

BASICITY OF SATURATED SOLUTIONS OF ALKALI METAL
HYDROXIDES IN DIMETHYLSULFOXIDEB. A. Trofimov, A. M. Vasil'tsov,
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The use of alkali-dipolar aprotic solvent **superbasic media in acetylene chemistry** has permitted developing the conditions for obtaining **previously inaccessible vinyl and divinyl chalcogenides** and their substituted, nitrogen-containing **heterocycles** and N-vinyl derivatives, etc., over the past 10 years [1-5]. Nevertheless, the **insufficient study** of even the most frequently used alkali-DMSO system does not permit **quantitatively explaining** the different catalytic activity of the alkalis and the effect of **water in vinylation reactions**.

In the present study, the solubility of **alkalis in DMSO as a function of the temperature and concentration of water**, and the ion pair interaction were studied, and the values of the acidity function H_- were found by the indicator method in the **alkali-DMSO system**.

Strongly basic (superbasic) media are defined in [6] as **media capable of ionizing weak acids to a greater degree than a 0.1 M solution of the alkalis in water**. For example, they include solutions of dimsylys(methylsulfinylcarbanions), **alkoxides**, and hydroxides of alkali metals in DMSO.

The reactivity of the charged nucleophil is **strongly dependent on the degree of its solvation**. In dipolar aprotic solvents,* it primarily **takes place due to the weak dispersion interaction of anions with the solvent molecules**. **"Soft" anions with a delocalized charge** such as thiolates and carbanions undergo a slight decrease in their energy due to the hydrogen bonds in comparison to the energy of the unsolvated state. **"Tough" anions with a localized charge**, for example, a hydroxide or an alkoxide, **on the contrary produce stable hydrogen bonds stabilized in aqueous solutions and alcohols [9]**. In dipolar aprotic solvents, they are unstable and capable of entering into reactions of **nucleophilic substitution, addition, and deprotonation of CH acids with the formation of carbanions much more effectively**.

The dependence of H_- on the composition of the **DMSO-water solution** for 0.01 M Me_4NOH at 25°C is given in [10, 11]. However, these data are **difficult to compare with the conditions in which organic reactions are usually conducted (high concentrations, high temperature)**.

Our data indicated that the solubility of **KOH in DMSO changes only in aqueous DMSO with an increase in the temperature, remaining stable ($3.7 \cdot 10^{-2}$ M) at 25°C and with a low concentration of water (0-9%) (Fig. 1)**. The solubility of **NaOH and LiOH is slightly lower, $2.6 \cdot 10^{-2}$ and $1.7 \cdot 10^{-2}$ M, respectively**. Alkali metal hydroxides are thus **very poorly soluble in DMSO**, as indicated in [12, 13], although erroneous data such as the use of a 0.1 M solution of KOH in anhydrous DMSO, for example, are cited in some early studies [14].

The study of the phase distribution of the **water between the solution and the excess alkali** is of greater interest, as the drying capacity of **KOH is well known**. The data reported in Fig. 2 show that with a fixed concentration of the **base in the system**, the concentration of water in DMSO is almost independent of the temperature, **decreases on addition of KOH to the system, and increases on addition of water**. The **lower the concentration of water, the more efficiently it is absorbed by the KOH in excess**. With a **decrease in the concentration of water in the system from 10 to 0.6%**, the ratio of its concentration in **KOH and DMSO increases from 5 to 50 (with 10% KOH in both cases)**. When **NaOH and LiOH are used**, the water contained in them as an impurity goes into the DMSO. A significant time: **from several hours to 1 day**, is required for attaining equilibrium concentrations of **KOH and water at 20°C, despite intense**

*Instead of the widely used term "dipolar aprotic," the use of the more correct "dipolar non-hydroxyl" is recommended in [7, 8].

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stirring and careful grinding of the alkali. Equilibrium can be attained in 5-10 min by heating the system to 85°C and higher with subsequent cooling. In addition, settling of the solution is necessary for precipitating the suspended finely disperse particles of KOH.

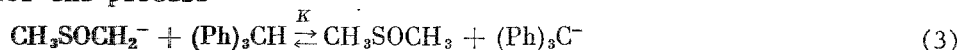
Fluorene, tri-, and diphenylmethanes, were used as indicators for establishing the range of values of acidity function H_- in the alkali (10%)-DMSO system. The calculations were performed with the equation

$$H_- = pK_a + \lg ([In^-]/[InH]) \quad (1)$$

using the known values of the ionization constants pK_a in DMSO in standard conditions (Table 1). Although LiOH ionizes fluorene insignificantly (~1%, $H_- = 20.5$), NaOH ionizes it almost totally (90%, $H_- = 23.5$). Potassium hydroxide even reacts with such a weak acid as triphenylmethane (ionized by 40%, $H_- = 30.5$)



The water formed is bound by the alkali present in excess, which permits obtaining a medium with a higher basicity than can be created with KOH in DMSO ($H_- = 29.5$; 0.01 M KOH [9]). After addition of an equimolar (to the KOH in the solution) amount of triphenylmethane, the intensity of the color slowly increases (rapidly when heated, as indicated above). It is subsequently possible to repeatedly add small portions of water to the prepared solution, each time attaining discoloration of the solution and subsequent restoration of the color. This indicates elevated buffering of the system with respect to the water. The indicator ratio $[In^-]/[InH]$ for triphenylmethane, and consequently the value of H_- in it, is even higher than in the KOBu-t-DMSO system, since t-BuOH is not removed from the solution. In light of these data, it is possible to assume the uniform ionization of diphenylmethane in the KOH-DMSO system, which is not indicated in the literature. Intense red coloration, which rapidly disappears due to oxidative processes, is observed even in air when a small amount of DMSO is added to a mixture of ground KOH and diphenylmethane. At the same time, ionization of diphenylmethane is not observed in the KOBu-t-DMSO system, although KOBu-t is much more soluble in DMSO than KOH. The latter is the salt of a stronger acid (see Table 1). Based on the value of the equilibrium constant $K = 3.0 \cdot 10^4$ [15] for the process



it is possible to estimate the concentration of the dimsyl ion in the KOH-DMSO system. The calculated value is $3 \cdot 10^{-4}$ M or approximately 1% of the concentration of the KOH in DMSO. It should be emphasized that equilibrium (3) is satisfied regardless of the method of preparation of the dimsyl ion, since equilibrium constant K is a thermodynamic value. The proportionality found between the increase in the conductivity and the concentration of triphenylmethane added indicates the constancy of the indicator ratio in the KOH-DMSO system and the presence of the dimsyl ion in the starting solution in approximately the same concentration ($3 \cdot 10^{-4}$ M).

It is well known that the basicity of equimolar solutions decreases in many solvents (for example, in water and alcohols [9]) in going from KOH to LiOH due to an increase in the association of ions



A similar dependence is observed in DMSO. Based on the findings of our conductometric measurements, we calculated the values of the association constants (Table 2) with the equation in [17]

$$K_{as} = (1 - \alpha)/\alpha^2 C f_{\pm}^2 \quad (5)$$

where $\alpha = \Lambda/\Lambda_0$, where Λ and Λ_0 are the apparent and limit equivalent conductivities; C is the concentration of alkali in the DMSO. The activity coefficient f_{\pm} was calculated as in [17]* with the equation

$$f_{\pm} = -0,7875 (\alpha C)^{1/2} / [1 + 1,207 (\alpha C)^{1/2}] \quad (6)$$

Table 2 shows that even for very dilute solutions of NaOH, the effect of the ion pairs is pronounced, and almost all of the LiOH is in the form of an associate. When KBr is added

*The equations for calculation of K_{as} and f_{\pm} in [17] include typographical errors.

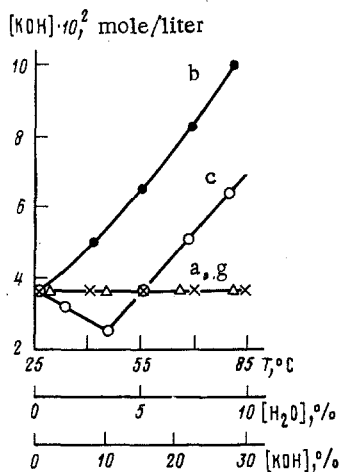


Fig. 1

Fig. 1. Dependence of the concentration of KOH in DMSO on the temperature (a, b), concentration of H_2O in the system at 55°C (c), and the total amount of KOH at 25°C (d). a) $[\text{KOH}] = 10\%$ without water; b) same, $[\text{H}_2\text{O}] = 9\%$; c) $[\text{KOH}] = 10\%$; d) without water.

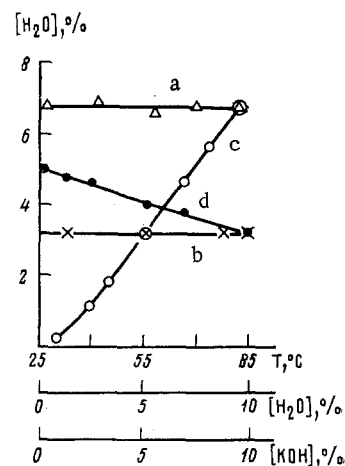


Fig. 2

Fig. 2. Dependence of the concentration of H_2O in DMSO on the temperature (a, b), concentration of H_2O in the system at 25°C (c), and total amount of KOH in the system at 25°C (d). a) $[\text{KOH}] = 10\%$, $[\text{H}_2\text{O}] = 10\%$; b) $[\text{KOH}] = 10\%$, $[\text{H}_2\text{O}] = 5\%$; c) $[\text{KOH}] = 10\%$; d) $[\text{H}_2\text{O}] = 5\%$.

TABLE 1. Acidity Scale in DMSO [15, 16]

| Acid | $\text{p}K_a$ | λ_{max} (In^-), nm | $\epsilon \cdot 10^4$ | Acid | $\text{p}K_a$ | λ_{max} (In^-), nm | $\epsilon \cdot 10^4$ |
|-----------------------------------|---------------|---|-----------------------|----------------------|---------------|---|-----------------------|
| DMSO | 35.1 | | | (Ph) ₃ CH | 30.6 | 500 | 4.51 |
| <i>t</i> -BuOH | 32.2 | | | PhC \equiv CH | 28.8 | | |
| (Ph) ₂ CH ₂ | 32.2 | 460 | 7.68 | Fluorene | 22.6 | 485 | 0.147 |
| H ₂ O | 34.4 | | | | | | |

to a solution of KOH and triphenylmethane, the color attenuates markedly, and when the more soluble KI is added, the solution discolors due to equilibrium (4). At the same time, association of dimethyl ion and other carbanions with the alkali metal cations is insignificant [17, 19].

With a fixed concentration of base in DMSO, even an insignificant increase in the concentration of water causes a sharp decrease in the basicity of the system due to hydration of the highly basic hydroxide ion



Equilibrium (7) is strongly shifted to the right ($\log K_h = 3.2$ [15]), which is also characteristic of alcohols [9, 17] and phenols [8], whose values of $\log K_h$ are within the limits of 3 to 4. However, hydrated ions tend to form ion pairs (according to our estimations, $\log K_{\text{as}} = 2.5$ and 3.5 for KOH and NaOH monohydrates, respectively), since with addition of up to 1 M water, dissociation of the alkalis increases insignificantly. For alcohols, the effect of the concentration of the hydroxyl component on the dissociation of ion pairs is much more pronounced. For methanol, for example, a 10-fold excess of the alcohol with respect to Na methoxide results in the almost total dissociation of the base in DMSO [17]. If we assume that the basicity of the system is due to hydrated OH^- ions with low concentrations of water, which are nevertheless higher than the concentration of the alkali, then by substituting $[\text{HO}^-]/[\text{H}_2\text{O}]$ instead of the indicator ratio in Eq. (1) in consideration of equilibria (7) and (8), it is

TABLE 2. Calculation of the Association Constants K_{as} from the Findings of Conductometric Measurements

| Alkali | $C_{MOH}^{10^4}$ | Λ_0 [17, 18], $cm^3/\Omega \cdot Eq$ | Λ/Λ_0^* | $lg K_{as}^\dagger$ | | | Proportion of ion pairs in a saturated solution |
|--------|------------------|---|-----------------------|---------------------|----------------------|-----------------------|---|
| | | | | MOH | MOH·H ₂ O | MOH·2H ₂ O | |
| LiOH | 2,4 | 23,2 | 0,07 | 5,9 | 4,6 | 3,7 | 99,2 |
| NaOH | 1,2 | 26,0 | 0,32 | 4,7 | 3,5 | 2,7 | 97,0 |
| KOH | 1,2 | 26,8 | 0,88 | 3,1 | 2,5 | 1,9 | 86,0 |

*In abs. DMSO.

†For hydrates, K_{as} were obtained with 0.01 and 1.0 M H₂O.

possible to estimate the hydration constant K_h ($\log K_h^I = 4.8 \pm 0.3$ and $\log K_h^{II} = 6.61 \pm 0.02$) based on the known values of H_- [10]. It qualitatively follows that the existence of the unhydrated HO^- ion is almost impossible, since the product of $[H_2O] \cdot K_h^I$ and consequently the ratio of the concentrations of the hydrated and free forms of the OH^- ion is large even for very low concentrations of water. The stability of the bond in the $(HO \cdot H_2O)^-$ ion can be judged by the fact that it is not destroyed by triphenylmethane salts [20]. The OH^- ion is extremely unstable in DMSO, and for this reason, the formation of stable hydrogen bonds together with association of the ions is one of the ways of stabilizing it, which results in a decrease in the basicity of solutions of alkalis in DMSO in comparison to the basicity expected from the value of the pK_a of water. Actually, in consideration of the maximum solubility of alkalis in DMSO even in the condition of transformation of a dissociated base into a dimsyl ion, the limit values of H_- for KOH, NaOH, and LiOH are 31.3, 30.5, and 29.8, respectively, which is lower than the pK_a of water. Nevertheless, it was observed in [21] that the basicity of the OH^- ion is comparable to or even higher than the basicity of the dimsyl ion. It is completely possible that the pK_a of water is even higher than the value of 31.4 measured in the presence of [2.2.2]-cryptand, which eliminates ionic association, since hydration of the anions has not been excluded.

The constants K_{as} and K_h obtained permit calculating the values of the acidity function H_- with low concentrations of water (less than 1 M) for solutions of alkali metal oxides in DMSO.

EXPERIMENTAL

Purification of DMSO. DMSO, previously dried with 4A molecular sieves, was distilled over CaH_2 in a vacuum at 50°C and stored over 4A molecular sieves in dry Ar. The specific conductivity of the DMSO was $<1 \cdot 10^{-7} \Omega^{-1} \cdot cm^{-1}$.

Determination of the Concentration of Alkali in DMSO. Here 1 ml of DMSO was added to 10 ml of an aqueous solution of MOH of known concentration, the pH of the prepared solution was measured with an OR-208 precision pH meter, and calibration graphs were plotted in pH-logarithm of the concentration of alkali coordinates. Then 1 ml of the solution studied was added to 10 ml of freshly prepared distilled water, the pH was measured, and the concentration of MOH was found with the calibration graph. The error of the measurements did not exceed 5% in a wide range of concentrations. The conductivity of the alkali solutions in DMSO was measured in Ar with a LM-301 conductivity apparatus. The cell constant was 0.96. The concentration of water in the DMSO was determined by preliminary calibration by GLC on a LKhM-80 instrument with an EI-2 integrator. The column was 0.85 m \times 3 mm, the solid phase was Polysorb-1, the detector was a catharometer, the carrier gas was He, the gas flow rate was 50 ml/min, the column temperature was 190°C, and the evaporator temperature was 210°C. The column was first held in a He current for 1 day at 230–240°C.

The values of H_- were estimated by determining the increase in the conductivity and the concentration of base in the solution studied after addition of an indicator.

CONCLUSIONS

1. Saturated solutions of alkali metal hydroxides in dimethyl sulfoxide are highly basic. The values of the acidity function H_- varied from 20.5 to 30.5 in going from LiOH to KOH.

2. The strong dependence of the basicity of the **alkali-DMSO** system on the nature of the cation is the result of an ion pair interaction in the **solution** which increases with a decrease in the radius of the cation and the varied **drying capacity** of the alkalis present in excess.

3. The KOH-DMSO pair is an example of the **superbasic medium** which is simplest to prepare and use; its basicity is located between potassium **tert-butylate** and potassium dimethyl in DMSO.

LITERATURE CITED

1. B. A. Trofimov, *Heteroatomic Derivatives of Acetylene [in Russian]*, Nauka, Moscow (1981), p. 147.
2. B. A. Trofimov and S. V. Amosova, *Divinyl Sulfide and Its Derivatives [in Russian]*, Nauka, Novosibirsk (1983), 262 pp.
3. B. A. Trofimov, *Sulf. Reports*, 3, 83 (1983).
4. B. A. Trofimov and S. V. Amosova, *Sulf. Reports*, 3, 323 (1984).
5. B. A. Trofimov and A. I. Mikhaleva, *N-Vinylpyrroles [in Russian]*, Nauka, Novosibirsk (1984).
6. K. Bowden, *Chem. Revs.*, 66, 119 (1966).
7. F. G. Bordwell, J. C. Branca, D. L. Hughes, and W. N. Olmstead, *J. Org. Chem.*, 45, 3005 (1980).
8. F. G. Bordwell, R. J. McCallum, and W. N. Olmstead, *J. Org. Chem.*, 49, 1424 (1984).
9. O. A. Reutov, I. P. Beletskaya, and K. P. Butin, *CH Acids [in Russian]*, Nauka, Moscow (1980).
10. R. A. Cox and R. Stewart, *J. Am. Chem. Soc.*, 98, 488 (1976).
11. D. Dolman and R. Stewart, *Can. J. Chem.*, 45, 911 (1967).
12. E. C. Steiner, J. D. Starkey, J. M. Tralmer, and R. O. Trucks, *Prep., Am. Chem. Soc., Div. Petrol. Chem.*, 12, C11 (1967).
13. E. C. Steiner, R. O. Trucks, J. D. Starkey, and J. H. Exner, *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.*, 13, 1135 (1968).
14. D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Amer. Chem. Soc.*, 81, 5774 (1959).
15. W. N. Olmstead, Z. Margolin, and F. G. Bordwell, *J. Org. Chem.*, 45, 3295 (1980).
16. E. M. Arnett and K. G. Venkatasubramanian, *J. Org. Chem.*, 48, 1569 (1983).
17. J. H. Exner and E. C. Steiner, *J. Am. Chem. Soc.*, 96, 1782 (1974).
18. R. Gortein and T. C. Bruice, *J. Phys. Chem.*, 76, 433 (1972).
19. W. N. Olmstead and F. G. Bordwell, *J. Org. Chem.*, 45, 3299 (1980).
20. E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, 85, 3054 (1963).
21. C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, 89, 1721 (1967).