Choosing a solvation model for simulating reactions in KOH(KOBu\textsuperscript{t})/DMSO superbasic media

V B Kobychev
Laboratory of Quantum Chemical Modeling of Molecular Systems, Irkutsk State University, 664003, 1 Karl Marx St, Irkutsk, Russia
A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033, 1 Favorsky St, Irkutsk, Russia
E-mail: gimli@cc.isu.ru

Abstract. The ability of protocols based on the B2PLYPD/6-311+G**//B3LYP/6-31+G* method with various schemes for accounting for nonspecific solvation to reproduce C–H, N–H, O–H and S–H acidity in a dimethyl sulfoxide medium is considered. For a selected set of 20 compounds, typical reagents for reactions in superbasic media, the IEFPCM scheme with UFF cavity and $\alpha = 1.35$ multiplier yields better results than the popular SMD model.

1. Introduction
Modern advances in the chemistry of acetylene are largely associated with the use of media with increased basicity (superbasic media) of the type “hydroxide or alkoxide of an alkali metal – dimethyl sulfoxide” [1]. The use of such media made it possible to significantly expand the possibilities of classical acetylene reactions such as ethynylation, vinylation, and acetylene-allene rearrangement [2], and also led to the discovery of a number of new reactions. In particular, the recently discovered reaction of ketone vinylation formed the basis for an impressive variety of cascade transformations ensuring assemblies of complex heterocyclic systems [3].

Modeling such reactions by means of quantum chemistry contributes to a better understanding of the laws governing their course. Adequate models, methods, and protocols are required to reliably describe the mechanisms of chemical transformations in a superbasic environment.

We have recently proposed several models of the reaction center of the superbasic system [4]. The most complete of them considers an alkali metal cation surrounded by up to five explicitly included solvent molecules. The remaining part of the bulk solvent is taken into account within the polarizable continuum model. At the same time, it was shown that simpler models, namely the “monosolvate” one, which includes explicitly only one solvent molecule, and even the so-called “anionic”, which does not include the metal cation at all and takes into account only the effects of nonspecific solvation, are capable of providing thermodynamic and kinetic characteristics of the reactions under study that are close to those obtained using a more complete model.

When choosing the level of theory, we settled on the B2PLYP functional [5], which provides good performance with relatively low resource intensity. It is noteworthy that this functional successfully copes with the problems arising in the description of the reactions of acetylenes and ketones in the presence of bases, which are traditionally difficult for most popular functionals, as well as for the \textit{ab initio} MP2 approach, such as acetylene-allene rearrangement [6] or the aldol reaction of acetone [7].
The subject of this publication is the selection of a design scheme for describing the effect of a solvent. Over the years, we have used the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) proposed by Tomasi et al. [8], limiting our consideration to electrostatic contributions only. At the same time, a different version of IEFPCM proposed by Truhlar et al. [9] and known as SMD (Solvation Model based on the quantum mechanical charge Density), has become widespread. In addition to the electrostatic term, the SMD scheme includes cavitation, dispersion and repulsion energies. In the current version of Gaussian program suite, this scheme is the recommended choice for computing $\Delta G$ of solvation.

The SMD model has presented a good performance for challenging neutral molecules in water solvent. The advantages of this model for describing anions in non-aqueous solvents are not so obvious. Thus, Pliego and Riveros [10] found that for six nucleophilic substitution reactions involving different anions, the SMD model is not quite suitable for dipolar aprotic solvents, giving a root mean square error (RMS) of 5.6 kcal/mol, while the PCM method with atomic cavities, suggested by Pliego and Riveros [11], gives an RMS of only 3.2 kcal/mol.

A good test for the method's ability to describe both neutral and anionic systems in solution is the calculation of C–H, N–H, O–H and S–H acidities. Here we present the acidity estimates of compounds that are typical reagents, intermediates and products of the superbase-promoted reactions obtained using the classical PCM and SMD approaches.

2. Computational details

According to Pliego et al. [12], the calculation of the pKa value in DMSO solution can be undertaken through the use of the following proton-transfer reaction:

$$\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$$  \hspace{1cm} (1)

This approach is more adequate than using the direct ionization of the HA acid, because it does not require the value of the experimental solvation free energy of the H$^+$ ion [12]. Considering the general chemical equilibrium relationship one can obtain

$$p\text{K}_a(\text{HA}) = p\text{K}_a(\text{H}_2\text{O}) + \Delta G/2.303RT,$$

where $\Delta G$ is given by

$$\Delta G = G(A^-) + G(\text{H}_2\text{O}) - G(\text{AH}) - G(\text{OH}^-)$$ \hspace{1cm} (3)

$$G = G^* + \Delta G_{\text{sol}},$$ \hspace{1cm} (4)

The Gibbs free energy in the solution is renormalized to a concentration of 1 mol/L, taking into account the entropy losses during solvation.

$$G^* = H - TS_{\text{sol}},$$ \hspace{1cm} (5)

and that the entropy in the DMSO solution $S_{\text{sol}}$ was obtained from the entropy for ideal gas in the harmonic approximation $S_{\text{harm}}$ as follows [6]:

$$S_{\text{sol}} = 0.74 \cdot S_{\text{harm}} - 3.21 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$ \hspace{1cm} (6)

We have also used the experimental pK$\alpha$ value of 31.4 for water reported by Bordwell [13].

Two approaches were used to estimate the free energies in the gas phase. One of them, considered as a reference, was the composite CBS-Q//B3 precision method [14,15] implemented in the Gaussian 09 program suite [16].

Another approach, less resource-intensive and, therefore, more practical for studying the mechanisms of complex reactions, is based on the double-hybrid B2PLYP-D functional, including the dispersion correction [17]. In this approach, the structural parameters of the studied molecules and their anions were optimized in the gas phase using density functional theory (DFT) at the B3LYP [18,19] level of theory with the 6-31+G$^*$ basis set. The vibrational corrections to enthalpies and Gibbs free energies were calculated at the same level of theory (B3LYP/6-31+G$^*$) at a standard temperature 298.15 K. Furthermore, the energies at the stationary points were refined by using the B2PLYP-D functional in combination with the extended 6-311+G** basis set.

Calculations of solvation free energies within the SMD model were carried out at the B3LYP/6-311+G** level of the theory with radii and non-electrostatic terms for Truhlar and coworkers’ SMD...
solvation model. An alternative model (we will refer to this model as PCM, although strictly speaking the SMD model also belongs to this family) builds up the cavity using the Universal force field (UFF) radii, which places a sphere around each solute atom, with the radii scaled by the electrostatic scaling factor \( \alpha \). Along with the default value of \( \alpha = 1.1 \), we used the \( \alpha = 1.35 \) recommended [12, 20] for DMSO acidities. This value was optimized for the HF/6-31+G* calculations, and we tested it in combination with B3LYP/6-31+G* and B3LYP/6-311+G** approaches.

3. Results

The following types of acidity are of interest for describing the reactions in superbasic media: i) O–H acidities, primarily O–H acidities of alcohols (their assessment is extremely important for describing the comparative strength of superbases based on alkali metal hydroxides and alkoxides, as well as for describing the classical reactions of vinylation of alcohols with acetylene and its derivatives) and oximes, intermediates of cascade transformations with the participation of hydroxylamine and its derivatives; ii) C–H acidities of acetylene and its derivatives (associated with ethynylation reactions), ketones (vinylation reaction of ketones and further transformations of the resulting vinyl ketones) and ketimines (of particular interest in connection with studies of the possibility of their vinylation with acetylenes); N–H acidities of amines, pyrroles (primarily due to the unique reaction of the formation of vinylnpyrroles) and imines (unfortunately, for the latter, there are very few experimental data available) and iv) S–H acidities of sulfides (starting materials on the way to divinylsulfides).

3.1. Gas phase acidities

Calculated within the framework of two approaches, CBS-Q/B3 and B2PLYP-D/6-311+G**//B3LYP/6-31+G, the Gibbs free energies of proton detachment are collected in table 1. The Gibbs free energy of the proton in gas phase was assumed to be \(-6.29 \text{ kcal/mol} [21]\). Comparison of theoretical estimates with experimental ones shows that the CBS-Q/B3 method provides, as expected, “chemical” accuracy, and the mean absolute deviation (MAD) for it is close to 1 kcal/mol. The B2PLYP-D/6-311+G**//B3LYP/6-31+G* approach yields a slightly larger MAD, 1.44 kcal/mol. It can be seen, however, that the largest error exceeding 3 kcal/mol is contributed by CF_{3}CH_{2}OH and 2-indanone. Elimination of these two compounds reduces the MAD to 1.12 kcal/mol.

Table 1. Calculated gas phase acidities \( \Delta G_{\text{calc}} \) [kcal/mol] compared to experimental ones (taken from Ref. 21, unless otherwise indicated).

|          | Experiment \( \Delta G_{\text{calc}} \) | CBS-Q/B3 \( \Delta G_{\text{calc}} \) | Deviation | CBS-Q/B3 \( \Delta G_{\text{calc}} \) | Deviation | B2PLYP \( \Delta G_{\text{calc}} \) | Deviation |
|----------|--------------------------------------|----------------------------------|-----------|----------------------------------|-----------|----------------------------------|-----------|
| H_{2}O   | 383.74 ± 0.060 [23]                  | 385.4                            | 1.7       | 383.0                            | −0.8      |
| Methanol | 376.02 ± 0.62 [24]                  | 375.5                            | −0.5      | 373.9                            | −2.1      |
| t-BuOH   | 368.1 ± 1.1 [25]                    | 367.7                            | −0.4      | 367.4                            | −0.7      |
| PhOH     | 340.8 ± 1.9 [26]                    | 341.8                            | 1.0       | 339.7                            | −1.1      |
| CF_{3}CH_{2}OH | 354.1 ± 2.0 | 353.2                            | −0.9      | 350.2                            | −3.9      |
| Acetoxime| 359.1 ± 2.0                        | 360.9                            | 1.8       | 357.0                            | −2.1      |
| E-Acetophenone oxime | 346.3 [27] | 347.4                            | 1.1       | 343.7                            | −2.6      |
| Acetone  | 361.9 ± 2.0                        | 363.2                            | 1.3       | 362.1                            | 0.2       |
| Acetophenone | 354.5 ± 2.0 | 355.1                            | 0.6       | 355.4                            | 0.9       |
| 2-Indanone | 343.5 ± 2.0 | 341.4                            | −2.1      | 340.1                            | −3.4      |
| Aniline  | 360.91 ± 0.67 [28]                 | 360.6                            | −0.4      | 359.7                            | −1.2      |
| Pyrrole  | 350.9 ± 2.0                        | 351.1                            | 0.2       | 350.9                            | 0.0       |
| t-BuSH   | 346.2 ± 2.0                        | 344.8                            | −1.4      | 346.0                            | −0.2      |
| PhSH     | 333.8 ± 2.0                        | 332.5                            | −1.3      | 332.0                            | −1.8      |
| PhC≡CH   | 362.9 ± 2.0                        | 363.2                            | 0.3       | 362.4                            | −0.5      |
| Cyclopentadiene | 347.7 ± 2.0 | 345.7                            | −2.0      | 346.0                            | −1.7      |
| MAD      |                                    |                                  |           | **1.06**                         |           | **1.44**                         |           |
Unexpectedly, the CBS-Q/B3 precision approach predicts a large enough error for the abstraction of a proton from a water molecule. Such an error can cause a systematic underestimation of the $pK_a$ values calculated by Equations 2–5 by 1.2 units.

3.2. CBS-Q/B3 based acidities

To calculate DMSO acidities, we used several schemes for accounting for the effects of solvation: i) the B3LYP/6-311+G** SMD model (SMD); ii) the B3LYP/6-311+G** PCM with non-electrostatic terms included and scaling factor $\alpha = 1.35$ (PCM-LB); iii) same as PCM-LB, but taking into account electrostatic term only, as recommended in Ref. 12 (PCM-ES). The results of these calculations collected in table 2 together with the experimental data show that the SMD scheme gives significantly worse results (MAD = 3.25 $pK_a$ units) than the classical PCM approach (MAD = 2.26 and 2.18 $pK_a$ units for PCM-LB and PCM-ES, correspondingly). The largest error, reaching 7.7 and even 7.8 $pK_a$ units in the calculation with the SMD method, is associated with the C–H acidities of phenylacetylene and cyclopentadiene. After excluding these points, the MAD decreases to 2.6 units, but still remains greater than the error of the PCM-LB and PCM-ES schemes.

Table 2. CBS-Q/B3 based acidities obtained using various schemes (see text for notation) compared to experimental [29] ones. The values in parentheses were obtained using the experimental value of the water deprotonation energy in the gas phase.

|                          | Experiment | SMD   | PCM-LB | PCM-ES |
|--------------------------|------------|-------|--------|--------|
| Methanol                 | 29.0       | 30.4  | (31.6) | 31.1   | (32.3) |
| t-BuOH                   | 32.2       | 30.1  | (31.3) | 30.4   | (31.6) |
| PhOH                     | 18.0       | 13.4  | (14.6) | 14.3   | (15.5) |
| CF$_2$CH$_2$OH           | 23.5       | 21.8  | (23.0) | 21.1   | (22.3) |
| Acetoxime                | 25.2       | 23.3  | (24.5) | 24.3   | (25.5) |
| E-Acetophenone oxime     | 21.1       | 19.4  | (20.6) | 19.7   | (20.9) |
| Ph$_2$C=NOH              | 20.1       | 18.1  | (19.3) | 17.6   | (18.8) |
| Acetone                  | 26.5       | 26.2  | (27.4) | 26.8   | (28.0) |
| Acetophenone             | 24.7       | 23.8  | (25.0) | 24.1   | (25.3) |
| 2-Indanone               | 16.9       | 17.2  | (18.4) | 16.7   | (17.9) |
| Aniline                  | 30.6       | 25.3  | (26.5) | 28.4   | (29.6) |
| Ph$_2$C=NH               | 31.0       | 31.5  | (32.7) | 35.9   | (37.1) |
| Pyrrole                  | 23.0       | 16.0  | (17.2) | 19.6   | (20.8) |
| t-BuSH                   | 17.9       | 12.2  | (13.4) | 13.4   | (14.6) |
| PhSH                     | 10.3       | 5.7   | (6.9)  | 6.8    | (8.0)  |
| PhC=CH                   | 28.8       | 21.0  | (22.2) | 27.6   | (28.8) |
| Cyclopentadiene          | 18.0       | 10.3  | (11.5) | 15.1   | (16.3) |
| MAD                      | 3.25       | (2.61) | 2.26   | (1.71) | 2.18   | (1.68) |
| Mean error (ME)          | −3.0       | (−1.8) | −1.4   | (−0.2) | −1.3   | (−0.1) |

The values of the mean error (ME) show that all methods are characterized by an underestimation of the $pK_a$, which is largely due to the above error in the gas phase acidity of water. The use of the experimental value for the water deprotonation energy brings a significant improvement in the results for the PCM-LB and PCM-ES schemes, while the error of the SMD scheme is still large, and even after elimination of the problem values for phenylacetylene and cyclopentadiene the MAE of the SMD scheme is 0.4 units higher than that of the PCM circuit. Thus, the PCM scheme with a scaling factor $\alpha = 1.35$ seems to be more preferable for describing both neutral molecules and their anions in dimethyl sulfoxide.

The MAD value obtained for the PCM-LB scheme turns out to be twice as large as that found within the framework of a similar calculation scheme (CBS-Q/B3 for the gas phase and B3LYP/6-311+G** IEFPCM for the energy of solvation) by Khursan and Ovchinnikov [30] in their article,
focused on precision description of DMSO acidities. Note, however, that the authors of [30] used different scale factors $\alpha$ for various acids, and, in addition, the error of the $pK_a$ calculation was decreased by correlation allowances for each kind of C–H, O–H, N–H and S–H acids. In contrast, our goal is not obtaining the accurate $pK_a$ values, but a comparison of different schemes for calculating the solvation energies of neutral and anionic forms in a uniform manner.

### 3.3. B2PLYP based acidities

In this series, the Gibbs free energy in the gas phase was calculated using the B2PLYP-D/6-311+G**//B3LYP/6-31+G* method. To calculate the solvation energies, in addition to the SMD, PCM-LB and PCM-ES schemes described above, we used i) the PCM-SB scheme, similar to PCM-LB, but with a reduced basis set 6-31+G*, and ii) the PCM-D scheme, also using the 6-31+G* basis set, the default in G09 value $\alpha = 1.10$, and taking into account only the electrostatic component.

| Table 3. B2PLYP/6-311+G**/B3LYP/6-31+G* based acidities obtained using various schemes (see text for notation) compared to experimental [29] ones. |
|---------------------------------|---------|--------|--------|--------|--------|--------|
| **Experiment**                  | **SMD** | **PCM-LB** | **PCM-ES** | **PCM-SB** | **PCM-D** |
| Methanol                        | 29.0    | 30.4   | 31.0   | 31.1   | 31.1   | 32.4   |
| t-BuOH                          | 32.2    | 31.3   | 31.7   | 31.7   | 31.8   | 33.4   |
| PhOH                            | 18.0    | 13.6   | 14.4   | 14.4   | 14.7   | 18.3   |
| C2F5CH2OH                       | 23.5    | 21.1   | 20.5   | 20.5   | 20.5   | 23.6   |
| Acetoxime                       | 25.2    | 22.3   | 23.3   | 23.5   | 23.4   | 25.6   |
| E-Acetophenone oxime            | 21.1    | 18.3   | 18.6   | 18.8   | 18.7   | 22.5   |
| Ph3C=NOH                        | 20.1    | 16.8   | 16.3   | 17.3   | 16.4   | 21.5   |
| Acetone                         | 26.5    | 27.4   | 27.9   | 28.5   | 28.1   | 31.5   |
| Acetophenone                    | 24.7    | 25.7   | 26.0   | 26.5   | 26.2   | 30.0   |
| 2-Indanone                      | 16.9    | 17.9   | 17.4   | 17.8   | 17.6   | 22.4   |
| Aniline                         | 30.6    | 26.6   | 29.6   | 29.8   | 29.7   | 33.5   |
| Ph3C=N–CH2–Ph                   | 24.3    | 21.5   | 20.9   | 22.2   | 21.1   | 28.1   |
| Ph3C=NH                         | 31.0    | 32.3   | 36.9   | 37.0   | 37.0   | 40.0   |
| Pyrrole                         | 23.0    | 17.6   | 21.2   | 21.3   | 21.5   | 25.2   |
| t-BuSH                          | 17.9    | 14.9   | 16.1   | 16.3   | 16.3   | 18.8   |
| PhSH                            | 10.3    | 7.2    | 8.3    | 8.5    | 8.5    | 12.2   |
| PhC=C=CH                        | 28.8    | 22.3   | 28.9   | 28.8   | 29.2   | 31.5   |
| Cyclopentadiene                 | 18.0    | 12.3   | 17.1   | 17.5   | 17.6   | 21.4   |
| **MAD**                         | **2.93**| **2.08**| **1.95**| **2.01**| **2.83** |

The results presented in table 3 show that all three PCM schemes using a factor of $\alpha = 1.35$ give similar acidities for the test compounds, which are in reasonable agreement with the experimental data. An unfortunate exception is 1,1-diphenylmethanimine, for which the calculated $pK_a$ value is 6 units higher than the experimental one. In the case of PCM-D, which uses a default multiplier, this error reaches 9 units, while the SMD scheme with the same cavity shape has no difficulty with this molecule. The exclusion of 1,1-diphenylmethanimine from the test set reduces the MAD value significantly, for example, for the PCM-ES the MAD decreases to 1.7 $pK_a$ units.

### 4. Discussion

The above results allow us to recommend the B2PLYP-D/6-311+G**//B3LYP/6-31+G* method in combination with the calculation of solvation energies in the framework of the continuous model (PCM)-B3LYP/6-311+G** with a scaling factor $\alpha = 1.35$ and taking into account only the electrostatic component (PCM-ES) to simulate the reactions in KOH(KOBu)/DMSO superbasic media. In conclusion, it is appropriate to make some remarks about its applicability to describe different classes of compounds exhibiting different types of acidity.
4.1. O–H acidities
Due to the specificity of the reactions under study, we limited the consideration of O–H acidities to alcohols and oximes.

Note that the chosen approach qualitatively correctly reproduces the relative acidities in the series pK_a(CH_3OH) < pK_a(H_2O) < pK_a(Bu'OH). This order is incorrectly reproduced in most approaches using the PCM scheme [12,20,30], with all the variety of methods for calculating the energy in the gas phase, methods for constructing a cavity, choosing thermodynamic relations, etc. Thus, in the case of calculations based on CBS-Q//B3, both SMD and PCM predict less acidity for methanol than for tert-butanol (see table 2). When using the experimental value of the water deprotonation energy, the calculated acidity of CH_3OH is even lower than the acidity of water. Most likely, the case of our approach is fortunate error compensation.

In the case of trifluoroethanol, a significant error is caused by the error in determining the energy of proton abstraction in the gas phase. At the same time, the large deviation in the case of more acidic phenol is most likely due to the neglect of the effects of specific solvation. Pliego demonstrated that with increasing acidity, the overestimation of this acidity in the PCM continual model increases [31]. Explicit consideration of even one solvent molecule often helps to improve the situation significantly.

The acidity of oximes in the proposed model is also somewhat overestimated. It is interesting to note that the inclusion of non-electrostatic contributions into consideration only increases the deviation of pK_a from the experimental values; this is especially pronounced in the case of benzophenone oxime.

4.2. C–H acidities
The proposed approach reproduces well the acidity of phenylacetylene. This circumstance is important, in particular, in assessing the preference of the competing reactions of ethynylation and vinylation of ketones and ketimines, as well as in the description of Michael reactions with the participation of the ethynide ion.

The acidity of ketones is somewhat overestimated relative to the experimental values. Accounting for non-electrostatic interactions (PCM-LB) improves the situation significantly. Note that the use of the default PCM procedure proposed in G09 with the standard scaling factor α = 1.10 leads to significant errors exceeding 5 pK_a units.

Unfortunately, N-benzyl-1,1-diphenylmethanimine is the only representative of N-benzyl ketimines for which the experimental pK_a value is available. The lack of experimental data on the deprotonation energy of N-benzyl-1,1-diphenylmethanimine in the gas phase does not allow us to unambiguously judge the reasons for the overestimation of its calculated acidity. It is noteworthy that, as in the case of oximes, the inclusion of non-electrostatic contributions into consideration only increases the deviation of pK_a from the experimental values. Nevertheless, reasonable agreement between calculation and experiment gives hope that the proposed approach can be used to study the recently discovered reaction of α-C–H vinylation of N-benzyl ketimines with acetylene gas yielding (E,Z)-2-azadienes [32].

Cyclopentadiene is an example of a system in which the anion is highly stabilized by conjugation. The C–H acidity of this molecule turns out to be a "stumbling block" for the default SMD and PCM-D procedures, while the proposed scheme copes well with this problem.

4.3. N–H acidities
Again, both SMD and PCM-D fail in assessing the acidities of pyrrole and aniline, while PCM-ES gives acceptable ratings for them. The 1,1-diphenylmethanimine case discussed above is the only example where the approach used is clearly unsuccessful. Unfortunately, 1,1-diphenylmethanimine is the only example of an imine for which the pK_a value has been experimentally determined.

4.4. S–H acidities
The proposed approach satisfactorily reproduces the high acidity of tert-butylthiol and thiophenol with an error less than 1.8 pK_a units.
5. Conclusion

The results obtained show that the B2PLYP-D/6-311+G**/B3LYP/6-31+G* method in combination with the estimation of the solvation energies within the (IEFPCM)-B3LYP/6-311+G** scheme with the scale factor $\alpha = 1.35$ (both with and without non-electrostatic interactions included) provides a balanced description of both neutral molecules and their anions in dimethyl sulfoxide solution and can be recommended for studying the mechanisms of reactions occurring in superbasic KOH/KOBu t /DMSO media.

Acknowledgments

This study was supported by Grant No. FZZE-2020-0025 from the Ministry of Science and Higher Education of the Russian Federation.

References

[1] Trofimov B 2002 Acetylene and its Derivatives in Reactions with Nucleophiles: Recent Advances and Current Trends Curr. Org. Chem. 6 1121–62
[2] Gusarova N K, Mikhail'eva A I, Shmidt E Y and Mal'kina A G 2013 Chemistry of Acetylene. New Chapters ed M P Egorov (Novosibirsk: Science)
[3] Trofimov B A and Schmidt E Y 2018 Acetylenes in the Superbase-Promoted Assembly of Carbocycles and Heterocycles Acc. Chem. Res. 51 1117–30
[4] Vitkovskaya N M, Orel V B, Kobylev V B, Bobkov A S, Absalyamov D Z and Trofimov B A 2020 Quantum-chemical models of KOH/KOBu t /DMSO superbasic systems and mechanisms of base-promoted acetylene reactions Int. J. Quantum Chem. 120 e26158
[5] Grimme S 2006 Semiempirical hybrid density functional with perturbative second-order correlation J. Chem. Phys. 124 034108
[6] Vitkovskaya N M, Kobylev V B, Bobkov A S, Orel V B, Schmidt E Y and Trofimov B A 2017 Nucleophilic Addition of Ketones To Acetylenes and Allenes: A Quantum-Chemical Insight J. Org. Chem. 82 12467–76
[7] Wheeler S E, Moran A, Pieniazek S N and Houk K N 2009 Accurate reaction enthalpies and sources of error in DFT Thermochemistry for aldol, mannich, and a-aminoxylation reactions J. Phys. Chem. A 113 10376–84
[8] Tomasi J, Mennucci B and Cancès E 1999 The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level J. Mol. Struct. THEOCHEM 464 211–26
[9] Marenich A V., Cramer C J and Truhlar D G 2009 Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions J. Phys. Chem. B 113 6378–96
[10] Miguel E L M, Santos C I L, Silva C M and Pliego Jr. J R 2016 How Accurate is the SMD Model for Predicting Free Energy Barriers for Nucleophilic Substitution Reactions in Polar Protic and Dipolar Aprotic Solvents? J. Braz. Chem. Soc. 27 2055–61
[11] Pliego J R and Riveros J M 2002 Parametrization of the PCM model for calculating solvation free energy of anions in dimethyl sulfoxide solutions Chem. Phys. Lett. 355 543–6
[12] Almerindo G I, Tondo D W and Pliego J R J 2004 Ionization of Organic Acids in Dimethyl Sulfoxide Solution: A Theoretical Ab Initio Calculation of the $pK_a$ a Using a New Parametrization of the Polarizable Continuum Model J. Phys. Chem. A 108 166–71
[13] N. Olmstead W, Margolin Z and G. Bordwell F 2002 Acidities of water and simple alcohols in dimethyl sulfoxide solution J. Org. Chem. 45 3295–9
[14] Montgomery J A, Frisch M J, Ochterski J W and Petersson G A 1999 A complete basis set model chemistry. VI. Use of density functional geometries and frequencies J. Chem. Phys. 110 2822–7
[15] Montgomery J A, Frisch M J, Ochterski J W and Petersson G A 2000 A complete basis set model chemistry. VII. Use of the minimum population localization method J. Chem. Phys.
112 6532–42

[16] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Petersson G A, Nakatsuji H, et al 1916 Gaussian 09, Revision C.01

[17] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comput. Chem. 27 1787–99

[18] Becke A D 1988 Density-functional exchange-energy approximation with correct asymptotic behavior Phys. Rev. A 38 3098–100

[19] Lee C, Yang W and Parr R G 1988 Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density Phys. Rev. B 37 785–9

[20] Fu Y, Liu L, Li R Q, Liu R and Guo Q X 2004 First-Principle Predictions of Absolute pKa’s of Organic Acids in Dimethyl Sulfoxide Solution J. Am. Chem. Soc. 126 814–22

[21] Fifen J J, Dhaouadi Z and Nsangou M 2014 Revision of the Thermodynamics of the Proton in Gas Phase J. Phys. Chem. A 118 11090–7

[22] Bartmess J E, Scott J A and McIver, Robert T. J 1979 Scale of acidities in the gas phase from methanol to phenol J. Am. Chem. Soc. 101 6046–56

[23] Smith J R, Kim J B and Lineberger W C 1997 High-resolution threshold photodetachment spectroscopy of OH Phys. Rev. A 55 2036–43

[24] Nee M J, Osterwalder A, Zhou J and Neumark D M 2006 Slow electron velocity-map imaging photoelectron spectra of the methoxide anion J. Chem. Phys. 125 014306

[25] Ramond T M, Davico G E, Schwartz R L and Lineberger W C 2000 Vibronic structure of alkoxy radicals via photoelectron spectroscopy J. Chem. Phys. 112 1158–69

[26] Angel L A and Ervin K M 2004 Competitive threshold collision-induced dissociation: Gas-phase acidity and O-H bond dissociation enthalpy of phenol J. Phys. Chem. A 108 8346–52

[27] Badal M M R and Mishima M 2010 Gas-Phase Acidities of Acetophenone Oximes. Substituent Effect and Solvent Effects Bull. Chem. Soc. Jpn. 83 58–65

[28] Wren S W, Vogelhuber K M, Ichino T, Stanton J F and Lineberger W C 2012 Photoelectron Spectroscopy of Anilinide and Acidity of Aniline J. Phys. Chem. A 116 3118–23

[29] Bordwell F G 1988 Equilibrium acidities in dimethyl sulfoxide solution Acc. Chem. Res. 21 456–63

[30] Khursan S L and Ovchinnikov M Y 2014 The pKa theoretical estimation of C-H, N-H, O-H and S-H acids in dimethylsulfoxide solution J. Phys. Org. Chem. 27 926–34

[31] Pliego J R J and Riveros J M 2001 The Cluster – Continuum Model for the Calculation of the Solvation Free Energy of Ionic Species J. Phys. Chem. A. 105 7241–7

[32] Bidusenko I A, Schmidt E Y, Protusk N I, Ushakov I A, Vashchenko A V., Afonin A V. and Trofimov B A 2020 KOBu t /DMSO-Mediated α-C–H Vinylation of N -Benzy1 Ketimines with Acetylene Gas: Stereoselective Synthesis of ( E , Z )-2-Azadienes Org. Lett. 22 2611–4