

Mechanistic aspects of superacid mediated condensation of polyphenols with ketones. Implications for polymer synthesis

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Received: 28 July 2014 / Accepted: 21 September 2014 / Published online: 9 October 2014
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Abstract A detailed computational study of possible reaction paths for methanesulfonic and triflic acid mediated polyhydroxyalkylation reaction between resorcinol and trifluoroacetone accompanied by cyclodehydration to give 9H-xanthene containing polymers has been carried out at M06-2X/6-311+G** level of theory. A cluster solvation model was used for the calculations. The calculations revealed that the most kinetically favorable reaction path involves the cyclodehydration occurring during the polymer forming step. In this case 9H-xanthene formation is promoted by the activated phenyl ring in Wheland intermediate assisting the aromatic nucleophilic substitution of OH group which leads to the cyclization. It has been demonstrated that the inability of methanesulfonic acid to catalyze the formation of 9H-xanthene containing polymers is due to the very high barrier of the rate limiting step of the polymer forming reaction and not the cyclodehydration process.

Keywords DFT · 9H-xanthene · Hydroxyalkylation · Protonation · Superacid · Trifluoromethyl group

Introduction

The reaction of ketones with aromatics in acid media is known as hydroxyalkylation reaction [1, 2]. An alcohol, a diaryl-compound or a mixture of those can be obtained depending on the monomer structures and the reaction conditions. Although this reaction is normally limited to the activated

arenes having electron-rich substituents, ketones with electron withdrawing groups react with benzene and even deactivated aromatic molecules giving derivatives of tetrasubstituted methanes in high yield. Thus, Kray and Rosser demonstrated that trifluoromethanesulfonic acid commonly referred to as triflic acid (TFSA) catalyzed the condensation of 2,2,2-trifluoroacetophenone with aromatic substrates affording diaryl-derivatives with moderate yield [3].

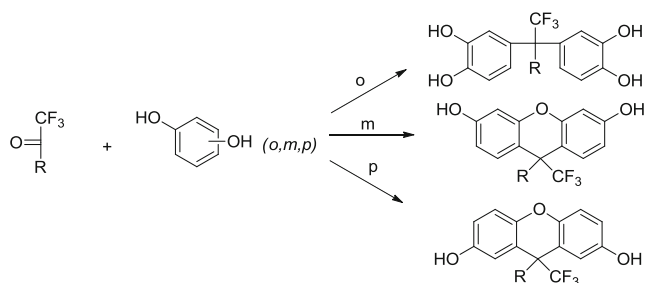
A number of hydroxyalkylation reactions have been carried out using superacids, mostly (TFSA) as catalysts or as a reaction medium [4–7]. Non substituted and substituted trifluoromethyl ketones were found to react smoothly with benzene and substituted arenes, including bisphenols [8, 9] in TFSA at room temperature to give di-aryl compounds. Klumpp recently reported on unusual chemo-, regio-, and stereoselectivities in TFSA catalyzed reactions of some trifluoromethylketones with aromatics [10].

Very recently [11], the reactions of trifluoromethyl activated ketones with catechol, resorcinol, and hydroquinone in TFSA media have been studied. While the reaction with catechol affords tetraphenols without any byproducts, resorcinol and hydroquinone form substituted 9H-xanthene diols (Scheme 1).

The dehydration in this case is facilitated by six member cycle formation. This reaction takes place under very mild conditions affording 9H-xanthene diols in 80–90 % yields. The reaction can also be used as a polymer forming process resulting in ladder type polymers (Scheme 2) using bisphenols as a nucleophilic monomer and activated ketones as electrophilic ones. The polyhydroxyalkylation reaction also takes place under very mild conditions producing polymers containing 9H-xanthene fragments with near 100 % chemoselectivity [12].

The reaction of aldehydes with phenols is a very well-known transformation [13–33] which is widely used for 9H-xanthens synthesis. The reaction normally occurs at elevated

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Scheme 1 Hydroxyalkylation of diphenols with trifluoromethyl substituted ketones

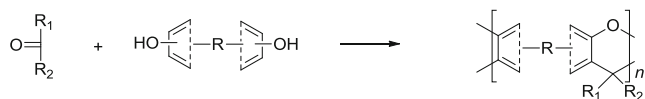
temperatures mediated by Lewis or protic acids giving 9H-xanthenes in moderate to high yields. Postulated conventional mechanism for this reaction involves dehydration as the last reaction step. This step is the aromatic nucleophilic substitution reaction where the catalyst increases the nucleofugality of the leaving hydroxyl group (Scheme 3, blue path) [34]. Other authors [11] proposed a slightly different mechanism where the cyclodehydration occurs after the formation of tetrahedral (Wheland) intermediate, thus activating the phenyl ring toward the nucleophilic substitution (Scheme 3, red path). Both postulated mechanisms have not been proved either experimentally or theoretically. Moreover, the mechanism of superacid mediated hydroxyalkylation reaction is drastically affected by the catalyst nature, which adds another variable to the puzzle of the reaction mechanism.

Given the recently discovered cyclodehydration reaction occurring during the superacid mediated polyhydroxyalkylation with 9H-xanthene formation between polyphenols and activated ketones, the mechanism investigation of this process becomes a priority to understand the mechanism of the whole polymer forming process.

Computational details

A flexible cluster-continuum solvation model has been used for the solvent modeling, where the inner solvation sphere contains an explicit solvent molecule whereas the outer sphere is modeled using SMD modification of polarizable continuum model [35]. This complex model has been shown to be superior to any continuum model [36]. For all calculations the Gaussian 09 suit of programs has been used [37]. M06-2X functional in combination with the 6-311+G** basis set has been applied. This model reproduces well the proton affinities and pKa's of organic acids [38].

For the inner solvation sphere one acid molecule (TFSA) or methanesulfonic acid (MSA) has been used, solvating the



Scheme 2 Formation of 9H-xanthene containing polymers

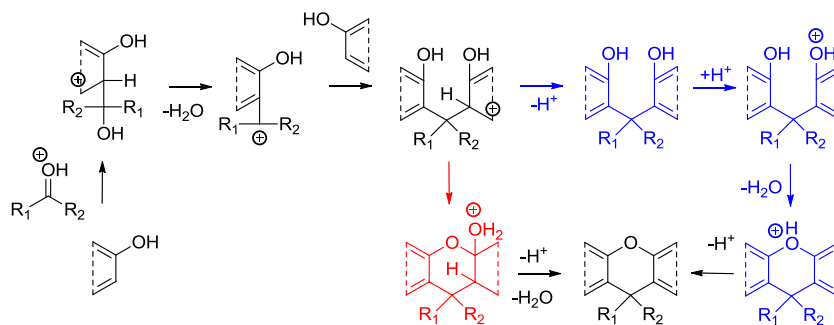
leaving phenol OH group. For the outer solvation sphere SMD continuous model was used as implemented in Gaussian 09, (dielectric constant of 77.4 and solvent radius of 2.60 Å were used for TFSA) while for MSA the dielectric constant of 70.0 and the solvent radius of 2.34 Å were applied. All the geometries 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

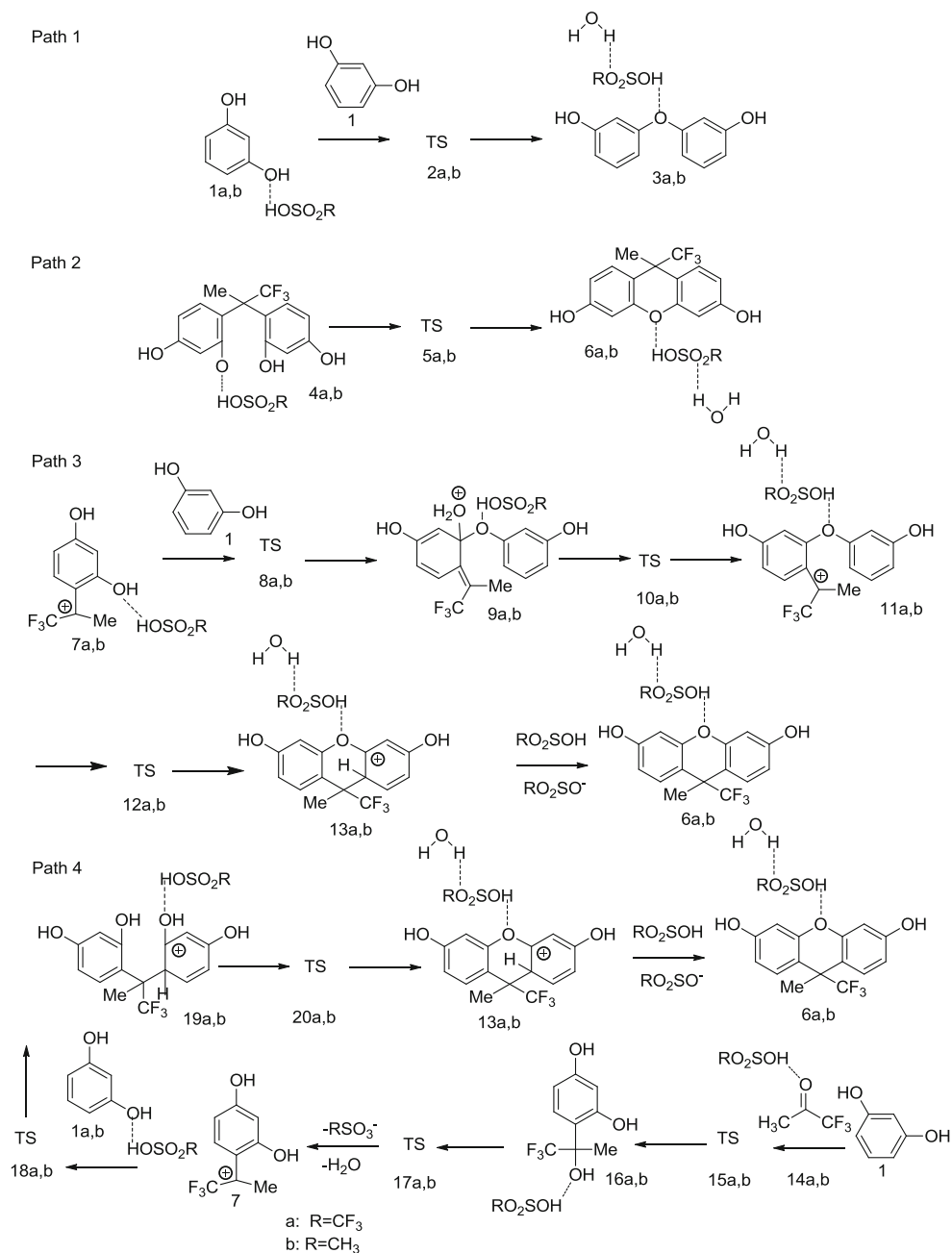
As a model reaction for the cyclodehydration accompanied by the polyhydroxyalkylation to give 9H-xanthene containing structures, the reaction between trifluoroacetone and resorcinol has been studied. TFSA and MSA mediated reaction have been studied to explore the effect of acidity media on the reaction kinetics and thermodynamics. The studied reaction paths are shown in Scheme 4

Four different reaction paths have been studied for the acid mediated model reactions of aromatic nucleophilic substitution in polyphenols. The direct formation of 3,3'-diphenoxide (3) from resorcinol (1), path 1. It is known that direct acid mediated formation of aromatic ethers from phenols does not occur at room temperature. Therefore, this reaction is a good reference point to validate the computational method and to estimate the effect of the hydroxyalkylation reaction on the cyclodehydration process leading to 9H-xanthene fragment formation. Paths 2, 3, and 4 describe possible mechanisms of the acid mediated cyclodehydration. In the first one (path 2) the cyclodehydration occurs *after* completing the hydroxyalkylation step. In the second one (path 3) the formation of ether bond between resorcinol 1 and carbocation 7 occurs *before* completing the hydroxyalkylation step, and in the third one (path 4) the cyclodehydration occurs *during* the hydroxyalkylation step. Revising the last three possible cyclodehydration mechanisms one can clearly see the differences between them. Path 2 is the “classic” mechanism of the intramolecular dehydration to form 9H-xanthene fragment. In the case of paths 3 and 4 the nucleophilic attack of hydroxyl group is apparently facilitated by the positively charged groups; carbocation 7 in the case of path 3 or the positively charged tetrahedral intermediate 12 (path 4). Carbocation 7 is formed during the hydroxyalkylation reaction of trifluoroacetone (13) and resorcinol followed by the dehydration of formed carbocation 14 to produce carbocation 7 (Scheme 4). The mechanism of this particular hydroxyalkylation step has been a subject of intense theoretical studies in our earlier papers [38–44].

Scheme 3 Alternative mechanisms of 9H-xanthenone fragment formation during the hydroxyalkylation reaction



Scheme 4 Studied reaction paths



Path 1

Figure 1 shows the reaction energy profile for the acid mediated dehydration reaction of two molecules of resorcinol and optimized geometries of transition states 2a and 2b. The calculations have been carried out for two different reaction media; TFSA and MSA. It is a matter of common knowledge that this reaction does not take place at room temperature. Calculations are in agreement with this observation. This reaction shows a very high activation barrier for both TFSA and MSA catalyzed reactions. Moreover, this process is not viable thermodynamically due to positive free Gibbs reaction energies. Nevertheless, it should be noted that the free Gibbs activation energy for the TFSA mediated reaction is some 6 kcal mol⁻¹ lower than that of MSA catalyzed reaction (Fig. 1). Higher acidity of TFSA compared to MSA allows for much better protonation of resorcinol hydroxyl group in the transition state 2 increasing its nucleofugality. As seen, the distance between TFSA proton and oxygen atom of triflic anion is notably longer in transition state 2a (1.78 Å) compared to that for MSA proton in 2b (1.62 Å)

Path 2

Path 2 describes the first possible mechanism of cyclodehydration taking place in a polymer as a polymeric reaction after the polymer forming step is completed. This mechanism is the commonly accepted one for the 9H-xanthene formation from phenols and ketones. Figure 2 depicts the reaction energy profile for this reaction and optimized geometries of the transition states 5a and 5b. Unlike

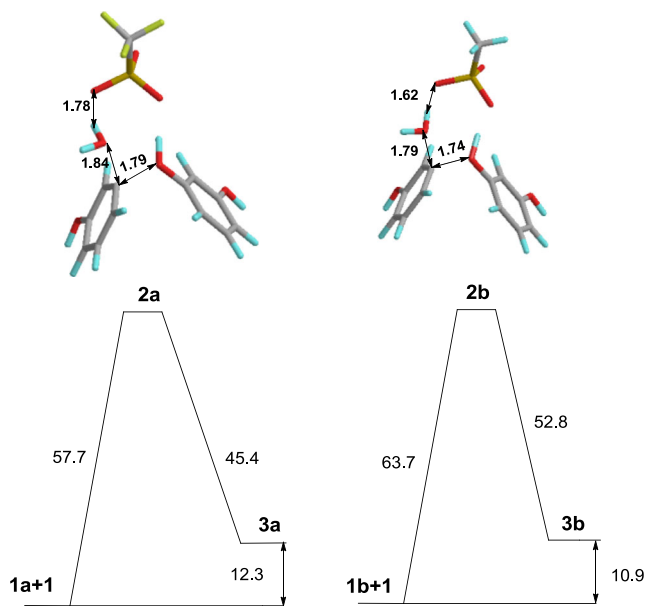


Fig. 1 The free Gibbs reaction energy profile (kcal mol⁻¹) and optimized geometries of transition states for path 1

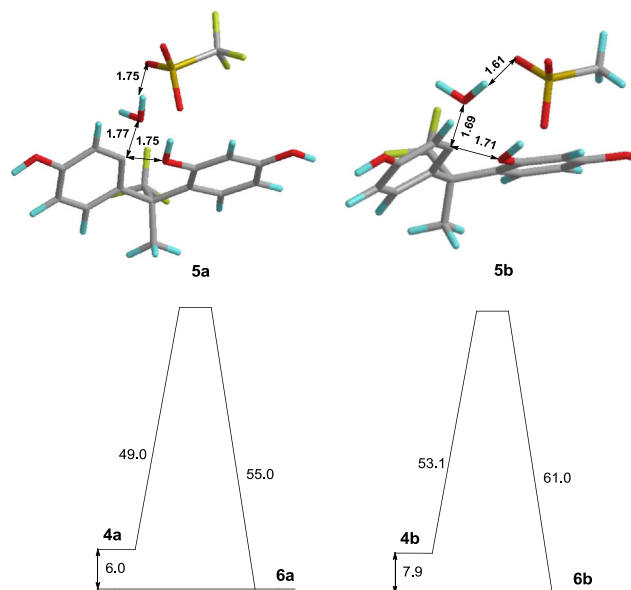


Fig. 2 The free Gibbs reaction energy profile (kcal mol⁻¹) and optimized geometries of transition states for path 2

path 1, path 2 is exergonic due to much more favorable entropic factor. Nevertheless, the free Gibbs activation energy remains too high for this reaction route to occur smoothly at

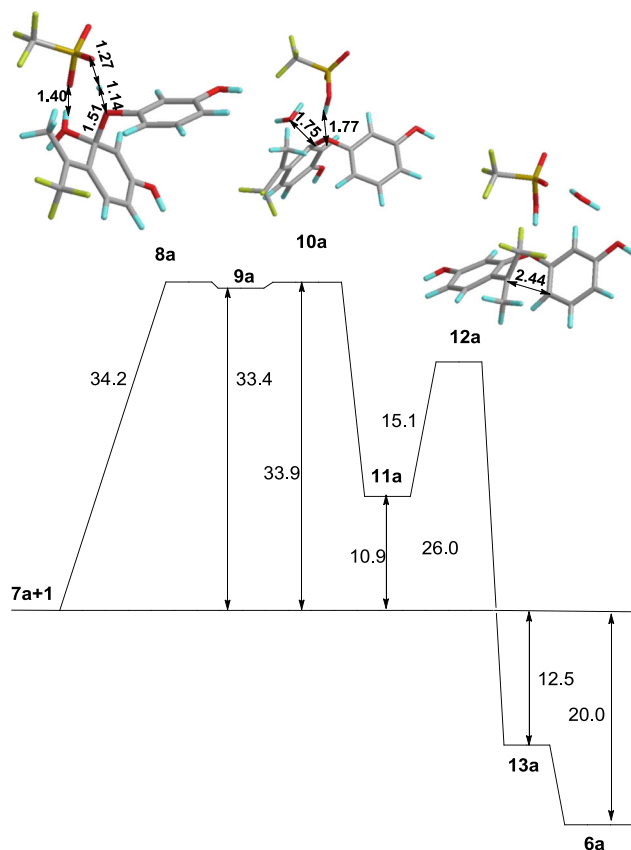


Fig. 3 The free Gibbs reaction energy profile (kcal mol⁻¹) and optimized geometries of the transition states for path 3 mediated by TFSA

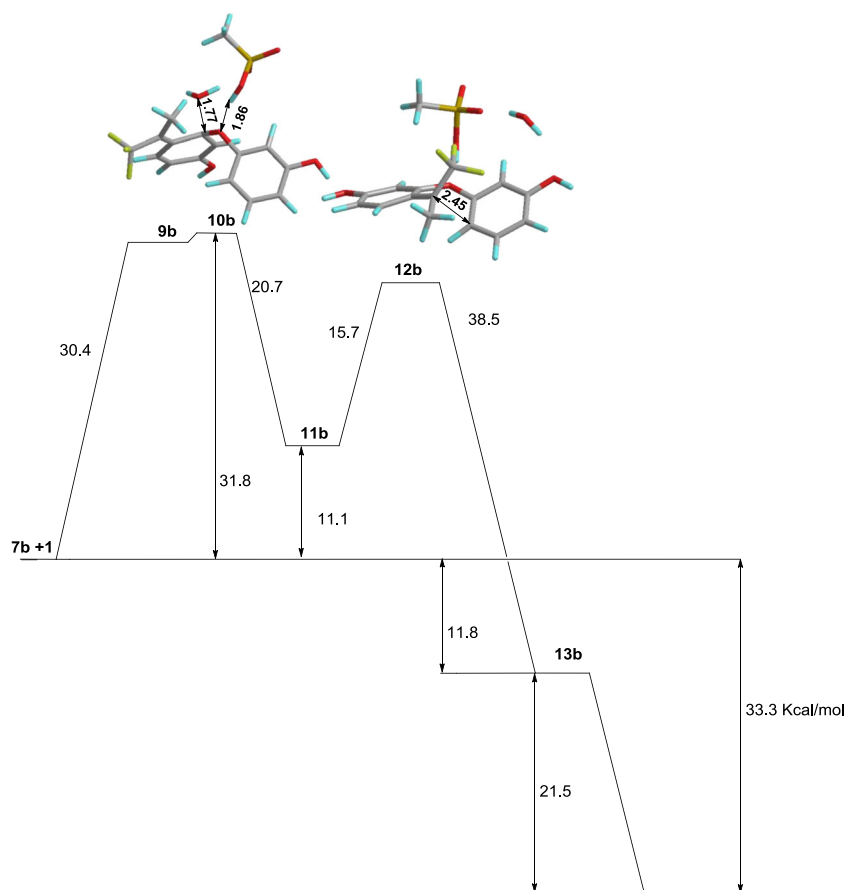
room temperature. The free Gibbs activation energy is 4 kcal mol⁻¹ less for TFSA mediated reaction compared to that mediated by MSA. The reason for that is similar to that mentioned for path 1; stronger triflic acid protonates better leaving hydroxyl group increasing its nucleofugality. The distance between proton of TFSA and oxygen atom of anion (1.75 Å) is notably longer than that for MSA (1.61 Å) and similar to those calculated for transition states 2a and 2b.

Path 3

This reaction route involves the formation of 9H-xanthenone fragment from carbocation 7 and resorcinol. Two different bonds form between the phenyl rings: C-O and C-C affording the 9H-xanthenone fragment. Path 3 considers the formation of C-O ether bond first, followed by the intramolecular electrophilic substitution reaction step. The aromatic nucleophilic substitution reaction between resorcinol and carbocation 7 is facilitated by formal positive charge at carbocation 7 activating it toward the nucleophilic attack. On the other hand, the next step; intramolecular electrophilic substitution reaction to form intermediate 13 becomes more difficult due to the electron donating effect of the phenoxy group in carbocation 11

reducing both the electrophilicity of the carbocationic center and the nucleophilicity of the adjacent phenyl ring. Figure 3 shows the calculated reaction energy profile for path 3. First, it can be noted, that the free Gibbs activation energy of Meisenheimer complex 9a formation is the lowest out of all activation energies calculated for paths 1 and 2 (34.2 kcal mol⁻¹). We were unable to locate the corresponding transition state 8b for 9b formation. The transition state search always led to the product 9b. Considering that 8a is a very late transition state where C-O bond is almost formed (Figs. 3 4) and the difference in total energy between 8a and 8b does not exceed 1 kcal mol⁻¹, we suggest that a similar situation occurs in the case of MSA mediated reaction, and the free Gibbs activation energy in this case can be approximated as the reaction energy 7b+1=9b; 30.5 kcal mol⁻¹. Further exploring the potential energy surface reveals two more transition states; the first one is the elimination of a water molecule to produce 11 and the second one is the ring closure of 11 to give 13. As seen the free Gibbs activation energies of 11 and 13 formation are much lower than that of Meisenheimer complex formation 9, being the rate determining step of the reaction. As seen, in this particular case the acidity of the media does not significantly affect the reaction barriers. The difference does not exceed 3 kcal mol⁻¹.

Fig. 4 The free Gibbs reaction energy profile (kcal mol⁻¹) and optimized geometries of the transition states for path 3 mediated by MSA

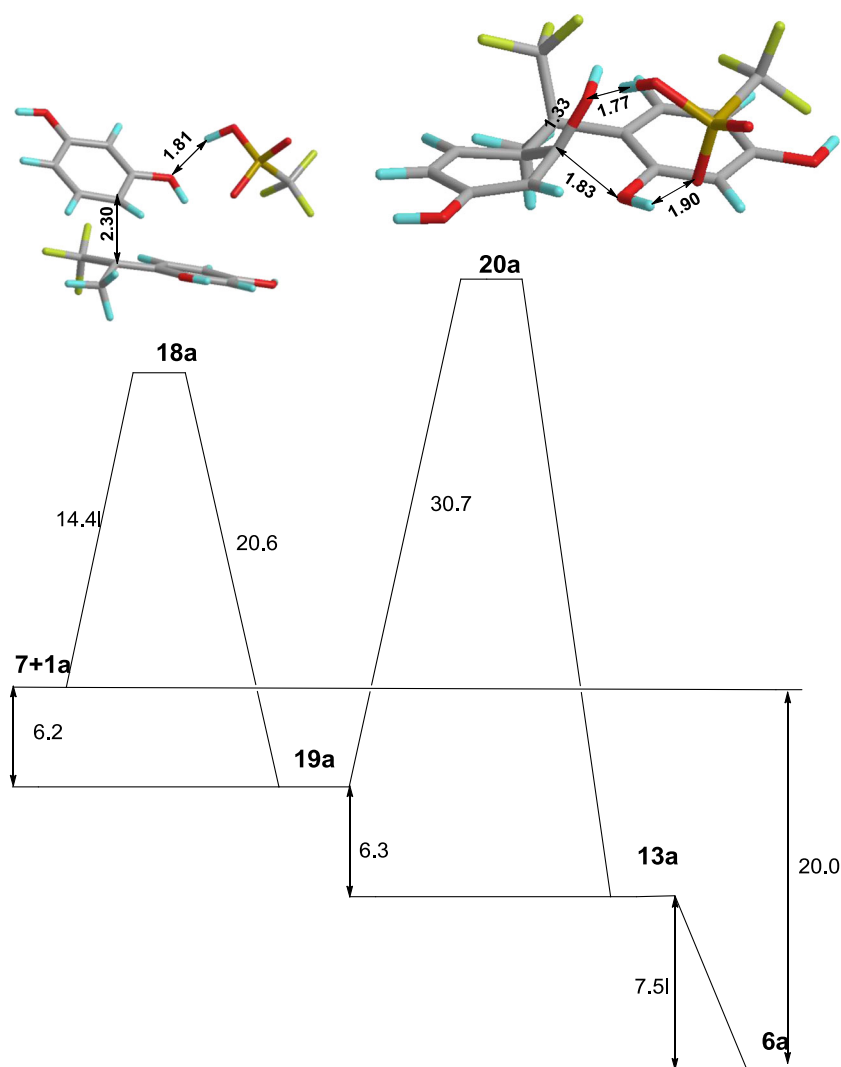


Path 4

Path 4 is an alternative reaction route to path 3. In this case the first step is the electrophilic attack of carbocation 7 at resorcinol resulting in the formation of intermediate 19, followed by the cyclodehydration promoted by the activated, positively charged phenyl ring producing intermediate 13, the same as in path 3. The last step of path 4 is the same as in path 3 generating the final 9H-xanthen product 6 by the aromatization of 13. Figures 5 and 6 show the reaction energy profile for path 4. As can be seen, the rate limiting step for this path is the cyclodehydration reaction with 9H-xanthen formation. This path shows the lowest total activation energy for both the TFSA and MSA mediated process, suggesting this mechanism to be the most probable reaction path for the polyhydroxyalkylation reaction resulting in 9H-xanthen containing polymers. As seen from Figs. 5 and 6 the hydroxyalkylation step shows low activation energy of $14.4 \text{ kcal mol}^{-1}$ and does not depend on the acidity media

due to the very active aromatic component involved in the reaction (resorcinol). As seen from the comparison of path 2 and 4, the activation of the phenyl ring undergoing nucleophilic attack is crucial for the cyclodehydration to occur; the activation energies for 9H-xanthen ring formation reduces by more than 20 kcal mol^{-1} . As seen from Figs. 5 and 6 the ring closure (formation the intermediate 13) is barely sensitive to the acidity media, suggesting that the activation energy of this step is determined by the electrophilicity of carbon atom and not by nucleofugality of the leaving OH group. This conclusion agrees well with the observation that the ring closure with 9H-xanthen formation is catalyzed by a great variety of protic and Lewis acids [13–27]. According to the calculations, both TFSA and MSA are able to mediate the ring closed. However, the fact is that the polyhydroxyalkylation reaction to give 9H-xanthen polymers does not advance in MSA. To explain this contradictory fact we explored the reaction path leading to the formation of carbocation 7, the key intermediate for the ring closure reaction according to path 4. The elemental steps

Fig. 5 The free Gibbs reaction energy profile (kcal mol^{-1}) and optimized geometries of transition states for path 4 mediated by TFSA



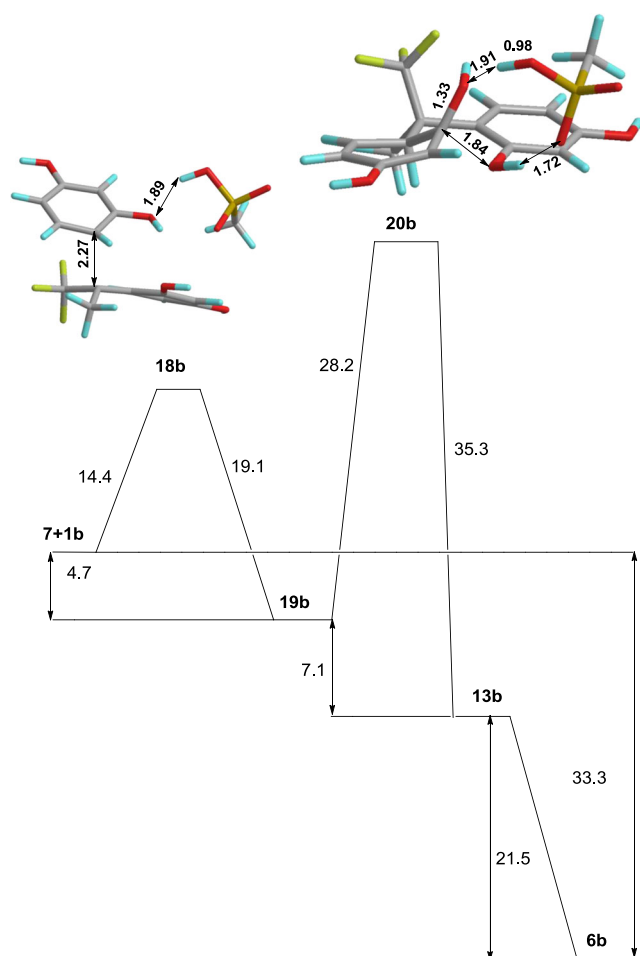


Fig. 6 The free Gibbs reaction energy profile (kcal mol^{-1}) and optimized geometries of transition states for path 4 mediated by MSA

involved in the carbocation 7 formation were described in details earlier [32–38]. The first step is the electrophilic attack of solvated ketone 14 at resorcinol producing tetrahedral intermediate (not shown in Scheme 4) which produces carbinol 16 after the aromatization. The heterolytic C-O bond cleavage of carbinol 16 results in carbocation 7 formation. It has been demonstrated that depending on the media acidity and the nature of the substituents in carbonyl component, both the formation of the tetrahedral intermediate or C-O bond cleavage in carbinol 16 can be the rate limiting step of this reaction [32]. Thus, the increase of the acidity media decreases the activation energy of two steps due to better protonation ability of the carbonyl group in the first step and the carbinol hydroxyl group in the second one. The free Gibbs activation energies of the 1+14a reaction is $17.1 \text{ kcal mol}^{-1}$, while the reaction 1+14b shows the free Gibbs activation energy of $24.7 \text{ kcal mol}^{-1}$. Higher activation energy of the reaction catalyzed by MSA is owing to the weaker acidity of this molecule compared to TFSA. Although MSA mediated reaction has higher activation barrier, both reactions can take place at room temperature (experimental conditions). The free

Gibbs activation energy of the next reaction step; C-O bond dissociation in carbinol 16 is $24.7 \text{ kcal mol}^{-1}$ in the case of TFSA mediated process and $34.6 \text{ kcal mol}^{-1}$ when MSA is used as the catalyst. In this case the TFSA mediated process still can proceed at room temperature resulting in carbocation 7 formation. The free Gibbs activation energy of MSA mediated reaction is too high to proceed at a reasonable rate at room temperature, thus impeding the carbocation 7 formation.

Therefore, the low activity of MSA as a catalyst for the formation of 9H-xanthene containing polymers is not due to its inability to mediate the ring closure in the intermediate 19 but due to the low activity in dehydration of carbinol 16 to generate carbocation 7.

Conclusions

The exploration of different reaction pathways for the acid mediated formation of 9H-xanthene containing polymers reveals that the most kinetically favored reaction route is path 4 where the phenyl ring is activated toward the nucleophilic aromatic substitution during the hydroxyalkylation step, first forming C-C and then C-O bond. This reaction path, first proposed as a possible reaction mechanism in [11], shows the activation barrier by some 20 kcal mol^{-1} lower compared to the “conventional” mechanism. The alternative mechanism where C-O bond is formed first (path 3) can be ruled out due to higher barrier of the cyclodehydration step. Interestingly, the cyclodehydration step is the rate determining reaction step in the 9H-xanthene containing polymer formation. The barrier of this step is barely affected by the acidity media. However, the dissociation of carbinol 16 to generate carbocation 7 is strongly affected by the acid nature. This step does not proceed in MSA at room temperature due to high activation energy, thus preventing the polymer formation and, therefore, the cyclodehydration leading to 9H-xanthene.

Acknowledgments The authors acknowledge the financial support from CONACyT Mexico (Grant 151842) and from DGAPA-UNAM (PAPIIT IN 105314).

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