# CHEMISTRY

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1963

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## Abstract

## Full Text

CHEMISTRY

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# THE INFLUENCE OF ETHER STRUCTURE ON THE SOLVATION EFFECT IN THE FORMATION OF SODIUM DIPHENYL AND SODIUM NAPHTHALENE

*(Presented by Academician V. A. Kargin, April 5, 1963)*

Scott and co-workers (⁀1) were the first to discover that the addition of sodium to diphenyl and naphthalene proceeds especially readily in a medium of 1,2-dimethoxyethane (DME). As was established later (⁀2), in these reactions the electron of the metal passes into the free orbital of the hydrocarbon molecule and an anion radical (AR) is formed. Consideration of the energy balance of the AR-formation reaction shows (⁀3) that, if the hydrocarbon and the metal are kept fixed and electron-donor solvents with similar dielectric constants (DC) are varied, then the difference in AR formation energies depends chiefly on the unequal energy of solvation of the cation by solvent molecules. Solvation occurs predominantly through forces of donor–acceptor character. There are indications ([4,]5) that in solvation complexes the coordination number of sodium is four.

Despite the existence of many works devoted to the synthesis, study of properties, and use of AR, the literature gives little attention to the question of the role of structural features of the solvent molecules in AR formation. Therefore, using as examples the reactions for obtaining sodium naphthalene (NN) and sodium diphenyl (ND), which are often used as polymerization initiators ([3,]6), we compared the solvating ability of more than twenty solvents (ethers of ethylene and diethylene glycol, five- and six-membered cyclic ethers with one and two oxygen atoms, and simple ethers). The solvation effects in AR-formation reactions and in other organic anionic reactions are in many respects similar ([7-]9). In view of this, the results have a more general significance.

The reactions were carried out between a solution of the hydrocarbon of specified concentration in the ether under study and a sodium mirror, under high vacuum at room temperature. To determine the equilibrium relative concentrations $C_{\mathrm{ND}}$ and $C_{\mathrm{NN}}$, the following were measured ([9,]10): I. The intensity of the electronic absorption spectrum of the solution (for ND at $\lambda = 625$ m$\mu$, for NN at $\lambda$: 365 and 810 m$\mu$. $C_{\mathrm{D}} = 0.002 \pm 0.0002$ mole/l; $C_{\mathrm{N}} = 0.006 \pm 0.0003$

mole/l). It was assumed that the AR concentration in DME is equal to 100 ($C_{\mathrm{ND}} = C_{\mathrm{NN}} = 100$); II. The intensity of the central component of the EPR spectrum of the ND solution. The comparison standards were the EPR spectrum of a crystal of $CuCl_2 \cdot 2H_2O$ and the EPR spectrum of an ND solution in 1,2-diethoxyethane (DEE), for which comparison with the intensity of the EPR spectrum of a solution with the equilibrium concentration of ND in DME gave $C_{\mathrm{ND}} = 14$. The concentration $C_{\mathrm{D}} = 0.003 \pm 0.0002$ mole/l. The values of the relative equilibrium concentrations $C_{\mathrm{ND}}$ (I) and $C_{\mathrm{ND}}$ (II), determined by the two methods, agree well with one another (Table 1). Differences in the concentrations of ND caused by changing the solvents are manifested more strongly than differences in $C_{\mathrm{NN}}$, since the electron affinity of the diphenyl molecule (0.41 eV) is less than that of naphthalene (0.65 eV) (⁀11).

It was of interest to compare the electron-donor ability of various ethers in the formation of their complex with the $Na^+$ ion and in the formation of a hydrogen bond with $CH_3OD$. For this purpose, in a separately published paper by I. M. Ginzburg with two of us (A. Sh. and E. P.), the magnitudes of the shift of the frequency of the valence vibration of the OD bond ($\Delta\nu_{\mathrm{OD}}$, $\mathrm{cm}^{-1}$) in the IR spectrum of a solution of $CH_3OD$ in $CCl_4$ upon addition of an ether were measured; according to Gordy ($^{12}$), these characterize the strength of ethers as bases ($\nu_{\mathrm{OD}} = 2689$ $\mathrm{cm}^{-1}$).

Table 1

| % | Ether | $C_{\mathrm{HD}}$ (I) | $C_{\mathrm{HD}}$ (II) | $C_{\mathrm{HH}}$ | K-Na | $\Delta\nu_{\mathrm{OD}}$, $\mathrm{cm}^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | $CH_3OC_2H_4OCH_3$ | 100 | 100 | 100 | ++ | 93 |
| 2 | $CH_3OC_2H_4OC_2H_5$ | 58 | 62 | 100 | + | 95 |
| 3 | $CH_3OC_2H_4OC_3H_7$ | 23 | 21 | 86 | 0 | 97 |
| 4 | $CH_3OC_2H_4OC_4H_9$ | 19 | 18 | 83 | 0 | 95 |
| 5 | $CH_3OC_2H_4OC_5H_{11}$ | 15 | 14 | 72 | 0 | 98 |
| 6 | $C_2H_5OC_2H_4OC_2H_5$ | 15 | 14 | 60 | 0 | 98 |
| 7 | $C_4H_9OC_2H_4OC_4H_9$ | 10 | 8 | 20 | 0 | 100 |
| 8 | $CH_3OCH_2OCH_3$ | 0 | – | 0 | 0 | 84 |
| 9 | $CH_3OCH(CH_3)OCH_3$ | 0 | 0 | 6 | 0 | 90 |
| 10 | $CH_3OC_3H_6OCH_3$ | 6 | 7 | 50 | 0 | 100 |
| 11 | $CH_3OC_4H_8OCH_3$ | 4 | 2 | 18 | 0 | 104 |
| 12 | $CH_3OCH_3$ | 2 | – | 20 | 0 | – |
| 13 | $CH_3OC_2H_5$ | 1 | – | 3 | 0 | – |
| 14 | $C_2H_5OC_2H_5$ | <1 | – | 2 | 0 | 106 |
| 15 | $CH_3OC_2H_4OC_2H_4OCH_3$ | 100 | – | – | ++ | 90 |
| 16 | $C_2H_5OC_2H_4OC_2H_4OC_2H_5$ | 100 | – | – | + | 98 |
| 17 | Tetrahydrofuran (THF) | 42 | 46 | 86 | + | 115 |
| 18 | 2,5-Diethoxy-THF | 0 | 0 | 5 | 0 | 92 |

| % | Ether | $C_{HD}$ (I) | $C_{HD}$ (II) | $C_{HH}$ | K-Na | $\Delta\nu_{OD}$, $cm^{-1}$ |
|---|---|---|---|---|---|---|
| 19 | 1,3-Dioxolane | 10 | – | 70 | 0 | 76 |
| 20 | Tetrahydropyran | 9 | 10 | 52 | 0 | 112 |
| 21 | 1,4-Dioxane | 4 | 3 | 34 | 0 | 100 |
| 22 | 1,3-Dioxane | 14 | 14 | 70 | + | 85 |

It is known ([13,14]) that in certain ethers, in particular in DME, alkali metals dissolve with formation of blue solutions and ionize. We assumed that in those ethers in which an alkali metal is soluble, AP will also be formed more readily, since solvation of the cation is an important factor determining the direction of both processes. Table 1 gives the results of qualitative experiments by Wilkinson and co-workers ([13]) on the solubility of the K-Na eutectic in ethers, supplemented by us (intense coloration, weak coloration, and its absence are denoted respectively: ++; +; 0). In addition, Table 1 lists the values of $C_{HD}$ (determined by two methods, I and II), $C_{HH}$, and $\Delta\nu_{OD}$.

From the data in Table 1 it is evident that replacement in DME of a methyl group (and especially replacement of both $CH_3$ groups) by an alkyl radical with a larger number of carbon atoms (Nos. 1-7) sharply lowers the equilibrium concentration of AP, despite the enhancement of the electron-donor properties of the ether as a result of the increase in the inductive effect of the alkyl group as it is lengthened. Shielding of the oxygen atoms by alkyl groups freely rotating around them hinders solvation of the $Na^+$ ion.

The inductive effect of the oxygen atom has the opposite sign compared with the inductive effect of an alkyl group. Therefore the strength of an ether as a base with respect to $CH_3OD$ decreases when a second oxygen atom is introduced into the molecule and when the distance between the oxygen atoms is decreased (cf. Nos. 14 and 6; Nos. 11, 10, 1, and 8; Nos. 17 and 19; Nos. 20, 21, and 22). We are again convinced that there is usually no direct relationship between the strength of an ether as a base and its solvating ability with respect to the $Na^+$ ion, since for formation of a strong complex with the cation, besides a sufficiently pronounced electron-donating ability of oxygen in the ether,

a favorable arrangement of the oxygen atoms in space is necessary. Thus, in the group of ethers differing in the length of the carbon bridge between two oxygen atoms (Nos. 8, 1, 10, and 11), the optimum configuration is that of the DME molecule. It is in this solvent that AR are readily formed and the K-Na eutectic dissolves. The significance of the spatial factor is also clearly revealed by the example of cyclic ethers—THF and its diethoxy derivative in positions 2 and 5 (Nos. 17 and 18). In the second solvent AR are almost not formed, although for it and for DME the value of $\Delta\nu_{OD}$ is the same.

The probability of complex formation may to a certain extent depend on the number of oxygen atoms in the molecule of an acyclic ether. Let us compare the data for simple ethers (Nos. 12, 13, and 14), ethylene glycol ethers (Nos. 1, 2, and 6), and diethylene glycol ethers (Nos. 15 and 16). The molecule of a diethylene glycol ether is, as it were, a doubled molecule of an ethylene glycol ether, and even the presence in it of two $C_2H_5$ groups does not prevent dissolution of the K–Na eutectic. In simple diethyl ether (No. 14), which proved to be the strongest proton acceptor of all the acyclic ethers we studied, even NN is almost not formed.* There is no dependence between the number of oxygen atoms in the molecule of a cyclic ether and its solvating ability.

Thus, although both cation solvation and hydrogen-bond formation are due to forces of donor-acceptor nature, there is no correspondence between the series of ethers established with respect to the two reactions. This can be explained by the fact that, for cation solvation to occur, coordination of several (probably four) oxygen atoms is required, and therefore it is important how they are arranged in space and whether there are obstacles to complex formation depending on the steric factor. In the formation of a hydrogen bridge with $CH_3OD$, only one oxygen atom participates; steric hindrance has comparatively little effect; the energy and polarity of the bond formed are determined mainly by the electron-donor properties of the oxygen atom in the given molecule.

The expected correspondence between the concentration of AR and the ability of an ether to dissolve an alkali metal does in fact exist (Nos. 1, 2, 15, 16, 17). At the same time, for the formation of AR, as for the dissolution of K-Na (13), the magnitude of the dielectric constant of the solvent apparently is not of particular importance—with almost identical dielectric constants the ND concentration differs a hundredfold:

| No. | 1 | 17 | 6 | 20 | 14 |
|---|---|---|---|---|---|
| DP | 5.5 | 6.0 | 5.1 | 5.4 | 4.2 |
| $C_{\mathrm{ND}}$ | 100 | 45 | 15 | 10 | <1 |

It should be noted that observations made in our laboratory (8) on the kinetics of certain organic anionic reactions testify to the same point—the decisive factor is not the magnitude of the dielectric constant of the solvent, but the structural features of its molecules, on which the solvation effect depends. This must be borne in mind when considering the important problem of theoretical chemistry concerning the influence of solvents on reaction kinetics, posed by N. A. Menshutkin. Since in the classical Menshutkin reaction of formation of substituted ammonium salts the polarity of the transition state is high, in this particular case the dielectric constant of the solvent indeed plays an essential role, but often excessive significance is attached to this parameter in the general interpretation of the problem.

We are continuing work aimed at expanding the range of solvents, including compounds containing nitrogen, and also toward obtaining–

* In sulfur analogues of ethers (tetrahydrothiophene and $C_2H_5SC_2H_4SC_2H_5$), it was not possible to obtain AR even of anthracene, despite the considerable affinity of its molecule for an electron (1,19 eV) (11). This may depend on the lower basicity of sulfur compounds in comparison with oxygen compounds (15,16).

tion of thermodynamic data characterizing the equilibria of AP formation in different solvents as a function of the structure of their molecules and of the alkali-metal cation.

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Received
1 IV 1963

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