

PROTON SOLVATION: COMPETITION BETWEEN ACETONE AND DIMETHYL SULFOXIDE

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This paper presents results of quantum-chemical study of proton exchange equilibrium between acetone (AC) and dimethyl sulfoxide (DMSO). Basing on the previous study of acid-base equilibria in AC with small additives of DMSO, the most probable composition of the lyonium ion is taken as $\text{H}(\text{DMSO})_2^+$. The equilibrium geometries and energies of solvents molecules and all possible combinations of proton complexes with one or two solvent molecules were calculated in DFT level of theory using B3LYP functional and 6-31G++(d,p) basis set. The energies of solvated proton complexes were then calculated using PCM method. The energy change corresponding to the equilibrium $\text{H}(\text{AC})_2^+ + 2 \text{DMSO} \rightleftharpoons \text{H}(\text{DMSO})_2^+ + 2 \text{AC}$ is $-63.1 \text{ kJ mol}^{-1}$ in the gas phase, which is in qualitative agreement with the standard Gibbs energy data, obtained experimentally in the gas phase by Kebarle's group, $-77.6 \text{ kJ mol}^{-1}$, and with $\Delta G_{298}^\circ = -49.3 \text{ kJ mol}^{-1}$ for AC solution with small additions of DMSO, determined by the Guss and Kolthoff method.

Keywords: proton solvation; acetone; dimethyl sulfoxide; quantum-chemical study; energy of proton exchange.

Introduction

This paper is devoted to the competition for proton between the molecules acetone and dimethyl sulfoxide (DMSO) using quantum-chemical calculations. The higher basicity of DMSO as compared with acetone is of common knowledge, see Table 1.

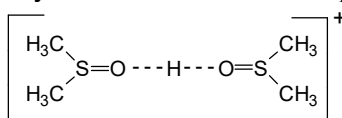
In addition to the numerical parameters gathered in Table 1, basing on experimental data, we decided to theoretically examine the proton exchange between these two solvents. Also, the same exchange equilibrium was estimated using our earlier published experimental results.

Table 1. Solvent descriptors characterizing the solvent basicity

Parameter	Acetone	DMSO
DN^N	0.44	0.77
β	0.48	0.76
B	224	362
B_p	12.6	13.3
PA	831	897

Note. The data are taken from ref. [1]. DN^N is the normalized Gutmann's donor number; β is the solvatochromic Kamlet-Taft parameter; B is the Koppel-Palm parameter; B_p is the "polar basicity" according to Fawcett [2]; PA is the proton affinity, kJ mol^{-1} .

More than ten years ago, we studied the acid-base and related equilibria in acetone (AC) containing small additives of DMSO [3, 4]. It was demonstrated that the likely composition of the lyonium ion is $\text{H}(\text{DMSO})_2^+$. In other words, the primary solvation shell can be represented in following manner:

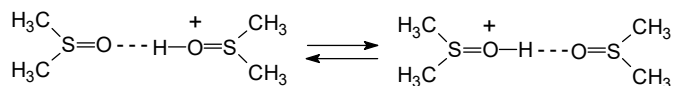


or, more strictly:

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(In this paper, we avoid discussing the likelihood of symmetric hydrogen bonds occurring.)

This was deduced from the dependence of the $\text{p}K_{\text{a}}$ of picric acid on the DMSO content in the binary acetone – DMSO solvent and confirmed by the proximity of the limiting molar conductivities, Λ_0 , at 25 °C of picric acid and tetraethylammonium picrate in acetone containing 5 mole % DMSO, a solvent with relative permittivity $\epsilon_r = 22.19$. These values are 162.0 ± 1.2 and $180.3 \pm 1.7 \text{ S mol}^{-1} \text{ cm}^2$, respectively [3, 4].

At the same time, the linear size of the ion $\text{H}(\text{DMSO})_2^+$, estimated as the distance between the most remote hydrogen atoms (Fig. 1a), is 900 pm. Crystallographic and various other experimental data available in the literature, as well as estimates using van der Waals radii of atoms, suggest that the diameter of the “pseudospherical” $\text{N}(\text{C}_2\text{H}_5)_4^+$ ion, which belongs to the “weakly solvated” category, is in the range from 674 to 800 pm [3, 4]. This amounts to (75–89) % of the linear size of the $\text{H}(\text{DMSO})_2^+$ ion, which indicates the consistency of the proposed proton solvation model. In any case, the existence of the lyonium ion in the form of $\text{H}(\text{DMSO})^+$ would be more difficult to reconcile with its lower mobility compared to the $\text{N}(\text{C}_2\text{H}_5)_4^+$ ion. As a result, we consider $\text{H}(\text{DMSO})_2^+$ as the most probable composition of the lyonium ion.

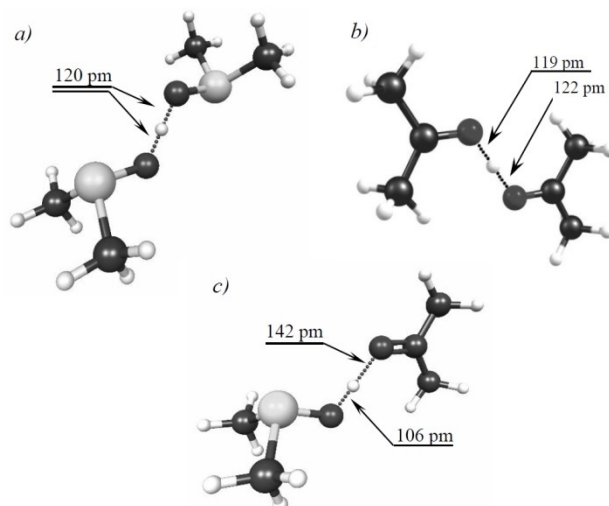


Fig. 1. Geometries of complexes a) $\text{H}(\text{DMSO})_2^+$; b) $\text{H}(\text{AC})_2^+$ and c) $\text{H}(\text{AC},\text{DMSO})^+$ from the quantum chemical calculations

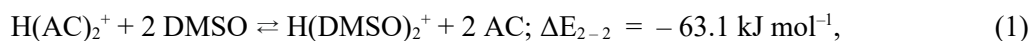
In pure DMSO, this composition is preferred on the basis of data from IR spectroscopy [5, 6].

The geometric and energy parameters of proton complexes with acetone and DMSO molecules were also estimated using quantum chemical calculations. All calculations were provided using Gaussian 09 program set [7]. The geometries of individual solvent molecules, as well as complexes of a proton with one or two solvent molecules in vacuum (Fig. 1) were optimized using DFT (density functional theory) method with the B3LYP hybrid functional and 6-31G++(d,p) basis set. Additional keywords `opt=tight` and `int=ultrafine` were used to ensure accuracy of optimization procedure. The vibrational frequencies were also calculated and imaginary vibration frequencies were absent. The energies of these solvate complexes in acetone were then calculated using the polarized continuum model (PCM). Zero-point energy and thermal correction to 298 K were taken into account when calculating the energies.

According to our calculations, the O – O distance in the $\text{H}(\text{DMSO})_2^+$ ion is 2.405 Å, which is in good agreement with the value of 2.403 Å calculated by Denisov *et al.* [8] at B3LYP/6-31G(d,p) level.

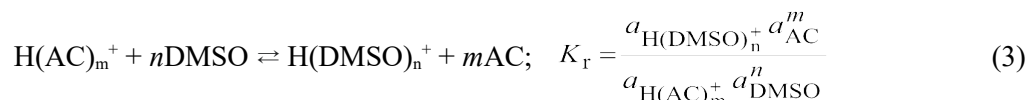
The transformation of structure 1a into structure 1b requires a cost of 20.9 kJ mol⁻¹. The greater basicity of the DMSO molecule is also clearly demonstrated by the bond lengths between the proton and oxygen atoms in two different structures. This result is very instructive, and a similar approach can be applied to other systems.

Energy changes corresponding to proton exchange between various proton solvates in acetone were also calculated:



The significantly higher basicity of DMSO compared to AC is also confirmed by the experimental data of the Kebarle group [9] on the values of the standard Gibbs energies of the indicated proton exchange reactions in the gas phase: ΔG_{298}° (1) = -77.6 kJ mol⁻¹ and ΔG_{298}° (2) = -64.8 kJ mol⁻¹.

In addition, the proton exchange between acetone and DMSO in acetone solution can be examined using the approach developed by Guss and Kolthoff [10]. If only one solvate complex can be taken into account and ruling out the possibility of mixed proton solvates, such as H(AC, DMSO)^+ , the following equilibria can be derived:



In this case, according to Guss and Kolthoff, the following equation is valid:

$$K_a = K_a^{\text{AC}} \left(1 + K_r \frac{a_{\text{DMSO}}^n}{a_{\text{AC}}^m} \right) \quad (4)$$

Using the experimental $\text{p}K_a$ values of picric acid in acetone – DMSO mixtures with molar fraction of DMSO from 0.005 to 0.06 [3, 4], taking $\text{p}K_a^{\text{AC}} = 9.2$ from the work by Foltin and Majer [11], and equating n and m to 2, we obtained a value $K_{r(2-2)} = (4.3 \pm 0.8) \times 10^8$. Accordingly, ΔG_{298}° (1) = $-2.303 RT \log K_{r(2-2)} = -49.3 \text{ kJ mol}^{-1}$, which is in qualitative agreement with the results of quantum chemical calculations for the gas phase.

Similar calculations can be carried out for the case $n = 2, m = 1$ ($K_{r(1-2)}$), etc. However, as quantum chemical calculations show, the addition of a second DMSO molecule to H(DMSO)^+ and a second AC molecule to H(AC)^+ in acetone is accompanied by such significant energy gains (60.26 and 54.68 kJ·mol⁻¹, respectively), that it is quite justified to take into account only the solvates H(DMSO)_2^+ and H(AC)_2^+ . A solvate of composition H(AC, DMSO)^+ is possible only in the case of DMSO deficiency, but under the conditions of our experiment, the proton concentration is 3–4 orders of magnitude lower than the DMSO concentration.

Thus, we have proven that in acetone with DMSO additives, the lyonium ion exists mainly in the form of H(DMSO)_2^+ , and that the proton exchange constant between the two solvents is very high and amounts to over 10^8 . Both theoretical and experimental data give new convincing support to the more strong basic properties of DMSO as compared with acetone.

Acknowledgements

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References

1. Reichardt C., Welton T. Solvents and Solvent Effects in Organic Chemistry. Wiley-VCH; Weinheim, 2011.
2. Fawcett W.R. Acidity and basicity scales for polar solvents. *J. Phys. Chem.*, **1993**, 97 (37), 9540-9546. <https://doi.org/10.1021/j100139a045>
3. Lebed A.V., Mchedlov-Petrosyan N.O., Filatov D.Yu., Goga S.T. Acid-base equilibrium in a mixture of protophobic and protophilic polar non-hydrogen bond donor solvents: Stoichiometry of proton solvation by dimethyl sulfoxide in acetone. *Proc. Nat. Acad. Sci. Ukraine*. **2008**, no. 9, 121-125. <http://dspace.nbuv.gov.ua/handle/123456789/5919>
4. Mchedlov-Petrosyan N.O., Filatov D.Yu., Goga S.T., Lebed A.V. Ionic equilibrium in mixtures of protophobic and protophilic polar non-hydrogen bond donor solvents: Acids, salts, and indicators in acetone containing 5 mol % DMSO. *J. Phys. Org. Chem.*, **2010**, 23(5), 418-430. <https://doi.org/10.1002/poc.1616>

5. Williams J.M., Kreevoy M. Structure and infrared spectrum of the solvated proton in dimethyl sulfoxide. *J. Am. Chem. Soc.* **1967**, 89(21), 5499-5501. <https://doi.org/10.1021/ja00997a062>
6. Kampschulte-Scheuing I., Zundel G. Tunnel effect, infrared continuum, and solvate structure in aqueous and anhydrous acid solutions. *J. Phys. Chem.*, **1970**, 74(11), 2363-2368. <https://doi.org/10.1021/j100705a021>
7. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
8. Denisov G.S., Koll A., Lobadyuk V.I., Schreiber V.M., Shurukhina A.V., Spevak V.N. Hydrogen bonding in coordination compounds containing homoconjugated bis-dimethylsulfoxide cation. Ab initio and IR studies. *J. Mol. Struct.*, **2002**, 605(2-3), 221-226. [https://doi.org/10.1016/S0022-2860\(01\)00783-9](https://doi.org/10.1016/S0022-2860(01)00783-9)
9. Lau Y.K., Saluja P.P.S., Kebarle P. The proton in dimethyl sulfoxide and acetone. Results from - phase ion equilibria involving $(\text{Me}_2\text{SO})_n\text{H}^+$ and $(\text{Me}_2\text{CO})_n\text{H}^+$. *J. Amer. Chem. Soc.*, **1980**, 102(25), 7429-7433. <https://doi.org/10.1021/ja00545a004>
10. Guss L.S., Kolthoff I.M. The distribution of protons between water and other solvents. *J. Amer. Chem. Soc.*, **1940**, 62(6), 1494-1496. <https://doi.org/10.1021/ja01863a047>
11. Foltin M., Majer P. Determination of dissociation constant of picric acid and calibration of potentiometric cell in acetone. *Coll. Czech. Chem. Commun.*, **1978**, 43(1), 95-102. <https://doi.org/10.1135/cccc19780095>

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О.В. Лебідь, Н.О. Мчедлов-Петросян, Д.Ю. Філатов, С.Т. Гога. Сольватація протона: конкуренція між ацетоном та диметилсульфоксидом.

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Ця стаття містить результати квантово-хімічного дослідження обміну протоном між ацетоном (AC) та диметилсульфоксидом (DMSO). Базуючись на попередніх дослідженнях кислотно-основних рівноваг в AC з малими домішками DMSO, як найімовірнішим складом іону ліонію прийнято $\text{H}(\text{DMSO})_2^+$. Рівноважна геометрія та енергії молекул розчинника та усіх можливих комбінацій комплексів протону з однією або двома молекулами розчинників обчислені на рівні DFT з використанням функціоналу B3LYP ьа базису 6-31G++(d,p). Енергії сольватації комплексів протону обчислені за допомогою методу PCM. Зміна енергії, яка відповідає рівновазі $\text{H}(\text{AC})_2^+ + 2 \text{DMSO} \rightleftharpoons \text{H}(\text{DMSO})_2^+ + 2 \text{AC}$, складає $-63.1 \text{ kJ mol}^{-1}$ в газовій фазі. Значення цієї величини якісно узгоджуються зі значенням стандартної енергії Гіббса, $-77.6 \text{ kJ mol}^{-1}$, знайденої для газової фази експериментально групою Кебарле, та значенням $\Delta G_{298}^\circ = -49.3 \text{ kJ mol}^{-1}$ для розчинів AC з малими домішками DMSO, знайденим методом Гасса і Кольтгофа.

Ключові слова: сольватація протона; ацетон; диметилсульфоксид; квантово-хімічне дослідження; енергія обміну протоном.

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