Kinetics and Catalysis, Vol. 41, No. 1, 2000, pp. 38–41. Translated from Kinetika i Kataliz, Vol. 41, No. 1, 2000, pp. 46–49.
Original Russian Text Copyright © 2000 by Kazanskii, Solkan.

Solvation of Protons in Anhydrous H_2SO_4 as the Main Factor Determining Its Superacidic Properties

V. B. Kazanskii and V. N. Solkan

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 117334 Russia

Received October 18, 1999

Abstract—The energies of solvation of $H_3SO_4^+$ cations and HSO_4^- anions by a sulfuric acid molecule in the gas phase are calculated at the 6-31++G** level using the GAMESS program. The energy of additional solvation of the resulting complexes with liquid sulfuric acid was modeled within the framework of the PCM continuum model. The results obtained enable almost quantitative description of the energy of self-dissociation of 100% liquid sulfuric acid. The energy of proton solvation by 100% sulfuric acid calculated in a similar way was ~20 kcal/mol lower than the heat of proton hydration in aqueous solutions. This result explains the superacidic properties of anhydrous H_2SO_4.

INTRODUCTION

The acids capable of protonating even very weak bases are called superacids. The strength of such acids is usually measured using the Hammet acidity function H_0. The use of dissociation constants K_0 or pK_a values makes no sense for this purpose because the degree of dissociation for superacids is very small. For instance, the dissociation constants of 100% sulfuric acid and hydrofluoric acid are only 10^{-4} and 10^{-10}, respectively [1]. It is paradoxical that the dilution of superacids with water increases the degree of dissociation but decreases their strength.

In our opinion, the specific features of superacids mentioned above are due to the fact that the main factor determining their specific properties is the low energy of proton solvation by superacid molecules rather than the degree of dissociation. The goal of this paper is to use the *ab initio* quantum-chemical calculations to estimate the proton solvation energy in 100% sulfuric acid and to analyze the energy balance of its self-dissociation taking into account solvent effects.

We chose anhydrous sulfuric acid because it is the universally accepted standard of a superacid, and the corresponding value of the Hammet acidity function H_0 for it (–12) is usually taken as a minimum value for superacids. In addition, starting from the 1940s, concentrated sulfuric acid is widely used as a commercial catalyst for alkylation of isoalkanes by olefins. Therefore, the data on the energetics of the dissociation of anhydrous sulfuric acid and on the solvation of resultant protons are also of interest for understanding the formation mechanism and the nature of sulfuric acid-solvated alkylcarbenium ions, which are the active intermediates of hydrocarbon conversions catalyzed by sulfuric acid.

METHOD OF QUANTUM-CHEMICAL CALCULATIONS

In the calculation of the energy of proton solvation by liquid sulfuric acid, we used the experimental value of the proton affinity of sulfuric acid in the gas phase (172 kcal/mol [2]) and the energy of solvation of resulting $H_3SO_4^+$ ions with liquid sulfuric acid calculated by a quantum-chemical technique. The solvation energy was calculated in two steps. First, the structure and formation energy of the $[H_3SO_4^+ \cdot H_2SO_4]$ ion in the gas phase were calculated in the cluster approximation using the GAMESS program [3]; the geometry was completely optimized, and the corrections for the zero-point energy were taken into account with the 6-31++G** basis set. Liquid sulfuric acid was modeled by a continuum medium with a dielectric constant ε of 110. The additional energy of the electrostatic interaction of these ions with the surrounding molecules of liquid sulfuric acid contributing the solvation energy was evaluated by the PCM method [4] within the framework of the continuum model of solvation.

To verify the validity of the results obtained, the energy of solvation of HSO_4^- anions with liquid sulfuric acid was calculated in a similar manner. The value obtained was then used to estimate the self-dissociation energy of liquid sulfuric acid, which we compared with the experimental value of the heat of self-dissociation (+3.4 kcal/mol [5]). The calculated total energies and

Total energies, zero-point energies, and the contribution of the electrostatic interaction of the solvated ions into the solvation energy

Molecule or ion	Total energy in the gas phase, a.u.*	Zero-point energy, kcal/mol	Interaction energy in the gas phase, kcal/mol	Electrostatic contribution, kcal/mol	Total solvation energy, kcal/mol
H_2SO_4	–698.05985093	26.37	–	–	–
$[H_2SO_4 \cdot H_2SO_4]$	–1396.15073365	55.01	19.47	–	19.47
$H_3SO_4^+$	–698.34747237	33.77	–	–	–
HSO_4^-	–697.55276521	18.58	–	–	–
$[H_3SO_4^+ \cdot H_2SO_4]$	–1396.45381238	61.68	27.6	64.3	79.9
$[HSO_4^- \cdot H_2SO_4]$	–1395.68258801	47.64	41.2	50.8	80.0

* Calculations at the RHF/6-31++G** level.

energies of the interaction of HSO_4^- anions and $H_3SO_4^+$ cations with sulfuric acid in the gas phase and with liquid sulfuric acid are presented in the table.

RESULTS AND DISCUSSION

Our calculation showed that the formation of a symmetric $[H_3SO_4^+ \cdot H_2SO_4]$ cation with three equal hydrogen bonds with a molecule of sulfuric acid did not correspond to the local minimum on the potential energy surface (PES). A dimer with two equal short hydrogen bonds (1.818 Å) between two sulfate groups turned out to be the most stable complex (Fig. 1). The energy of its formation in the gas phase corrected for the zero-point energy was 27.6 kcal/mol. According to the estimates within the framework of the continuum model, the electrostatic interaction with surrounding molecules of liquid sulfuric acid contributed an additional 64.3 kcal/mol to the solvation energy.

To find the total energy of $H_3SO_4^+$ cation solvation by liquid sulfuric acid, the correction for the transfer of an acid molecule to the gas phase was subtracted from the calculated solvation energy. This correction can be set equal to the experimental value of the heat for 100% sulfuric acid evaporation that was found equal to 12 kcal/mol [6]. Thus, the total energy of $H_3SO_4^+$ cation solvation by liquid sulfuric acid was 79.9 kcal/mol.

The affinity of the proton to liquid sulfuric acid can then be determined from the following cycle:

$$H_2SO_{4\,l} \longrightarrow H_2SO_{4\,g} + 12\ \text{kcal/mol}$$

$$H_2SO_{4\,g} + H^+ \longrightarrow H_3SO^+_{4\,g} - 172\ \text{kcal/mol}$$

$$H_3SO^+_{4\,g} \xrightarrow{H_2SO_{4\,l}} H_3SO^+_{4\,l} - 79.9\ \text{kcal/mol}$$

$$H^+ + H_2SO_{4\,l} \longrightarrow H_3SO^+_{4\,l} - 239.9\ \text{kcal/mol.}$$

The value obtained was ~20 kcal/mol lower than the heat of proton hydration in aqueous solution (261 kcal/mol [7]).

To verify the accuracy of our quantum-chemical calculations, we also calculated the energy of self-dissociation for liquid sulfuric acid and compared it to an experimental value of +3.4 kcal/mol [5]. For this purpose, using the scheme similar to that used for the $H_3SO_4^+$ cation, we first determined the energy of interaction of HSO_4^- anions with one molecule of sulfuric acid in the gas phase. Then, using the continuum model, we evaluated the contribution of the additional energy of anion interaction with surrounding molecules of liquid sulfuric acid to the total solvation energy.

Figure 2 presents the structure of the most stable $[HSO_4^- \cdot H_2SO_4]$ complex formed by the interaction of an HSO_4^- anion with one sulfuric acid molecule. In this case, the HSO_4^- anion binds to a sulfuric acid molecule by two equal short hydrogen bonds with lengths of 1.66 Å and by the third, longer (2.05 Å) hydrogen bond with a smaller contribution to the energy of intermolecular interactions. The shorter lengths of two hydrogen bonds and the formation of the third hydrogen bond between the HSO_4^- anion and a sulfuric acid molecule

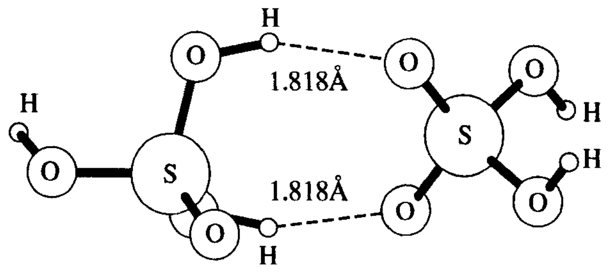

Fig. 1. Calculated structure of an $[H_3SO_4^+ \cdot H_2SO_4]$ cation.

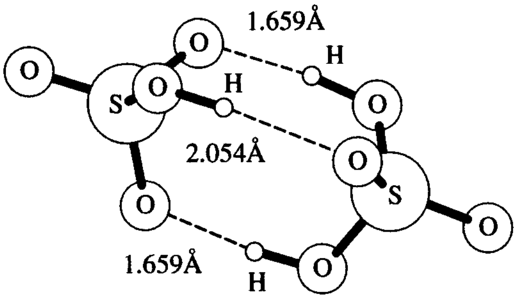

Fig. 2. Calculated structure of $[HSO_4^- \cdot H_2SO_4]$ anion.

undoubtedly point to the greater solvation energy of the anion as compared to the solvation energy of the $H_3SO_4^+$ cation. Indeed, the energy of HSO_4^- anion solvation by one molecule of the acid in the gas phase was found to be 41.2 kcal/mol, which is 13.6 kcal/mol higher than the solvation energy of the $H_3SO_4^+$ cation.

The additional contribution to the total solvation energy of HSO_4^- anions due to the electrostatic interaction of these ions with liquid sulfuric acid was calculated within the framework of the continuum model and found to be 50.8 kcal/mol. Thus, the total energy of HSO_4^- anion solvation corrected for the energy of hydrogen bond dissociation in liquid sulfuric acid was 80.0 kcal/mol.

To estimate the self-dissociation energy of liquid sulfuric acid, we used the experimental value for the self-dissociation energy for sulfuric acid in the gas phase, which is equal to 141 kcal/mol [8]. Then, taking into account the calculated solvation energies for $H_3SO_4^+$ cations and HSO_4^- anions, the balance of the self-dissociation for liquid sulfuric acid is as follows:

$$2H_2SO_{4\,l} \longrightarrow 2H_2SO_{4\,g} + 24\ \text{kcal/mol}$$

$$2H_2SO_{4\,g} \longrightarrow H_3SO^+_{4\,g} + HSO^-_{4\,g} + 141\ \text{kcal/mol}$$

$$H_3SO^+_{4\,g} \xrightarrow{H_2SO_{4\,l}} H_3SO^+_{4\,l} - 79.9\ \text{kcal/mol}$$

$$HSO^-_{4\,g} \xrightarrow{H_2SO_{4\,l}} HSO^-_{4\,l} - 80.0\ \text{kcal/mol}$$

$$2H_2SO_{4\,l} \longrightarrow H_3SO^+_{4\,l} + HSO^-_{4\,l} + 5.1\ \text{kcal/mol.}$$

Almost quantitative agreement of the calculated value with the experimental value obtained for the heat of self-dissociation indicates the high accuracy of our calculations.

An abnormally high chemical activity of protons in concentrated and anhydrous sulfuric acid was repeatedly noted in the literature [9–11]. A nonlinear growth of the Hammet acidity function observed for very concentrated sulfuric acid points to the peculiar properties of its protons. Our results naturally explain all these facts because the heat of proton hydration in 100% sulfuric acid, which is 20 kcal/mol lower than that in aqueous solutions, makes the chemical activity of protons much higher.

In connection with this, it should be emphasized that, although the solvation is a necessary condition for acid dissociation, it substantially decreases the chemical activity of protons. For example, it is well known that the electron affinity of a free proton is 13.6 eV, while the electron affinity of a hydrated proton in an aqueous solution is only several electron-volts. This is due to the fact that, after neutralization of the proton positive charge by the electron, the energy of proton hydration (–261 kcal/mol or 11.3 eV) transforms into the heat of water vapor condensation, which is only 9.8 kcal/mol per one H_2O molecule. Therefore, it is natural that the chemical properties of free protons have very little in common with those of hydrated protons. A 20-kcal/mol decrease in the proton solvation energy in 100% sulfuric acid as compared to aqueous solutions undoubtedly has a pronounced effect on the activity and chemical potential of protons since one pK_a unit corresponds to the energy difference of only ~1.5 kcal/mol at room temperature.

This conclusion is quite natural because protons are solvated by superacids much more weakly than by more basic water molecules. Thus superacids represent a compromise between the weakest possible solvation of protons and a rather high overall heat of proton and anion solvation, which is favorable for the heterolytic dissociation. This is possible because the energy of anion solvation by superacid molecules is higher than the heat of hydration of this anion in aqueous solutions. For example, the energy of HSO_4^- anion solvation by anhydrous sulfuric acid was calculated to be 80 kcal/mol, that is almost 10 kcal/mol higher than the heat of hydration for this ion in aqueous solutions. Thus, the value of the dissociation constant is not the determining factor for superacids, while their strength depends on the abnormally high chemical activity of protons due to their low solvation energy.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-03-32173.

REFERENCES

1. Cotton, F. and Wilkinson, J., *Advanced Inorganic Chemistry. A Comprehensive Text*, New York, 1965, pt. 2.
2. Do, K., Klein, T.P., Pomerening, C.A., *et al.*, *J. Am. Chem. Soc.*, 1998, vol. 120, no. 24, p. 6093.
3. Schmidt, W.W., Baldridge, K.K., Boatz, J.A., *et al.*, *J. Comput. Chem.*, 1993, vol. 14, no. 12, p. 1347.

4. Miertus, S., Scrocco, E., and Tomasi, J., *Chem. Phys.*, 1981, vol. 55, p. 117.
5. Gillespie, R.J., Robinson, E.A., and Solomons, C., *J. Chem. Soc.*, 1960, p. 4320.
6. Malin, K.M., Arkin, N.L., Boreskov, G.K., and Slin'ko, M.G., *Tekhnologiya sernoi kisloty* (Sulfuric Acid Technology), Moscow: Goskhimizdat, 1950, p. 570.
7. Bell, R.P., *The Proton in Chemistry*, London: Chapman and Hall, 1973.
8. Lias, S.G., Bartmess, J.E., Holmes, J.L., *et al.*, *J. Phys. Chem. Ref. Data*, 1988, vol. 17, suppl. 1.
9. Nekrasov, B.V., *Osnovy obshchei khimii* (Foundations of General Chemistry), Moscow: Khimiya, 1969, vol. 1, p. 518.
10. Hammett, L.P., *Physical Organic Chemistry*, New York: McGraw Hill, 1970.
11. Vinnik, M.I., *Usp. Khim.*, 1966, vol. 35, no. 11, p. 1922.