

Reactions of ketones with aromatics in acid media. The effect of trifluoromethyl groups and the acidity media. A theoretical study

Ulises Jiménez Castillo · Mikhail G. Zolotukhin ·
Lioudmila Fomina · Daniel Romero Nieto ·
Lilian Olivera Garza · Serguei Fomine

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Abstract The reactions of acetone, 2,2,2-trifluoroacetone and hexafluoroacetone in methanesulfonic (MSA) and triflic acids (TFSA) with benzene have been studied at M06-2X/6-311+G(d,p) level using cluster-continuum model, where the carbonyl group is explicitly solvated by acid molecules. The introduction of a trifluoromethyl group into the ketone structure reduces the activation energy of the tetrahedral intermediates formation due to an increase of the electrophilicity of the carbonyl group and raises the activation and the reaction energies of the C-O bond cleavage in formed carbinol due to the destabilization of the corresponding carbocation. The introduction of the second trifluoromethyl group inhibits the hydroxyalkylation reaction due to a very strong increase of the reaction and activation energies of the C-O bond cleavage which becomes the rate determining step. The most important catalytic effect of TFSA compared to MSA is not the protonation of the ketone carbonyl, but the reduction of the activation and reaction energies of the carbinol C-O bond cleavage due to better protosolvation properties. Even for TFSA no complete proton transfer to carbonyl oxygen has been observed for free ketones. Therefore, the protonation energies

of free ketones cannot be considered as a measure of ketone reactivity in the hydroxyalkylation reaction.

Keywords DFT · Hydroxyalkylation · Protonation · Superacid · Trifluoromethyl group

Introduction

The reaction of ketones with aromatics in acid media is known as hydroxyalkylation reaction [1, 2]. Depending on the monomer structures and the reaction conditions, an alcohol, a diaryl-compound or a mixture of those can be obtained. Although this reaction is often limited to activated, electron-rich arenes, ketones bearing electron withdrawing groups may react with benzene and even deactivated arenes giving derivatives of tetrasubstituted methanes in high yield. Thus, Kray and Rosser reported on trifluoromethanesulfonic acid (TFSA) catalyzed condensation of 2,2,2-trifluoroacetophenone with aromatic substrates affording diaryl-derivatives with moderate yield [3].

The concept of superelectrophilic activation proposed by Nobel Prize winner Olah and co-workers to explain the high reactivities of electrophilic species in superacidic media [4], and its application for hydroxyalkylation reactions turned out to be remarkably successful. Numerous hydroxyalkylation reactions have been carried out using superacids, mostly (TFSA) as catalysts or as a reaction medium [5–8]. Non substituted and substituted trifluoromethyl ketones were found to react smoothly with benzene and substituted arenes in TFSA at room temperature to give diaryl compounds [9]. Klumpp recently reported on unusual chemo-, regio-, and stereoselectivities in TFSA catalyzed reactions of some trifluoromethylketones with aromatics [10]. High efficiency of polymer-forming superacid catalyzed polyhydroxyalkylations

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U. J. Castillo · M. G. Zolotukhin · L. Fomina · L. O. Garza ·
S. Fomine (✉)

Instituto de Investigaciones en Materiales Universidad
Nacional Autónoma de México,
Apartado Postal 70-360, CU, Coyoacán,
México DF 04510, México
e-mail: fomine@servidor.unam.mx

D. R. Nieto
University of Trieste,
Via Valerio 10,
34127 Trieste, Italy

involving trifluoromethyl aryl ketones and aromatics have allowed for the variety of new polymers with trifluoromethyl groups and promising gas-separating properties [11–14].

An interesting and rear possibility to control the degree of branching of hyperbranched polymers by means of the acidity of the reaction medium in the course of self condensation of 2,2,2-trifluoro-1-[4-(4-phenoxyphenoxy)phenyl] ethanone was demonstrated [15]. An intensive research in the area of superacid catalyzed reactions of trifluoromethyl ketones, new products and opportunities stimulated theoretical studies of these reactions [12, 16–22].

The electron-withdrawing groups enhance the electrophilicity of the carbonyl center, decreasing the LUMO energy of carbonyl component. At the same time the basicity of the carbonyl oxygen is declined and stronger acids are required for the protonation of the carbonyl group. For instance, 2,2,2-trifluoroacetophenone reacts smoothly in $\text{CF}_3\text{SO}_3\text{H}$ (triflic acid, TFSA) with biphenyl giving a high molecular weight polymer, however, the reaction does not advance in methanesulfonic acid (MSA) [11]. Similar situation holds for 2,2,2-trifluoroacetone (TFA) [23]. Thus, the calculations have shown that the Gibbs free energies of the protonation of 2,2,2-trifluoroacetophenone and acetophenone in TFSA are of 7.8 and -6.8 kcal/mol, respectively.[16] Hexafluoroacetone (HFA), however, does not react at all with biphenyl even in TFSA [13, 24]. This fact might be explained by the very positive free Gibbs protonation energy of HFA (32.4 kcal/mol) impeding the formation of an active protonated species [16]. The recent experimental proofs of the HFA reactivity [25], however, suggest that a simple picture of the protonated ketone as a reactive species is not totally correct. To clarify this point we decided to carry out a detailed computational study of the reaction energy profiles for the reactions of acetone, TFA and HFA with benzene to reveal the effect of the trifluoromethyl group and the acidity media on the reactivity of ketones in the reaction of hydroxyalkylation using a solvation model with explicit solvent molecules for the inner solvation sphere of the ketone molecule.

Computational details

A flexible cluster-continuum solvation model has been used for the solvent modeling, where the inner solvation sphere contains explicit solvent molecules whereas the outer sphere is modeled using SMD modification of polarizable continuum model [26]. This complex model has been shown to be superior to any continuum model [27]. For all calculations the Gaussian 09 suit of programs has been used [28]. A modified method successfully used for the modeling of hydroxyalkylation reaction in TFSA, MSA and sulfuric acid media has been used for the calculations [23]. Instead of the

originally used PBE0 functional the M06-2X functional has been used with the 6-311+G(d,p) basis set. It has been shown, that the M06-2X functional reproduces much better the thermodynamics and especially the barrier heights compared to PBE0 [29]. The calculation of the aqueous pK_a of acetic at 298.15 K using the M06-2X functional (4.16) is in very good agreement with experiment (4.76) [30]. To test the performance of M06-2X/6-311+G(d,p) model we estimated gas phase proton affinities for acetone and TFA and compared them with available experimental data [31]. The calculated and experimentally determinate proton affinities were found to be 193.6 and 194.2 kcal/mol respectively, for acetone and 170.0 and 173.0 kcal/mol for TFA, respectively.

For the inner solvation sphere the number of explicit molecules was equal to the number of the lone pairs at oxygen atoms; two for ketones and three for carbinols. For the outer solvation sphere SMD continuous model was used as implemented in Gaussian 09, (dielectric constant of 77.4 and solvent radius of 2.60 Å were used for TFSA) while for MSA the dielectric constant of 70.0 and the solvent radius of 2.34 Å were applied. All the geometries were fully optimized without imposing any symmetry restrictions and frequency calculations were ran to insure that a ground state (0 imaginary frequencies) or a transition state (1 imaginary frequency) is found. The frequency calculations data were used for calculations of the reaction thermochemistry.

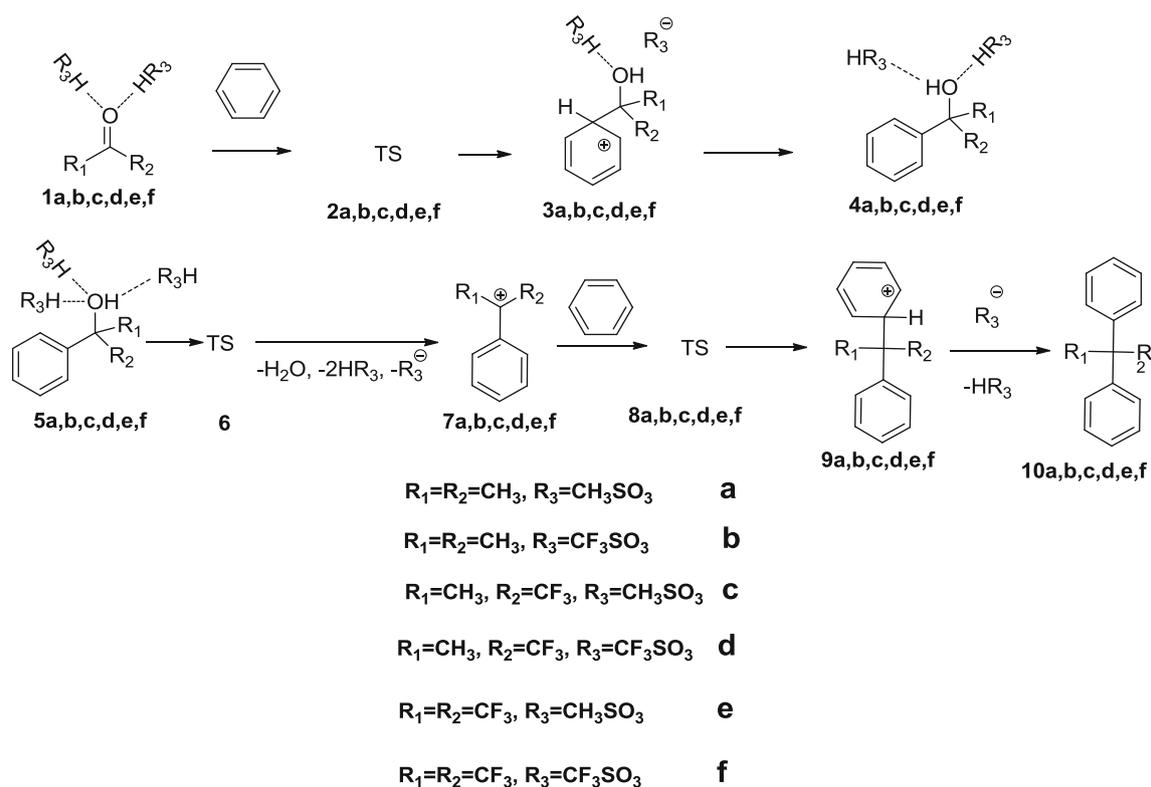
Results and discussion

The schematic representation of the reaction mechanism for the acid mediated hydroxyalkylation reaction between benzene and ketones is shown in Scheme 1. The solvated ketone **1** forms solvated tetrahedral intermediate **3**, passing through the transition state **2**. This step is considered to be the rate limiting step of the aromatic electrophilic substitution [32]. The tetrahedral intermediate is then aromatized producing solvated carbinol (**4** (solvated with two acid molecules) and **5** (three acid molecules)).

The next step is the cleavage of carbinol C-O bond to give carbocation **7**. The carbocation **7** reacts with another benzene molecule to generate tetrahedral intermediate **9** through the transition state **8** giving the final product **10** after the aromatization. The standard Gibbs free energies of activation and reaction of each elementary step have been determined to get a deeper insight into the reactivity of selected ketones.

The reaction of acetone with benzene in MSA

Figures 1 and 2 show the optimized geometry of explicitly solvated intermediates **1a-5a**. In the case of solvated acetone **1a** the distances between the carbonyl group oxygen and



Scheme 1 Elementary steps in the mechanism of the hydroxyalkylation reactions studied

MSA protons (1.625 Å) are equal, suggesting strong hydrogen bond, not a protonation. According to the calculations the complete proton transfer occurs in the transition state **2a**, where one proton is transferred to the carbonyl oxygen while the other one forms a strong hydrogen bond with O-H distance of 1.54 Å. Figure 4 shows the free Gibbs energy profile for the reaction of solvated acetone **1a** with benzene in MSA. As seen, in this particular case the formation of the first tetrahedral intermediate **3a** is the rate limiting step with the free Gibbs activation energy of 36.6 kcal/mol.

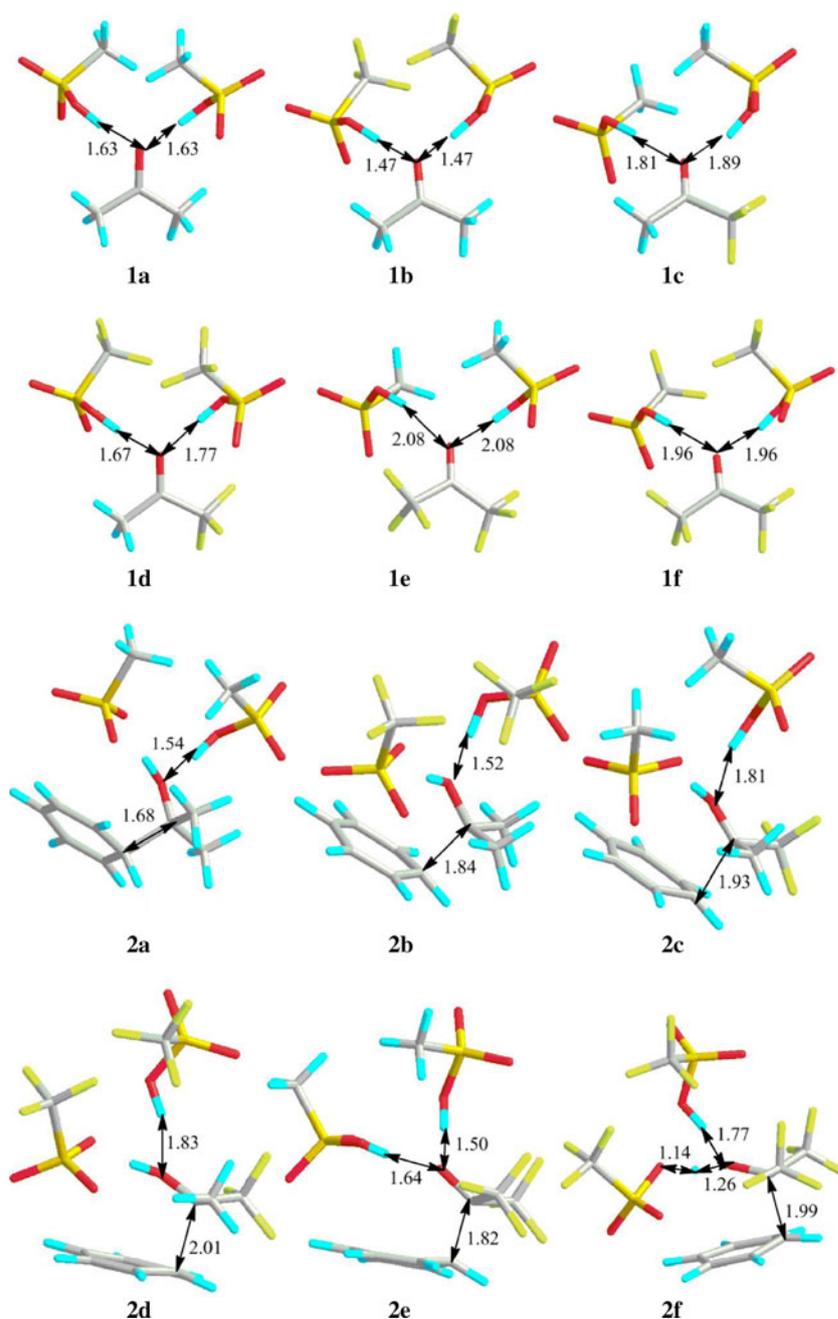
The carbonyl oxygen in the tetrahedral intermediate **3a** becomes almost diprotonated even in MSA due to the increase of its basicity. Thus, the distances O-H between acid protons and the tetrahedral intermediate oxygen are of 0.99 and 1.41 Å, respectively. The aromatization of **3a** produces a carbinol, represented by two models **4a** and **5a**, where the oxygen atom is protonated by two or three explicit MSA molecules, respectively. The difference between those two models essentially consists in a slightly larger C-O bond and a significantly larger O-H distance between acid protons and carbinol oxygen in the case of **5a**. Therefore, the explicit solvation of all available lone electron pairs is of importance. The heterolytic cleavage of C-O bond in **5a** leads to the buildup of the electron density at oxygen, resulting in stronger protosolvation of the carbinol oxygen in the transition state **6a** (Fig. 3). The Gibbs free activation energy for the formation of the carbocation **7a** is less than half of that

for the formation of **3a**. The second substitution requires 22.0 kcal/mol to form the tetrahedral intermediate **9a**. After the aromatization the final product **10a** is formed with the total free Gibbs reaction energy of -6.5 kcal/mol.

The reaction of acetone with benzene in TSFA

The use of TFSA as a solvent causes remarkable changes in the reaction energy profile compared to MSA, reducing significantly the free Gibbs activation energies of all reaction steps where the solvation of the carbonyl oxygen is involved. On the other hand, the free Gibbs activation energy of the second step remains almost unchanged (Fig. 4). Comparing the geometry of acetone molecule solvated with TFSA (**1b**) with that solvated with MSA (**1a**) (Fig. 1) it can be noticed that the distance between the carbonyl oxygen and TFSA protons is much shorter being only of 1.47 Å, which can be considered as a very tight hydrogen bond, not a diprotonation. A similar difference is noted for the transition state **2b** where the carbonyl oxygen is protonated and the second proton forms a tight hydrogen bond with O-H distance of 1.52 Å, 0.02 shorter than in that **2a**, revealing a better protosolvation of **2b** compared to **2a**. Unlike **3a**, the tetrahedral intermediate **3b** is clearly diprotonated in TFSA with O-H distances of 1.02 Å for two acid protons. The aromatization of **3a** produces a carbinol, represented by two models **4b** and **5b**, where oxygen is

Fig. 1 M06-2X/6-311+G(d,p) optimized geometry of optimized structures 1 and 2



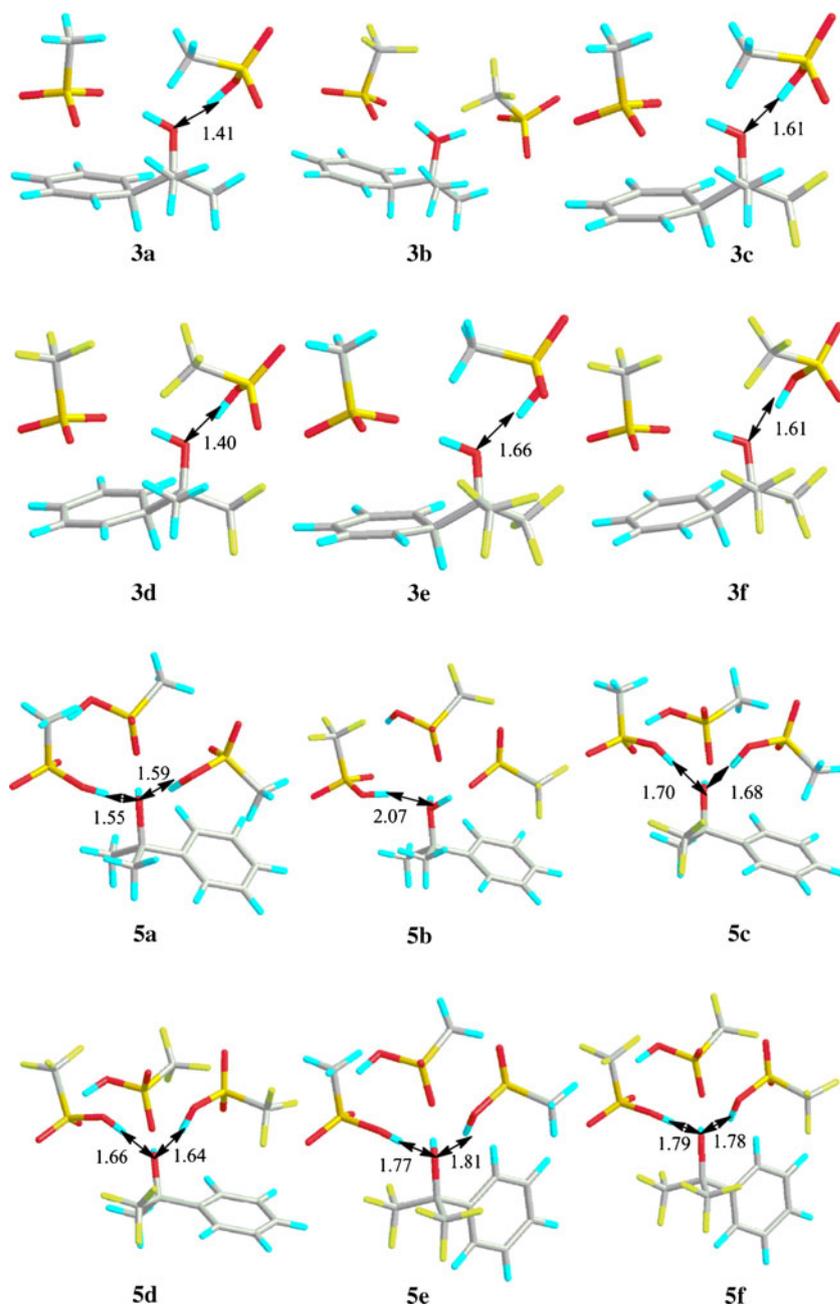
protonated by two and three explicit MSA molecules, respectively. When comparing **5a** and **5b** a remarkable difference can be seen due to better protosolvation of **5b** (Fig. 2). The C-O carbinol bond is elongated from 1.47 Å for **5a** to 1.51 Å for **5b**. This results in much lower free Gibbs activation energy of carbocation **7b** formation (3.9 vs. 16.6 kcal/mol, Fig. 4). The difference reflects better protosolvation of carbinol oxygen in the transition state **6b**, where the third proton forms a very tight hydrogen bond (the O-H distance is 1.45 Å against 1.54 for **6a**, Fig. 3). The total free Gibbs reaction energy is not affected significantly by the media acidity being only slightly more negative for TFSA,

−7.5 kcal/mol. Therefore, the acidity of the media affects mostly the reaction kinetics and not the thermodynamics. The most significant difference between the effect of MSA and TFSA on the reaction of acetone with benzene is a drastic decrease of the free Gibbs activation energy of the carbocation **7** formation.

The reaction of 2,2,2-trifluoroacetone with benzene in MSA

As has been shown earlier the introduction of the electron withdrawing groups reduces the activation energy of the tetrahedral intermediates formation [12]. This effect can be

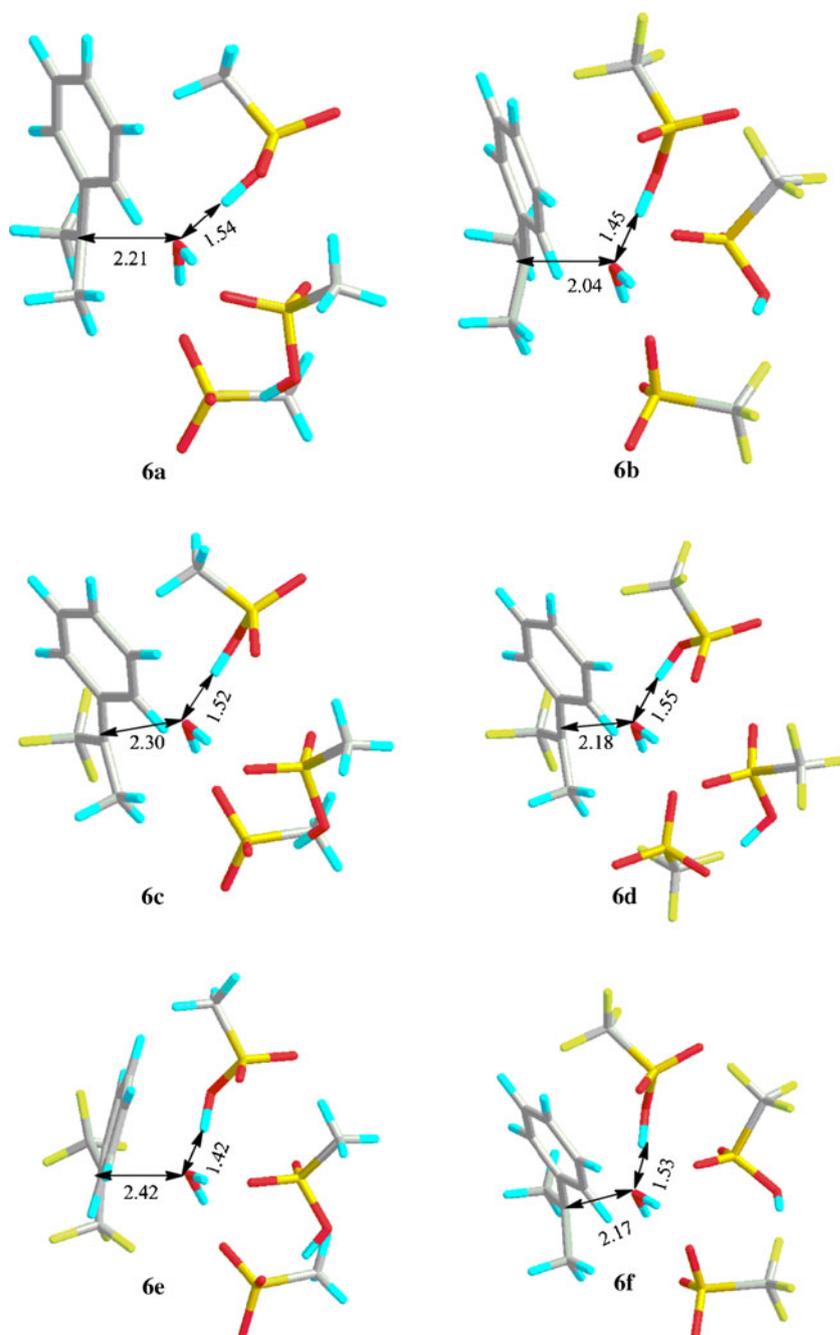
Fig. 2 M06-2X/6-311+G(d,p) optimized geometry of optimized structures **3** and **5**



noticed comparing Figs. 4 and 5. The free Gibbs activation energy formation of **3c** decreases by 7–8 kcal/mol compared to **3a**. At the same time the total free Gibbs reaction energy decreases from -6.5 kcal/mol for acetone to -22.8 kcal/mol. This change is related with the poorer protosolvation of TFA carbonyl compared to that of acetone. When comparing geometries of acetone and TFA solvated in MSA (**1a** and **1c**, respectively) (Fig. 1), it can be seen that the distances between carbonyl oxygen and MSA protons are about 0.2 Å longer in **1c**. In fact, in all cases the corresponding distances are longer for TFA due to the electron withdrawing effect of CF_3 group. The most important difference, however, is a strong increase of the free Gibbs reaction and activation

energies of carbocation **7c** formation, from 16.6 to 28.0 kcal/mol for the activation, and from 8.1 to 18.7 kcal/mol for the reaction energy. In fact, the free Gibbs activation energy of **7c** formation becomes almost identical to that of the tetrahedral intermediate **3c** formation. This effect is due to CF_3 group which destabilizes the carbocation raising the reaction and activation energies. The difference in the solvation energies of the carbinol oxygen seems not to be as important, since the C-O distances in the transition states of **6a** and **6c** (2.20 and 2.30 Å, Fig. 3) are large, thus decreasing the inductive effect of CF_3 group. This follows from the very close distances between the carbinol oxygen and the acid protons (Fig. 3). It can be suggested analyzing the

Fig. 3 M06-2X/6-311+G(d,p) optimized geometry of transition states 6



reaction energy profile (Fig. 5) that low reactivity of TFA in MSA is related not only to the high activation energy of the tetrahedral intermediate **3c** formation but also to the high activation and the reaction energies of the carbocation **7c** formation.

The reaction of TFA with benzene in TFSA

Unlike MSA, the reaction of TFA with aromatics in TFSA gives high molecular weight polymers [23]. Comparing the reaction energy profiles obtained for MSA and TFSA (Fig. 5) it can be noticed that the most important difference between

them is a strong decrease of the free Gibbs activation and reaction energy formation for carbocation **7**; confirming the hypothesis that this step is the crucial one for the reactivity of TFA in the polymer forming reactions. Similar to acetone, the use of TFSA instead of MSA as a reaction media results in the decrease of the free Gibbs activation energies for the steps involving the carbonyl oxygen due to better protosolvation properties of TFSA compared to that of MSA. Similar to acetone, in all cases the acid proton and the carbonyl oxygen distances are shorter for TFSA (Figs. 1, 2 and 3).

Higher activation and reaction energy estimated for the formation of the carbocation **7** in CF_3 substituted ketones

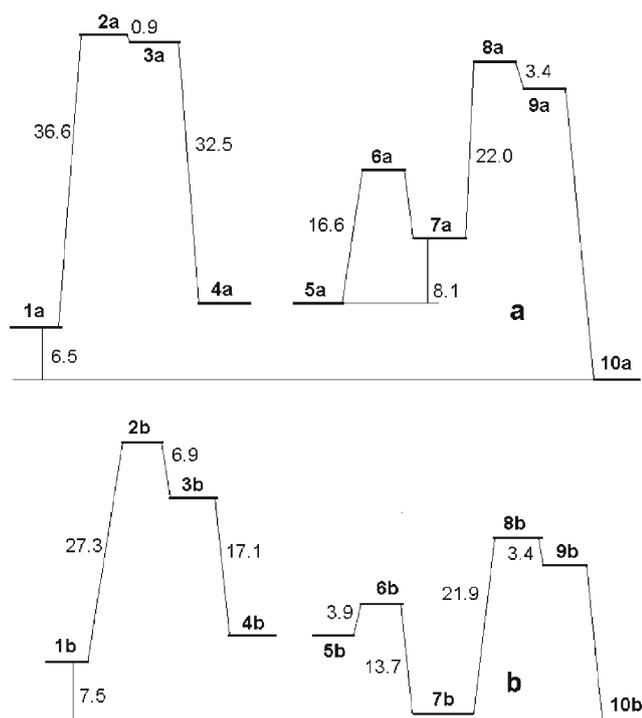


Fig. 4 The free Gibbs reaction energy profile for the reaction of acetone with benzene in MSA (a) and TFSA (b) (kcal/mol)

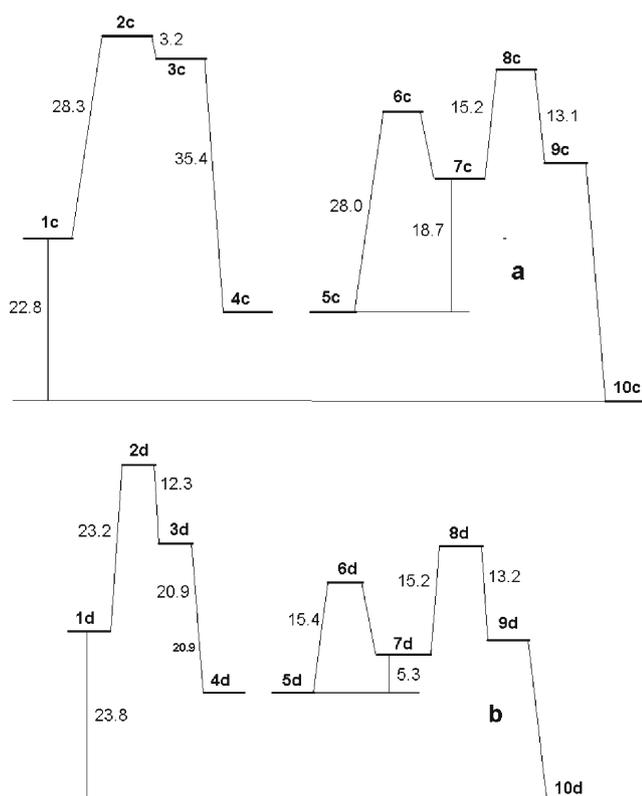


Fig. 5 The free Gibbs reaction energy profile for the reaction of TFA with benzene in MSA (a) and TFSA (b) (kcal/mol)

explains the experimental finding first demonstrated by Klumpp [10] that CF_3 substituted ketones show high chemoselectivity in the formation of the monosubstituted carbinols which are relatively stable in the superacid media.

The reaction of HFA with benzene in MSA

HFA does not give polymers with non-activated aromatics like biphenyl [13, 24] either in MSA or in TFSA. It has been originally suggested that the low reactivity of HFA is related to the reduced basicity of the carbonyl oxygen leading to very positive protonation energies [16]. However, the explicit solvation model shows that the protonation energies cannot be used as a measure of the carbonyl group reactivity, since even in the case of acetone solvated in TFSA (1b) (the combination of the most basic carbonyl and the strongest acid, (Fig. 1)) the complete proton transfer to the carbonyl group does not take place. When revising the reaction energy profile (Fig. 6) the low reactivity of HFA can be understood. Unlike the commonly accepted statement that the rate limiting step of the

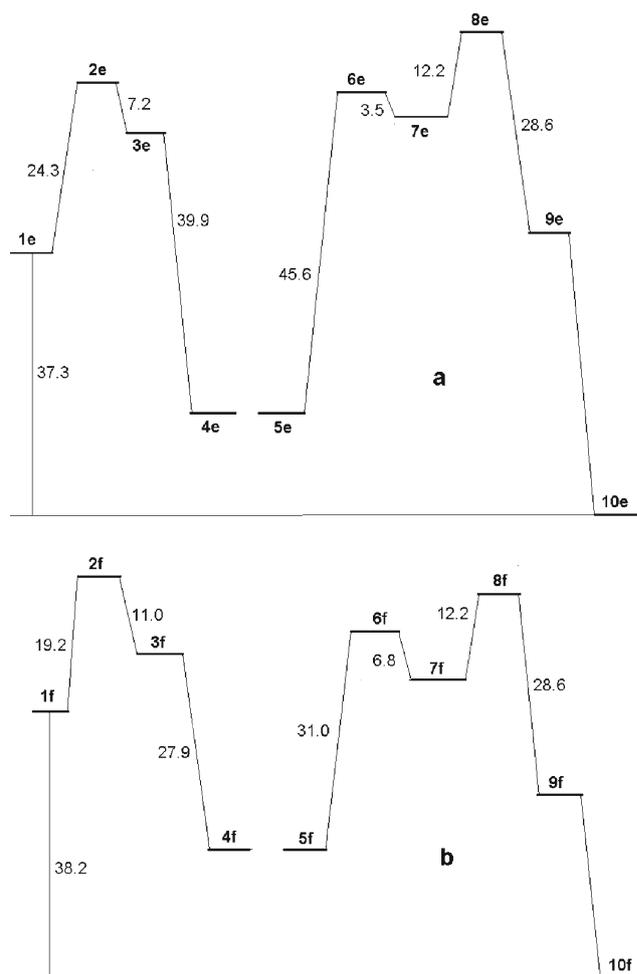


Fig. 6 The free Gibbs reaction energy profile for the reaction of HFA with benzene in MSA (a) and TFSA (b) (kcal/mol)

aromatic electrophilic substitution is the formation of the tetrahedral intermediate [32], this is not true for the reaction of HFA with benzene in MSA where the rate limiting step is the formation of carbocation **7** requiring 45.6 kcal/mol (Fig. 6).

In fact, the activation energies for the formation of **3e** and **3d** are very similar (24.3 and 23.4 kcal/mol, respectively) although TFA is very reactive and HFA is not, demonstrating that the most important factor for the formation of intermediate **3** is not the protonation but the effect of electron withdrawing groups on the carbocation stability. The basicity of HFA carbonyl is very low, which can be appreciated by the very long distance (2.08 Å) between the carbonyl oxygen and MSA protons (Fig. 1) and by the very negative total free Gibbs reaction energy (−37.3 kcal/mol), reflecting very weak protosolvation of HFA carbonyl by MSA. However, a strong electron withdrawing effect of two CF₃ groups of HFA greatly destabilizes carbocation **7e** resulting in very high activation and reaction energies for this reaction step. The high activation and reaction energies completely inhibits the second substitution step despite a very low activation barrier (12.2 kcal/mol) (Fig. 6), thus, making the polymer formation impossible.

The reaction of HFA with benzene in TFSA

Similar to other cases TFSA reduces the activation and the reaction energies of the reaction steps involving the solvation of oxygen atoms (Fig. 6). Thus, the activation energy of tetrahedral intermediate **3** formation reduces to 19.2 kcal/mol compared to 24.3 kcal/mol and that of **7** drops from 45.6 to 31.0 kcal/mol. At the same time the reaction energy of **5**→**7** step is reduced from 43.1 to 24.2 kcal/mol. Better protosolvation properties of TFSA compared to MSA can be appreciated in shorter O-H distances between HFA carbonyl and TFSA protons in the intermediates **1f**, **3f**, and **5f** (Figs. 1 and 2).

Similar to the MSA mediated reaction the cleavage of C-O bond in the carbinol **5** is the rate limiting step of the entire reaction. Even in the case of TFSA mediated aromatic electrophilic substitution the reaction and the activation energies of **5f**→**7f** step is too positive to allow the polymer formation. The free Gibbs activation energy of the second benzene molecule substitution (step **7f**→**9f**) is the same as in the case of MSA solvation; 12.2 kcal/mol. Revising the reaction energy profile (Fig. 6) it can be clearly seen that the low reactivity of HFA in the polyhydroxyalkylation reaction is related to the high activation and the reaction energies of the carbocation **7** formation and not to the high protonation energies of the HFA carbonyl. The use of a very electron reach aromatic component could be a solution for the low reactivity of HFA. After the first substitution the electron donating aromatic fragment would stabilize the carbocation **7**, thus facilitating the cleavage of C-O bond in the carbinol **5**. This hypothesis is supported by the very recent successful

synthesis of fluorinated bisphenols and tetraphenols [25] from HFA and polyphenols.

Conclusions

The use of the cluster-continuum solvation model reveals that the protonation energy of the ketone carbonyl has no direct impact on their reactivity in the reaction of hydroxyalkylation since even in the case of the most favorable pair TFSA – acetone there is no complete proton transfer to the carbonyl group, the complete proton transfer occurs only in the transition state. However, the acid strength has a significant impact on the activation energy due to the differences in their ability to solvate the transition states, explaining higher efficiency of TFSA compared to MSA as a catalyst. The introduction of a strong electron withdrawing group in ketone, reduces the activation energy of the tetrahedral intermediates formation, and increases the activation and the reaction energy of the C-O bond cleavage in the carbinol making more difficult the substitution of a second aromatic molecule. This effect becomes very important in HFA where the cleavage of the carbinol C-O bond becomes the rate limiting step. Those opposite trends tune the reactivity of the ketones in such a way that the first trifluoromethyl group increases the overall ketone reactivity in the reaction of hydroxyalkylation, while the second one decreases it. Therefore, TFA becomes the most reactive ketone out of the three studied.

References

- Hofmann JE, Schriesheim A (1964) In: Olah GA (ed) Friedelcrafts and related reaction. Wiley, New York
- March J (1992) Advanced organic chemistry. Wiley, New York.
- Kray WD, Rosser RW (1977) Synthesis of multifunctional triaryl-fluoroethanes. 1. Condensation of fluoro ketones. J Org Chem 42:1186–1189
- Olah GA (1993) Superelectrophiles. Angew Chem Int Ed 32:767–788
- Olah GA, Klumpp DA (2008) Superelectrophiles and their chemistry. Wiley, New York
- Klumpp DA (2009) Superelectrophiles in heterocyclic ring-forming reactions. ARKIVOC Part I:63–80
- Olah GA, Klumpp DA (2004) Superelectrophilic Solvation. Acc Chem Res 37:211–220
- Zielinski ME, Tracy AF, Klumpp DA (2012) Utilization of the hydroxyalkylation reaction to prepare bis(benzocrown ethers). Tetrahedron Lett 53:1701–1704
- O'Connor MJ, Boblak KN, Spitzer AD, Gucciardo PA, Baumann AM, Peter JW, Chen CY, Peter R, Mitton AA, Klumpp DA (2010) Condensations of aryl trifluoromethyl ketones with arenes in acidic media. Tetrahedron Lett 51:4984–4987
- O'Connor MJ, Boblak KN, Topinka MJ, Kindelin PJ, Briski JM, Zheng C, Klumpp DA (2010) Superelectrophiles and the effects of Trifluoromethyl substituents. J Am Chem Soc 132:3266–3267
- Zolotukhin MG, Fomine S, Salcedo R, Khalilov L (2004) Remarkable enhancement of reactivity of carbonyl compounds for

- polymerizations with non-activated aromatic hydrocarbons. *Chem Commun* 8:1030–1031
- Peña ER, Zolotukhin MG, Fomine S (2004) Factors enhancing the reactivity of carbonyl compounds for polycondensations with aromatic hydrocarbons. A computational study. *Macromolecules* 37:6227–6235
 - Diaz AM, Zolotukhin MG, Fomine S, Salcedo R, Manero O, Cedillo G, Velasco VM, Fritsch D, Khalizov AF (2007) A novel, one-pot synthesis and novel 3F, 5F, and 8F aromatic polymers. *Macromol Rapid Commun* 28:183–187
 - Guzmán T, Rios H, Ruiz-Trevino A, Zolotukhin MG, Balmaseda J, Fritsch D, Prokhorov E (2011) Structure-properties relationship for the gas transport properties of new fluoro-containing aromatic polymers. *J Membr Sci* 385–386:277–284
 - Segawa Y, Higashihara T, Ueda M (2010) Hyperbranched polymers with controlled degree of branching from 0 to 100 %. *J Am Chem Soc* 132:11000–11001
 - López A, Zolotukhin MG, Fomina L, Fomine S (2007) Triflic acid mediated polycondensation of carbonyl compounds with aromatic hydrocarbons. A theoretical study. *Macromol Theory Simul* 16:227–239
 - Ramos E, Zolotukhin M, Fomine S (2005) Reaction pathways of superelectrophilic polycondensation of 2,2,2-Trifluoroacetophenone and biphenyl. A computational study. *Polymer* 46:7494–7503
 - López A, Zolotukhin MG, Fomina L, Fomine S (2007) Super-electrophilic activation of 4-Heterocyclohexanones. Implications for polymer synthesis. A theoretical study. *J Phys Chem A* 111:13606–13610
 - Romero D, Fomine S, Zolotukhin MG, Fomina L, Gutiérrez M (2009) Superelectrophilic activation of N-substituted isatins. Implications for polymer synthesis. A theoretical study. *Macromol Theor Simul* 18:138–144
 - Romero D, Zolotukhin MG, Fomina L, Fomine S (2010) Super-acid mediated hydroxyalkylation reaction of 1,2,3-indanetrione. *J Phys Org Chem* 23:878–884
 - Rasul G, Prakash GKS, Olah GA (2006) Ab Initio/GIAO–CCSD (T) study of propenoyl ($\text{H}_2\text{C}=\text{CH}-\text{CO}^+$) and isopentenoyl ($(\text{CH}_3)_2\text{C}=\text{CH}-\text{CO}^+$) cations and their superelectrophilic protonated dications. *J Phys Chem A* 110:1041–1045
 - Olah GA, Prakash GKS, Rasul G (2008) Comparative ab initio/GIAO–CCSD(T) study of protonated propionaldehyde, isobutyraldehyde and pivalaldehyde cations and their superelectrophilic diprotonated dications. *J Mol Struct* 890:9–17
 - Guzman-Gutierrez MT, Nieto DR, Fomine S, Morales SL, Zolotukhin MG, Gutierrez M, Kriecheldorf H, Wilks ES (2011) Dramatic enhancement of superacid-catalyzed polyhydroxyalkylation reactions. *Macromolecules* 44:194–202
 - Rusanov AL, Chebotarev VP, Lovkov SS (2008) Superelectrophiles in the synthesis of condensation monomers and polymers. *Russ Chem Rev* 77:547–553
 - Tao L, Yang H, Liu J, Fan L, Yang S (2012) Synthesis and characterization of fluorinated bisphenols and tetraphenols via a simple one-pot reaction. *Synthetic Commun* accepted
 - Marenich AV, Cramer CJ, Truhlar DG (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* 113:6378–6396
 - Pliego JR Jr, Riveros JM (2002) Theoretical calculation of pK_a using the cluster–continuum model. *J Phys Chem A* 106:7434–7439
 - Frisch MJ et al. (2010) Gaussian 09 Revision B.01 Gaussian Inc. Wallingford, CT
 - Zhao Y, Truhlar DJ (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor Chem Acc* 120:215–241
 - Pliego JR Jr, Riveros JM (2002) Gibbs energy of solvation of organic ions in aqueous and dimethyl sulfoxide solutions. *Phys Chem Chem Phys* 4:1622–1627
 - Hunter EP, Lias SG (1998) Evaluated gas phase basicities and proton affinities of molecules: an update. *J Phys Chem Ref Data* 27:413–656
 - Solomons TWG (1997) *Fundamentals of organic chemistry*, 5th edn. Wiley, New York