1953).

18. A. G. Evans, B. Tabner, J. Chem. Soc., **1963**, 4613.

19. E. R. Zabolotny, J. F. Garst, J. Am. Chem. Soc., **86**, 1645 (1964).

Note: Figure translations are in progress. See original paper for figures.