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# Theoretical study on the nucleophilic fluoroalkylation of propylene oxide with fluorinated sulfones

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*Abstract*: The paths of nucleophilic fluoroalkylation reaction of propylene oxide with $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$, respectively) in the gas phase and in $Et_2O$ solvent were studied theoretically. The nucleophilic fluoroalkylation of propylene oxide with fluorinated carbanions was probed by comparison of the reactivities (phenylsulfonyl)monofluoromethyl anion ($PhSO_2CHF^-$), the (phenylsulfonyl)difluoromethyl anion ($PhSO_2CF_2^-$), and the bis(phenylsulfonyl)monofluoromethyl anion ($(PhSO_2)_2CF^-$). The nucleophilicity reactivity order of $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$) is $(PhSO_2)_2CF^-$ > $PhSO_2CHF^-$ > > $PhSO_2CF_2^-$, which indicates that the introduction of another electron-withdrawing phenylsulfonyl group is an effective way to significantly increase the nucleophilicity of fluorinated carbanions. For comparison, the nucleophilic addition reaction of propylene oxide with the chlorine-substituted carbanion $PhSO_2CHCl^-$ was investigated. The calculated results show that the nucleophilicity of $PhSO_2CYF^-$ is better than that of $PhSO_2CHCl^-$ in the ring opening reaction with propylene oxide. The calculated results are in good agreement with the available experimental ones.

*Keywords*: nucleophilic fluoroalkylation; propylene oxide; $PhSO_2CYF^-$ (Y = F, H and $PhSO_2$).

## INTRODUCTION

Nucleophilic fluoroalkylation, typically involving the transfer of a fluorine-bearing carbanion to an electrophile, has been widely studied and applied to synthesize fluorine-containing materials and bioactive molecules.[1–7] The nucleophilic fluoroalkylation of simple epoxides with fluorinated sulfones was achieved to give *α*-fluoroalkyl alcohols in one-step. Although there are a variety of examples of nucleophilic fluoroalkylation of various substrates,[6,7] the study of nucleophilic fluoroalkylation of simple epoxides is rare. The possible reason could be

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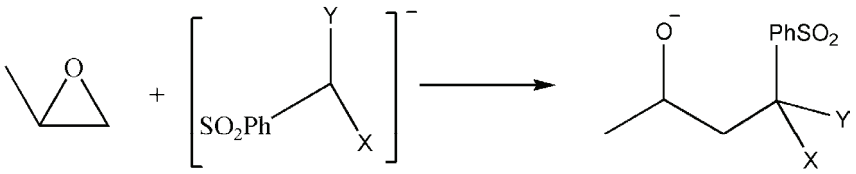
attributed to the intrinsic properties of fluorine-bearing carbanions and weak nucleophilicity toward epoxides.[1]

The exploration of the ring-opening reactions of epoxides from various sources of carbanions can be fully employed in drug design, organic synthesis and other fields. In the present work, the ring-opening mechanisms of epoxides by some sources of carbanions, *i.e.*, $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$), applied in the literature[1] were theoretically investigated (as shown in Scheme 1). Propylene oxide ($C_3H_6O$) was selected as a model molecule of epoxides to study the nucleophilic fluoroalkylations. Correspondingly, the nucleophilic chloroalkylation of propylene oxide with $PhSO_2CHCl^-$ was also studied. The following reaction of propylene oxide with $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$) was considered:

$$C_3H_6O + PhSO_2CYF^- \rightarrow \textit{gauche}\text{-product} \rightarrow \textit{anti}\text{-product}$$

In the above equation, Y is F, H, or $PhSO_2$; the *gauche*-product anion and *anti*-product anion (Scheme 1) for the reaction are distinguished by the F atom being in the *gauche*-conformation or *anti*-conformation to the O atom in this conformer.




X=F, Y=F, H, and $PhSO_2$
X=Cl, Y=H

Scheme 1. The ring opening reaction of propylene oxide by nucleophilic alkylation with halogenated sulfones.

## COMPUTATIONAL METHODS

The reactions were studied using the MP2 and B3LYP methods for the calculations of the reaction path in gas phase, which included geometry optimization, frequency analysis, and IRC (intrinsic reaction coordinate)[8,9] calculations.

Due to the high computational cost required for the full optimization of the large system, investigation of the reaction pathways was realized using the ONIOM approach.[10-13] The ONIOM methodology has been shown to be quite successful in the description of computationally time-consuming systems, by allowing the partitioning of a large cluster computation into various levels of accuracy, for example the active region treated with an advanced level of theory and the remaining region treated with an inexpensive, less accurate method. In the present work, the DFT-B3LYP, two layer ONIOM (MP2:B3LYP) and MP2 levels of theory were used. In the ONIOM (MP2:B3LYP) method, the extended framework environment (benzene ring) was considered with a less expensive level of B3LYP/6-311+g(d,p), while the remainder was treated with the high-level method of MP2/6-311+g(d,p) level.

In order to verify the reliability of the basis set used, BP91/6-311+g(d,p) calculations were also performed for the extended framework environment (benzene ring) of several representative intermediates and transition states, including IM1-2, TS1-2, *s-gauche*, and TS2 for the reaction of $PhSO_2CF_2^-$ with $C_3H_6O$. It was found that the energy barriers from IM1-2 to TS1-2, and from *s-gauche* to TS2, are 20.62 and 7.68 kcal $mol^{-1}$, respectively. These results are comparative with corresponding ones obtained using B3LYP/6-311+g(d,p) (20.53 and 7.44 kcal $mol^{-1}$), meaning that using BP91 does not change the conclusions obtained using B3LYP. Therefore, it can be assumed with confidence that the basis set used in the manuscript can give a reliable potential energy surface of the reaction.

In the gas phase, the geometry optimization calculations were performed for stationary points located along the reaction paths. The frequency analysis calculations were performed at the same level for characterizing stationary points as intermediates (IMn) or transition states (TSn). The reported energies are the zero-point energy (*ZPE*) corrected Gibbs free energies in the gas phase ($\Delta G_{gas}$). The nature of a given transition state was analyzed by IRC computations at the same level.

For locating and characterizing the stationary points along the reaction coordinates of the reaction in diethyl ether ($Et_2O$) solvent, Gibbs free energy calculations in solution ($\Delta G_{sol}$) were performed based on the gas-phase optimized geometries and calculations using the CPCM model (conductor-like polarizable continuum model)[14,15] of the self-consistent reaction field theory were used to simulate the solution effects. Unless otherwise noted, all discussed relative energies in the subsequent sections are referred to $\Delta G_{sol}$. All the calculations were realized using Gaussian 03 program.[16] The atom labelings used are shown in Fig. 1.

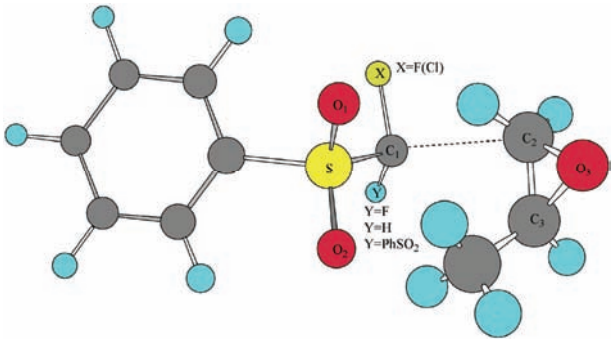
## RESULTS AND DISCUSSIONS

### *Nucleophilic fluoroalkylation of propylene oxide with $PhSO_2CYF^-$ (Y = F, H and $PhSO_2$)*

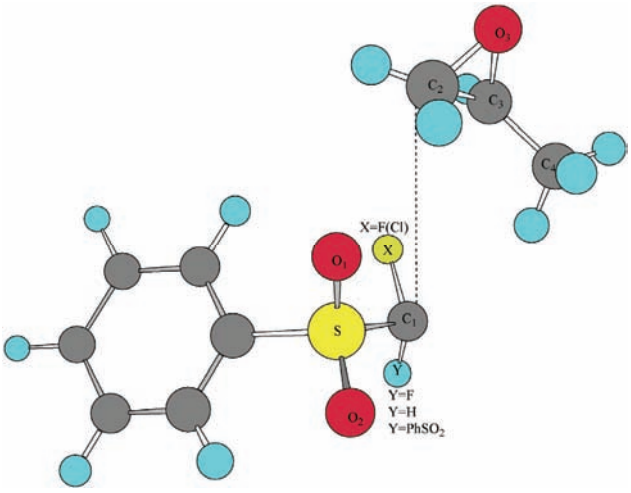
The calculations predicted the same reaction path (the same mechanism) for nucleophilic fluoroalkylation of propylene oxide with $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$) in the gas phase and in $Et_2O$ solvent. The obtained potential energy curve is shown in Fig. 2, along which there are two transition states (TS1 and TS2) and one intermediate (IM1). The relative free energies (in gas phase and in $Et_2O$ solvent) of the corresponding species involved in Fig. 2 are given in Table I. Two conformations for IM1, TS1, and *s-anti*, respectively, differing in the position of the benzene ring, were found, but optimization of TS1-1 was unsuccessful. The relative energies to the reactants ($PhSO_2CYF^-$ + $C_3H_6O$) were used in the discussions in the sections unless otherwise noted. The optimized structures of IM1 (IM1-1 and IM1-2), TS1 (TS1-2), *s-gauche*, TS2, and *s-anti* for $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$, respectively) are shown in Fig. 1, and the important geometric parameters are given in Table II.

The calculations indicated that the reaction involves the formation of IM1-1 and IM1-2, followed by a decomposition process of the $C_2$–$O_3$ bond in IM1-1 and IM1-2 *via* TS1-1 and TS1-2 (a stable structure for TS1-1 could not be obtained), respectively, leading to the *gauche*-product (*s-gauche*), which transformed into the more stable *anti*-product (*s-anti*) *via* TS2. Therefore, the reaction

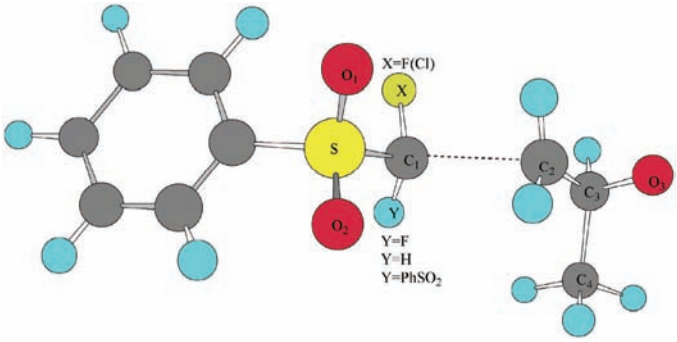
is considered to consist of steps 1 and 2. In the decomposition process of IM1 (step 1), the $C_2$–$O_3$ bond breaks and the $C_1$–$C_2$ bond forms. With the $C_2$–$C_3$ bond rotating along the $C_1$–$C_2$ bond, a conformational isomer of the product (s-*gauche*) transforms to another more stable isomer of the product *s-anti via* TS2 (step 2).



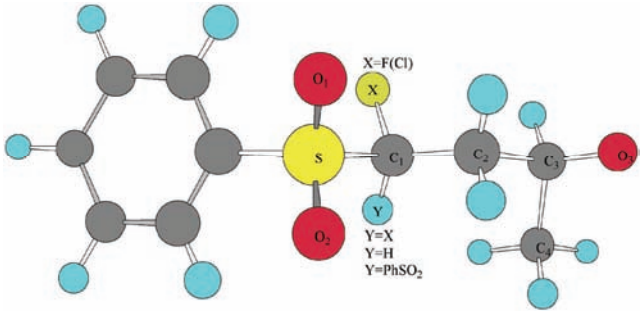

IM1-1



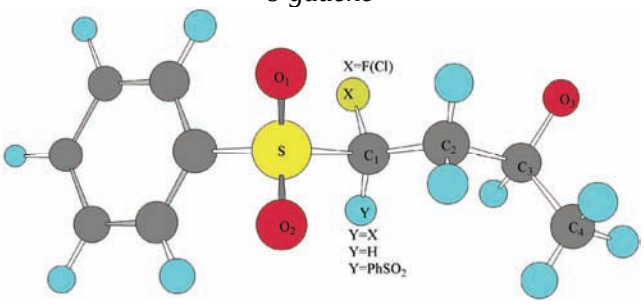

IM1-2



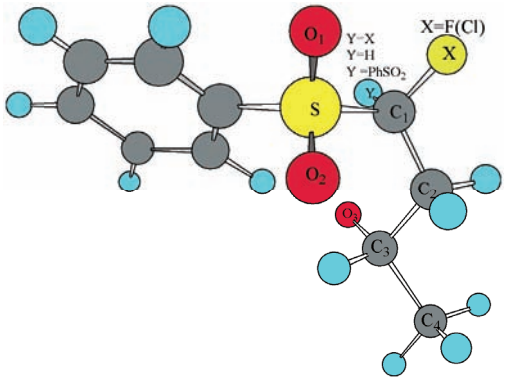

TS1-2




*s-gauche*




TS2




*s-anti*

Fig. 1. The gas phase structures of the intermediate complexes (IM1-1 and IM1-2), transition states (TS1-2 and TS2) and products (*s-gauche* and *s-anti*) for $PhSO_2CYF^-$ (Y = F, H and $PhSO_2$, respectively) and $PhSO_2CHCl^-$ along the reaction coordinates optimized using the ONIOM method.

The $C_2$–$O_3$ bond distances in the structure of IM1-1 and IM1-2 for $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$) are all significantly longer than the normal $C_2$–$O_3$ single-bond length of 1.434 Å in the free propylene oxide (Table II). The primary difference between the structures of IM1-1 and IM1-2 is the relative position of the propylene oxide part to the benzene ring, as shown in Fig. 1. As given in Table II,

the $C_3C_2C_1F$ dihedral angle values of IM1-1 in $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$) are 173.8, –178.1 and –177.6°, respectively, while the corresponding values for IM1-2 are –88.6, –66.4 and 68.7°, respectively.

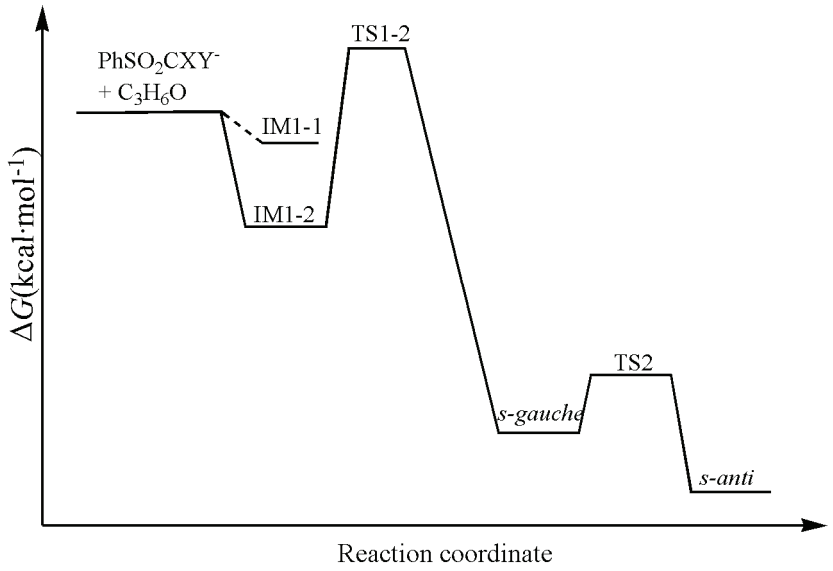



Fig. 2. Schematic diagram of the potential energy curves along the reaction coordinates for the nucleophilic halogenalkylation of propylene oxide with $PhSO_2CXY^-$ (X = F, Y = F, H and $PhSO_2$; X = Cl, Y = H) in the gas phase.

TABLE I. The relative free energies (kcal* $mol^{-1}$) of the intermediate complexes (IM1-1 and IM1-2), transition states (TS1-2 and TS2), and products (*s-gauche* and *s-anti*), to the reactant ($PhSO_2CYF^-$ (Y = F, H and $PhSO_2$) + $C_3H_6O$) or the reactant ($PhSO_2CHCl^-$ + $C_3H_6O$) in the gas phase and $Et_2O$ solvent; the values in parentheses are the relative free energies in the $Et_2O$ solvent based on the geometrical considerations

| Reactant | IM1-1 | IM1-2 | TS1-2 | *s-gauche* | TS2 | *s-anti* |
|---|---|---|---|---|---|---|
| $PhSO_2CF_2^-$ + $C_3H_6O$ | –8.12 | –8.15 | 12.38 | –36.61 | –29.17 | –43.00 |
| | (–2.26) | (–2.45) | (18.79) | (–23.10) | (–16.35) | (–35.21) |
| $PhSO_2CHF^-$ + $C_3H_6O$ | –8.82 | –8.97 | 7.86 | –38.16 | –33.88 | –51.92 |
| | (–3.08) | (–3.73) | (14.33) | (–26.99) | (–22.96) | (–41.72) |
| $(PhSO_2)_2CF^-$ + $C_3H_6O$ | –7.39 | –8.33 | 6.96 | –38.93 | –35.47 | –67.95 |
| | (–2.01) | (–2.65) | (13.11) | (–27.52) | (–24.29) | (–61.49) |
| $PhSO_2CHCl^-$ + $C_3H_6O$ | –9.06 | –9.22 | 14.01 | –30.53 | –27.34 | –41.20 |
| | (–2.85) | (–3.13) | (21.72) | (–17.17) | (–14.21) | (–36.45) |

The IRC calculations indicated that TS1-2 is connected to IM1-2. The barrier heights for step 1 of reaction (1) (the relative free energies of TS1-2 to IM1-2)

* 1 kcal = 4.184 kJ

were predicted to be 21.24, 18.06, and 15.76 kcal mol$^{-1}$ for $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$), respectively, in $Et_2O$ solvent.

TABLE II. Geometric parameters (ONIOM calculations, see text for details; for labelings, see Fig. 1) of the intermediate complex (IM1–1 and IM1–2), the transition states (TS1–2 and TS2), and the products (*s–gauche* and *s–anti*) for $PhSO_2CYF^-$ (Y = F, H and $PhSO_2$) and $PhSO_2CHCl^-$; bond distances are given in Å, and dihedral angles in degrees

| Bond or angle | IM1–1 | IM1–2 | TS1–2 | *s-gauche* | TS2 | *s-anti* |
|---|---|---|---|---|---|---|
| $C_1$–X | 1.411; | 1.417; | 1.395; | 1.370; | 1.387; | 1.377; |
| | 1.434; | 1.441; | 1.421; | 1.398; | 1.390; | 1.394; |
| | 1.441; | 1.396; | 1.430; | 1.401; | 1.392; | 1.411; |
| | 1.828 | 1.835 | 1.817 | 1.818 | 1.809 | 1.816 |
| $C_1$–$C_2$ | 3.860; | 4.391; | 2.282; | 1.481; | 1.486; | 1.509; |
| | 4.014; | 4.371; | 2.319; | 1.496; | 1.490; | 1.506; |
| | 4.086; | 3.787; | 2.323; | 1.512; | 1.493; | 1.505; |
| | 4.059 | 4.342 | 2.281 | 1.508 | 1.500 | 1.515 |
| $C_2$–$C_3$ | 1.460; | 1.460; | 1.467; | 1.653; | 1.646; | 1.570; |
| | 1.460; | 1.458; | 1.462; | 1.615; | 1.639; | 1.568; |
| | 1.460; | 1.460; | 1.463; | 1.616; | 1.635; | 1.566; |
| | 1.459 | 1.459 | 1.466 | 1.611 | 1.638 | 1.569 |
| $C_2$–$O_3$ | 1.450; | 1.447; | 1.818; | – | – | – |
| | 1.451; | 1.448; | 1.809 | | | |
| | 1.452; | 1.448; | 1.812; | | | |
| | 1.449 | 1.447 | 1.842 | | | |
| $\angle C_1C_2C_3C_4$ | –91.2; | –65.6; | –67.9; | –63.1; | –131.3; | –179.7; |
| | –84.4; | –68.7; | –69.6; | –59.7; | –125.5; | 168.0; |
| | –82.7; | –69.7; | –68.8; | –56.6; | –123.4; | 172.3; |
| | –98.0 | –67.5 | –68.0 | –58.2 | –125.9 | 169.1 |
| $\angle C_3C_2C_1X$ | 173.8; | –88.6; | –63.1; | –61.2; | –61.2; | 172.7; |
| | –178.1; | –66.4; | –73.2; | –70.9; | –70.9; | –165.4; |
| | –177.6; | 68.7; | –76.7; | –72.7; | –72.7; | –158.9; |
| | –161.2 | –84.4 | –78.0 | –68.7 | –68.7 | –161.3 |
| $\angle O_3C_3C_2C_1$ | 163.4; | 171.2; | 178.1; | 172.2; | 103.3; | 56.4; |
| | 170.2; | –174.3; | 176.6; | 176.0; | 109.2; | 43.2; |
| | 173.1; | –175.6; | 178.3; | 176.2; | 113.1; | 41.7; |
| | 156.7 | –173.2 | 177.6 | 177.6 | 108.8 | 44.4 |

The low free energies of *s-gauche* for $PhSO_2CYF^-$ (–23.10, –26.99, and –27.52 kcal mol$^{-1}$) in the $Et_2O$ solvent indicate that the *s-gauche* is a stable product. In the structures of *s-gauche* for $PhSO_2CYF^-$, the $C_2$–$O_3$ and $C_2$–$C_3$ bond distances are longer and the $C_1$–$C_2$ distance is shorter than the corresponding values in the structure of TS1-2 (as shown in Table II). The $O_3$, $C_3$, $C_2$, and $C_1$ atoms in the structures of $PhSO_2CYF^-$ are almost co-planar (see the $O_3C_3C_2C_1$ dihedral angle values given in Table II).

With the $C_2$–$C_3$ bond rotating along the $C_1$–$C_2$ bond, *s-gauche* transforms to *s-anti via* TS2. The most obvious differences in the structures of *s-gauche*, TS2,

and *s-anti* are the values of the $C_1C_2C_3C_4$ and $O_3C_3C_2C_1$ dihedral angle. For example, the $O_3C_3C_2C_1$ dihedral angle value in the structure of *s-gauche* for $PhSO_2CYF^-$ is almost 180.0° (176.0°), while the corresponding values in the structures of TS2 and *s-anti* are 109.2° and 43.2°, respectively. The IRC calculations indicated that TS2 is connected to *s-gauche* in the back direction and to the *s-anti* product in the forward direction.

The product *s-anti* is predicted to be lower in energy than the reactant ($PhSO_2CYF^- + C_3H_6O$) by 35.21, 41.72 and 61.49 kcal $mol^{-1}$ for $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$), respectively, in $Et_2O$ solvent, which demonstrates the reactions are exothermic. The barrier heights for step 2 of the reaction (the relative energies of TS2 to *s-gauche*) were predicted to be 6.75, 4.03, and 3.46 kcal $mol^{-1}$, for $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$, respectively) in $Et_2O$ solvent. Since TS1 is obviously higher in energy than TS2, the relative free energies of TS1-2 to the IM1-2 are the overall barrier heights for the reaction. The overall barrier heights for the reaction of $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$) in the $Et_2O$ solvent are predicted to be 21.24, 18.06, and 15.76 kcal $mol^{-1}$, respectively.

The nucleophilicity order of $PhSO_2CYF^-$ ($PhSO_2CF_2^-$, $PhSO_2CHF^-$ and $(PhSO_2)_2CF^-$) can be estimated by the thermodynamic fact (the relative energies of *s-anti* to the reactant) and the kinetic fact (the overall barrier heights for reaction).

The relative free energies of *s-anti* of monofluoro-substituted carbanion, (phenylsulfonyl)monofluoromethyl ($PhSO_2CHF^-$) to the reactant ($PhSO_2CHF^- + C_3H_6O$) are 8.92 and 6.51 kcal $mol^{-1}$ lower than the corresponding values of *s-anti* of (phenylsulfonyl)difluoromethyl anion ($PhSO_2CF_2^-$) to $PhSO_2CF_2^- + C_3H_6O$ in the two phases. The overall barrier heights of 20.53 and 21.24 kcal $mol^{-1}$ for the reaction of $PhSO_2CF_2^-$ are higher than the overall barrier height of 16.83 and 18.06 kcal $mol^{-1}$ for the reaction of $PhSO_2CHF^-$. All these results indicate that the $PhSO_2CHF^-$ has better nucleophilicity than $PhSO_2CF_2^-$ for the ring opening reaction with propylene oxide, confirming that the fluorine substitution of a carbanion will decrease the nucleophilicity of the latter (negative fluorine effect).[1]

To study further the nucleophilicity of a fluorinated carbanion toward epoxides, the reactivity of the bis(phenylsulfonyl)monofluoromethyl anion ($(PhSO_2)_2CF^-$) was analyzed from the thermodynamic the kinetic viewpoint. The relative energies of *s-anti* of $PhSO_2CHF^-$ to the reactant ($PhSO_2CHF^- + C_3H_6O$) are 16.03 and 19.77 kcal $mol^{-1}$ higher than the corresponding value of *s-anti* of $(PhSO_2)_2CF^-$ to $[(PhSO_2)_2CF^- + C_3H_6O]$ in the gas phase and $Et_2O$ solvent. In addition, the overall barrier heights for the reaction of $(PhSO_2)_2CF^-$ are lower than the overall barrier height for the reaction of $PhSO_2CHF^-$ (as shown in Table I). From the results above, it could be concluded that ($(PhSO_2)_2CF^-$) has a better nucleophilicity than $PhSO_2CHF^-$. A possible reason for this is that the phenylsul-

fonyl functionality is able to delocalize the electron density from the carbanion center; bis(phenylsulfonyl) substitution on a fluorinated carbanion can thus increase its stability and nucleophilicity by diminishing the electron repulsion between the electron pairs on the small fluorine atom and the electron lone pair occupying the p-orbital of the carbanion center.[1] The calculated nucleophilicity reactivity order of $PhSO_2CYF^-$ (Y = F, H, and $PhSO_2$, respectively) is $(PhSO_2)_2CF^- > PhSO_2CHF^- > PhSO_2CF_2^-$, which is exactly consistent with the experimental order.[1]

*Nucleophilic chloroalkylation of propylene oxide with $PhSO_2CHCl^-$*

For comparison, the nucleophilic addition reactions of propylene oxide with chlorine-substituted carbanion $PhSO_2CHCl^-$ were also studied (see Scheme 1). The reaction path for the nucleophilic chloroalkylation of propylene oxide with $PhSO_2CHCl^-$ is shown in Fig. 2, together with the relative free energies of respective species for the reaction in the gas phase (with *ZPE* corrections) and in the solvent $Et_2O$. The optimized structures of IM1 (IM1-1 and IM1-2), TS1 (TS1-2, the stable structure of TS1-1 could not be found in the present calculation), *s-gauche*, TS2, and *s-anti* for $PhSO_2CHCl^-$ are shown in Fig. 1 and important geometric parameters are given in Table II.

The reaction mechanism for the nucleophilic chloroalkylation of propylene oxide with $PhSO_2CYCl^-$ is similar to that with $PhSO_2CYF^-$ as shown in Fig. 2: $PhSO_2CHCl^- + C_3H_6O \rightarrow$ IM1 (IM1-1 and IM1-2) $\rightarrow$ TS1-2 $\rightarrow$ *s-gauche* $\rightarrow$ $\rightarrow$ TS2 $\rightarrow$ *s-anti*.

IRC calculations indicated that TS1-2 is connected to IM1-2. The relative free energy of TS1-2 to IM1-2 for $PhSO_2CHCl^-$ was predicted to be 23.23 and 24.85 kcal $mol^{-1}$ in gas phase and in $Et_2O$ solvent, respectively. As shown in Table II, the $C_2$–$O_3$ bond distance in TS1-2 for $PhSO_2CHCl^-$ (1.842 Å) is longer than that (1.809 Å) in TS1-2 for $PhSO_2CHF^-$, while the $C_1$–$C_2$ distances are 2.281 and 2.319 Å in $PhSO_2CHCl^-$ and $PhSO_2CHF^-$, respectively.

Comparing with the relative free energy of *s-gauche* for $PhSO_2CHF^-$ (–26.99 kcal $mol^{-1}$) in the $Et_2O$ solvent, the relative free energy of *s-gauche* for $PhSO_2CHCl^-$ of –17.17 kcal $mol^{-1}$ indicates that $PhSO_2CHCl^-$ is not as thermodynamically stable as $PhSO_2CHF^-$.

The structure of *s-gauche* transforms to *s-anti via* TS2 with the $C_2$–$C_3$ bond rotating along the $C_1$–$C_2$ bond, which could be found by examining the $C_1C_2C_3C_4$ and $O_3C_3C_2C_1$ dihedral angle values (see Table II). The IRC calculations indicate that TS2 is connected to *s-gauche* in the back direction and to *s-anti* product of the reaction in the forward direction.

The *s-anti* products of the reaction are predicted to be lower in energy than the reactant ($PhSO_2CHCl^- + C_3H_6O$) by 36.45 kcal $mol^{-1}$ in $Et_2O$ solvent and that the reaction is also exothermic. The barrier heights for this step (the relative

energies of TS2 to *s-gauche*) are predicted to be 3.19 and 2.96 kcal mol$^{-1}$ in the two phases. The relative free energy of TS1-2 is considered as the overall barrier height for the reaction.

The relative free energy of *s-anti* of $PhSO_2CHCl^-$ to the reactant ($PhSO_2CHCl^-$ + $C_3H_6O$) is 5.27 kcal mol$^{-1}$ higher than the corresponding value of *s-anti* of $PhSO_2CHF^-$ to ($PhSO_2CF_2^-$ + $C_3H_6O$) in the $Et_2O$ solvent. On the other hand, the overall barrier height for the reaction of $PhSO_2CHCl^-$ is higher than the overall barrier height for the reaction of $PhSO_2CHF^-$ in the $Et_2O$ solvent (see Table I). Estimated from the thermodynamic and the kinetic facts, the nucleophilicity of $PhSO_2CYF^-$ is better than that of $PhSO_2CHCl^-$ for the ring opening reaction with propylene oxide, although negative fluorine effects exist for $PhSO_2CYF^-$. These calculated results are in agreement with the experiment phenomena that the reaction provided satisfactory to good product yields for alkyl monosubstituted epoxides.[1] On the other hand, as stated in the experimental study,[1] the reaction yields dropped in the cases of aryl monosubstituted and disubstituted epoxides. It is supposed that a possible reason is that there is a competition between the negative fluorine effect and the size effect of the chlorine atom. For nucleophilic reactions with alkyl monosubstituted epoxides, such as propylene oxide, the size effect of chlorine atom is more obvious and the nucleophilicity for $PhSO_2CHF^-$ is better. However, the better nucleophilicity of $PhSO_2CHCl^-$ and the negative fluorine effect are primarily important in nucleophilic reactions with aryl monosubstituted and other disubstituted epoxides. Therefore, it can be concluded that the nucleophilicity of $PhSO_2CHCl^-$ is better in nucleophilic reactions with aryl-substituted epoxides, while the nucleophilicity of $PhSO_2CHF^-$ is better in nucleophilic reaction with alkyl-substituted epoxides.

Comparing with a previous study,[17] it could be stated that the nucleophilicity of $CH_2F^-$ is better than that of $PhSO_2CHF^-$, although the electron-withdrawing phenylsulfonyl group is an effective way to increase the nucleophilicity. The reason could be attributed to the fact that the steric hindrance of the phenylsulfonyl group decreases nucleophilicity in nucleophilic fluoroalkylation reactions.

## CONCLUSIONS

The path of nucleophilic fluoroalkylation reaction of propylene oxide with $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$) in gas phase and in $Et_2O$ solvent were studied. The nucleophilic fluoroalkylation of propylene oxide with fluorinated carbanions was probed by a reactivity comparison between $PhSO_2CHF^-$, $PhSO_2CF_2^-$ and $(PhSO_2)_2CF^-$. As stated in an experimental study,[1] introducing another electron-withdrawing phenylsulfonyl group is an effective way to increase significantly the nucleophilicity of fluorinated carbanions. The present theoretical calculations confirmed the experiment results and the nucleophilicity reactivity order of $PhSO_2CYF^-$ (Y = F, H or $PhSO_2$) is $(PhSO_2)_2CF^-$ > $PhSO_2CHF^-$ > $PhSO_2CF_2^-$.

For comparison, the nucleophilic addition reaction of propylene oxide with chlorine-substituted carbanion $PhSO_2CHCl^-$ was also studied. Although the negative fluorine effect exists for $PhSO_2CYF^-$, the nucleophilicity of $PhSO_2CYF^-$ is better than that of $PhSO_2CHCl^-$ for the ring opening reaction with propylene oxide.

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И З В О Д

## ТЕОРИЈСКА СТУДИЈА НУКЛЕОФИЛНОГ ФЛУОРОАЛКИЛОВАЊА ПРОПИЛЕН-ОКСИДА ФЛУОРОВАНИМ СУЛФОНИМА

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Теоријски је проучаван ток нуклеофилне реакције пропилен-оксида са $PhSO_2CYF^-$ (Y = F, H и $PhSO_2$) у гасној фази и у $Et_2O$ као растварачу. Нуклеофилно флуороалкиловање пропилен-оксида са флуорованим карбањонима је испитивана упоређивањем реактивности (фенилсулфонил)монофлуорметил ($PhSO_2CHF^-$), (фенилсулфонил)дифлуорметил ($PhSO_2CF_2^-$) и бис(фенилсулфонил)монофлуорметил анјона (($PhSO_2)_2CF^-$). Редослед нуклеофилности за $PhSO_2CYF^-$ (Y = F, H или $PhSO_2$) је $(PhSO_2)_2CF^- > PhSO_2CHF^- > PhSO_2CF_2^-$, што указује на то да је увођење додатне електрон-привлачне фенилсулфонилне групе, начин да се знатно појача нуклеофилност флуорованих карбанјона. Резултати прорачуна и постојећи експерименти се добро слажу.

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