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Halogen migration vs. hydrogen halogenide elimination in reactions of 1-chloro-2,2,2-trifluoroethansulfonyl chloride and 1,2,2,2-tetrafluoroethansulfonyl fluoride with amines: theoretical and experimental investigation

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ABSTRACT

A simple and useful method has been proposed for preparing of 1-chloro-2,2,2-trifluoroethan sulfonylchloride. By aminolysis of 1-chloro-2,2,2-trifluoroethansulfonylchloride the chlorine migration proceeds forming the corresponding salts of 1,1-dichloro-2,2,2-trifluoroethansulfinic acid. This process as well as the alternative reaction, elimination of hydrogen halogenide, has been studied using quantum chemistry (DFT and MP2) methods. As the calculation data indicate, an intermediately formed anion undergo intramolecular chlorine migration via a three-membered cyclic transition state. The latter is characterized by the low activation energy (ΔE = 27.0 kcal/mol). The barrier of activation in the case of 1,2,2,2-tetrafluoroethansulfonylfluoride is considerably higher (ΔE = 41.6 kcal/mol). The structures of the 1,1-dichloro-2,2,2-trifluoroethan sulfinic acid and 1,1,2,2,2-pentafluoroethansulfinic acid anions can be considered as donor–acceptor complexes of perhalogenoalkyl anions with SO_2.

1. Introduction

Since the 80s of the past century the 2,2,2-trifluoroethansulfonyl chloride (tresyl chloride) has been finding a wide application in biochemistry and medicine as a reagent for the hydroxyl group activation at the surface of various materials [1]. A selective activation of the mGlu2 receptor using 2,2,2-trifluoroethansulfonylamides as allosteric modulators was reported recently [2–4]. Therefore, elaboration of a simple and useful method for preparing of new analogues of 2,2,2-trifluoroethansulfonyl chloride from the accessible starting materials is an important goal.

2. Results and discussion

We have elaborated a useful method of synthesis of the previously unknown 1-chloro-2,2,2-trifluoroethansulfonyl chloride (**1a**) (Scheme 1). The accessible sodium 1-chloro-2,2,2-trifluoroethansulfinate [5,6] has been treated with sulfuryl chloride yielding the desired product with a high yield. In contrast to the known 1-chloro-2,2,2-trifluoroethansulfonyl fluoride [7], **1a** is a stable compound and can be stored for a long time under laboratory conditions. This demonstrates chloride **1a** as an especially perspective reagent for the preparative organic synthesis.

We have found that **1a** reacts with pyridine to give a product which has undergone a chlorine rearrangement, pyridinium salt of 1,1-dichloro-2,2,2-trifluoroethansulfinic acid (**2a**) (Scheme 2). A

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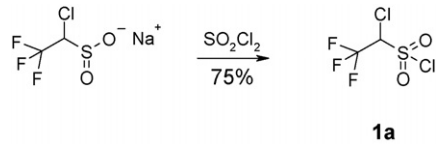
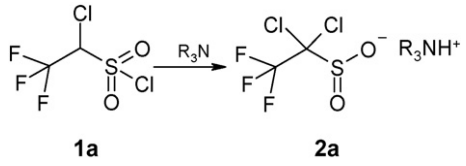


Scheme 1. Preparation of 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**).



Scheme 2. Rearrangement of **1a** in the presence of amines.

similar behaviour was reported for dichloromethanesulfonyl chloride [8]. The formation of the 1,1-dichloro-2,2,2-trifluoroethansulfinic acid has been confirmed by comparing the ^{19}F and ^{13}C NMR spectra of the pyridinium salt with those for the known sodium salt [5].

In the reactions of **1a** with more basic amines such as morpholine or ammonia, the corresponding sulfonylamides **3a** and **3b**, respectively have been isolated along with the migration products, ammonium salts of 1,1-dichloro-2,2,2-trifluoroethansulfinic acid (approximately 20%). Alternatively, the application of a weaker base, such as, e.g. 3-(trifluoromethyl)aniline, only sulfonylamide **3c** arises as the reaction product. Probably, the basicity of 3-(trifluoromethyl)aniline is not enough to provide deprotonation of **1a** at the first stage of the reaction (Scheme 3).

It was demonstrated previously [9] that 1,2,2,2-tetrafluoroethansulfonyl fluoride **(1b)** reacted with pyridine via alternative pathway giving rise to a stable pyridine adduct of sulfene, as a product of the hydrogen fluoride elimination. It should be noted here that no such adducts have been identified in reaction of **1a** with amines, even as by-products.

In order to explain the difference in chemical behaviour of **1a** and **1b** by treatment with pyridine and to elucidate the thermodynamic and kinetic peculiarities of these two different transformation pathways (elimination and migration), we have decided to investigate these two reactions using quantum chemistry methods. In the first part of the current paper we analyze the results of calculations carried out for small model structures using the gas phase approximation and empirically corrected level for description of the solvent effects using the polarizable continuum model (PCM).

The equilibrium structures for **1a** and **1b** are shown in Fig. 1.

The first stage for either the hydrogen halogenide elimination or the halogen migration is deprotonation of sulfonyl halogenide and

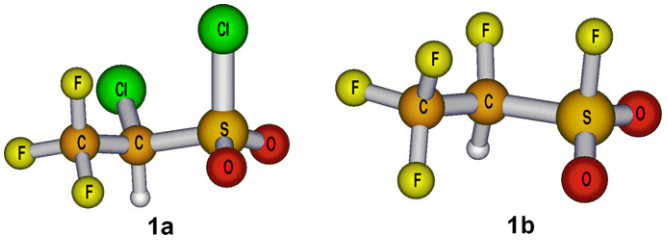


Fig. 1. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **1a,b**.

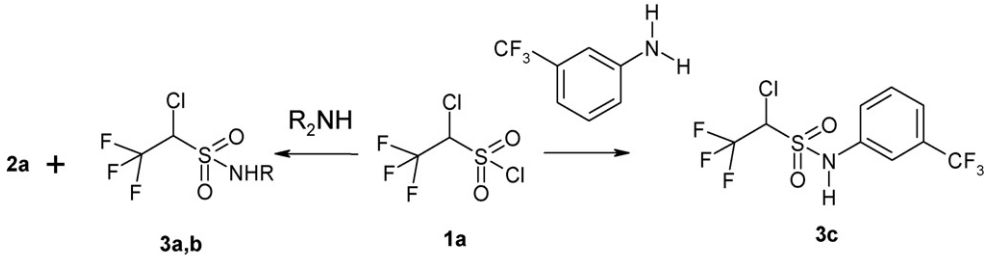
formation of the corresponding anion. The reaction energies for such processes have been estimated using Eq. (1):

$$F_3C{-}CH(Hal){-}SO_2Hal + Py \rightarrow F_3C{-}C^{(-)}Hal{-}SO_2{-}Hal + PyH^{(+)} + \Delta E^1 \quad (1)$$

Structures of anions $F_3C{-}C^{(-)}Cl{-}SO_2Cl$ (**4a**) and $F_3C{-}C^{(-)}F{-}SO_2F$ (**4b**), calculated as isolated molecules at the MP2(fc)/6–311++G** approximation level, are shown in Fig. 2. The structural data resulting from the DFT (B3LYP/6–311++G**) calculations differ only slightly and, if nothing specially noted, will not be further discussed here. More detailed data set (Cartesian coordinates for the MP2 and DFT optimized structures, total energy values, ZPE correction values, etc.) are included in the Supplementary Material for this paper. Within the gas phase approximation, reaction (1) is strongly endothermic (ΔE^1 = 111.0 and 101.3 kcal/mol at the MP2 level of theory). Calculations for the solution in dichloromethane using the COSMO procedure [10] (see Section 5) reduce the energies for the C–H bond cleavage to 22.0 and 14.1 kcal/mol, respectively. Taking into account the effect of counterion will additionally stabilize the anions (see the next chapter).

In structures **4a,b** the C–S bonds are rather short (1.672 and 1.686 Å, respectively), whereas the sulfur–halogen distances are significantly lengthened (2.292 and 1.741 Å). For comparison, the S–F bond length for SO_2F_2 determined using the electron diffraction method in the gas phase totals 1.552 Å, whereas the S–Cl bond length for sulfuryl chloride SO_2Cl_2 is found to be 2.011 Å [11]. Thus, **4a,b** might be represented as the adducts of sulfenes $F_3C{-}C(Hal){=}S(=O)_2$ (**5a,b**) with the corresponding halide anions. A shorter C–S bond in **4b** than in **4a** and a larger sum of the bond angles at the sulfur atom in the $-S(=O)_2$ moiety (345.3° for **4a** vs. 343.5° for **4b**) indicate stronger S–Hal interactions in **4b** than in **4a**. High negative NBO charges on the halogen atom attached to the SO_2 group calculated for **4a,b** (−0.57 on fluorine in **4b** and −0.47 on chlorine in **4a**) are in agreement with the representation as the above mentioned donor–acceptor adducts.

Equilibrium structures of sulfenes **5a,b** are shown in Fig. 3. Formation of sulfenes can arise via halide anion elimination from **4a,b** (Eq. (2)). These reactions are in the both cases endothermic



Scheme 3. Effect of amine basicity on the products of aminolysis of **1a**.

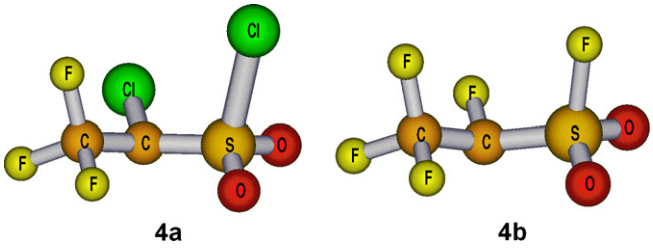


Fig. 2. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **4a,b**.

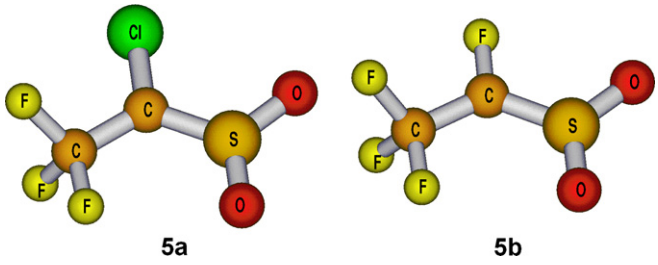


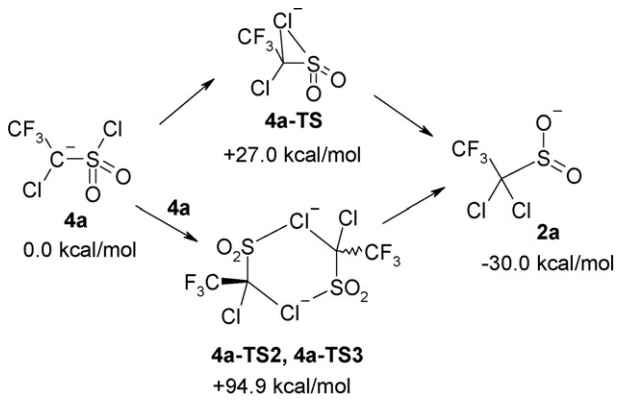
Fig. 3. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **5a,b**.

within the gas phase approximation (ΔE^2 = 12.9 and 20.0 kcal/mol, respectively). This is not contrary to the experimental data evidencing sulfenes as highly unstable species. They easily undergo further transformations, for example, as substrates in the Diels-Alder reactions [12,13] or in the reaction with amines [9,14,15]. Structures and relative stabilities for series of sulfene adducts with amines were analyzed recently in the theoretical paper of Bucher [16].

In accordance with our experimental finding, anion **4a** undergoes a halotropic rearrangement of the halide anion towards carbon giving an isomeric anion **2a** as the product (reaction (2a)). The reaction is exothermic (ΔE^{2a} = −30.5 kcal/mol) and proceeds via transition state **4a-TS** (Scheme 1). The total energy for the mentioned transition state structure is only 27.0 kcal/mol higher (B3LYP/6–311++G**) than that calculated at the same level of theory for **4a**. In contrast to sulfene **5b**, the formation of the migration product **2b** is favoured (ΔE^{2a} = −24.9 kcal/mol). However, a significantly higher activation energy (ΔE^{TS} = 41.6 kcal/mol) has been predicted in this case for the corresponding transition state structure, **4b-TS**, compared to that calculated for the chlorine migration via **4a-TS** (27.0 kcal/mol):

$$F_3C{-}C^{(-)}Hal{-}SO_2{-}Hal \rightarrow F_3C{-}CHal_2{-}SO_2{}^{(-)} + \Delta E^2 \quad (2)$$

$$F_3C{-}C^{(-)}Hal{-}SO_2{-}Hal \rightarrow F_3C{-}CHal{=}SO_2 + Hal^{(-)} + \Delta E^{2a} \quad (2a)$$



Scheme 4. Monomolecular and bimolecular mechanisms of thansformation of **4a**.

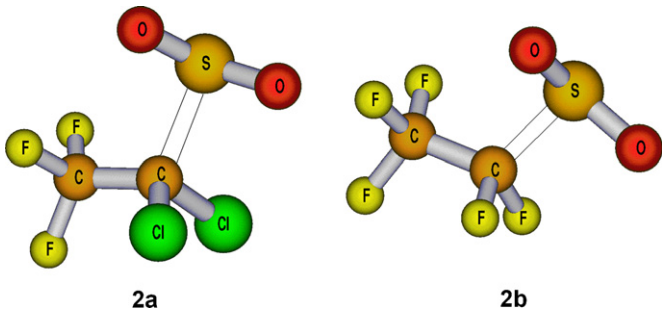
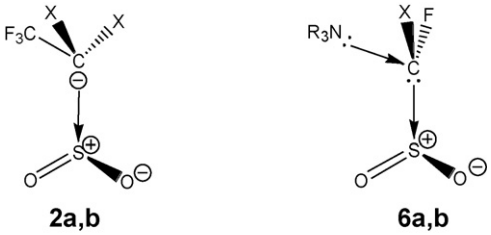


Fig. 4. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **2a,b**.

We have also analyzed the intermolecular rearrangement for **4a** proceeding via the cyclic transition state (Scheme 4). The corresponding transition state structures **TS2** (C_2 symmetry) and **TS3** (C_1 symmetry, see Supplementary Material for more details) correspond to the practically identical activation energy values, which are definitely higher (ΔE^{TS2} = 47.5 kcal/mol, ΔG^{TS2} = 54.1–54.3 kcal/mol of **4a**), than that calculated for the intramolecular process. Thus, the bimolecular mechanism of the rearrangement can be excluded from consideration.

The C–S bonds in anions **2a,b** (Fig. 4) are significantly elongated (1.962 and 2.123 Å, respectively. Taking into account solvent effects (dichloromethane) imply some shortening of these bonds (1.921 and 2.011 Å, respectively). Such bond lengths allow us to consider **2a,b** as the donor–acceptor adducts of perhalogenoalkyl anions CF_3–$C(Hal)_2{}^{(-)}$ with the SO_2 molecule (Scheme 1). A similar significant bond elongation was also reported previously for the trialkylammonium salts of trichloromethanesulfonic acid $R_3NH^{(+)}Cl_3C{-}SO_2{}^{(-)}$ [17] and for salts **6a,b** [14]) in solid. Such coordination character of the C–S bonds in **2a,b** is a consequence of the increased stabilities of the CF_3–$C(Hal)_2{}^{(-)}$ anions, due to the charge delocalization on the electronegative halogen atoms. It is easy to recognize in **6a,b** donor–acceptor complexes of the halocarbene with the amine as a donor and SO_2 as an acceptor. Such a consideration is in line with the dual nature of carbenes [18]. Despite the rather high level of approximation (MP2(fc)/6–311++G**), the calculated C–S bond lengths for **6a,b** (2.026 and 2.070 Å, respectively) are longer than the experimental ones (1.904 and 1.949 Å) [14]. A possible explanation for the observed discrepancies is probably the gas phase approximation used for geometry optimization, which poorly describes the structures in solid state. For comparison, the C–S bond length calculated for the $Cl_3C{-}SO_2{}^{(-)}$ anion (2.055 Å) is also too long compared to the experimental value for $R_3NH^{(+)}Cl_3C{-}SO_2{}^{(-)}$ (1.91 Å) [17]. However, similarly to **4a,b**, correction for the solvent effects using the COSMO routine significantly shortens the C–S bond (to 1.962 Å).



2a X= Cl; **2b** X= F; **6a** X= H; **6b** X= F

Therefore, the C–S bond lengthening should always be expected for species R–$SO_2{}^{(-)}$, where R can form a rather stable free anion. In this connection, the calculated C–S distance in the series of haloalkyl sulfinic acids increases as follows: R = $-CH_3$ (1.843 Å) < $-CF_3$ (1.922 Å) < $-CF_2CF_3$ (2.026 Å) < $-CCl_3$ (2.055 Å) < $-CCl_2CF_3$ (2.070 Å) < $-CF(CF_3)_2$ (2.184 Å). The ΔE and ΔG values for the

Table 1
Calculated reaction energy values for SO_2 elimination from X–$SO_2^{(-)}$ (ΔE and ΔG, kcal/mol).

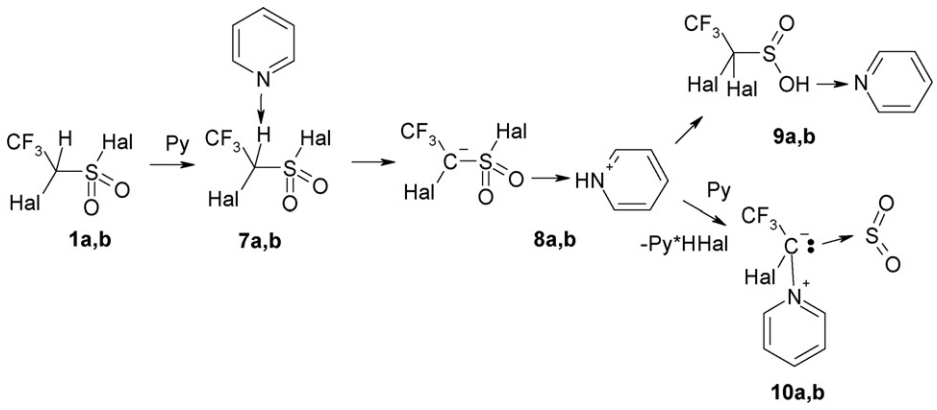
X	B3LYP/6–311++G**				MP2(fc)/6–311++G**			
	Gas phase		CH_2Cl_2 solution		Gas phase		CH_2Cl_2 solution	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
CH_3	71.8	61.8	70.2	59.8	65.0	55.0	64.6	54.5
CCl_3	29.2	17.6	24.9	12.2	36.2	24.3	33.1	20.6
CF_3	41.6	30.3	30.4	18.3	38.2	26.5	28.0	15.9
CF_3CF_2	38.2	26.9	29.9	17.6	36.0	24.3	28.9	16.7
$(CF_3)_2CF$	24.8	14.1	18.3	5.9	25.3	13.8	19.8	7.4
CF_3CCl_2	30.0	18.7	28.3	16.0	33.0	21.4	28.4	16.0
$Et_3N^{(+)}CHF$	29.2	17.4	–	–	27.5	15.7	–	–
$Et_3N^{(+)}CF_2$	19.1	6.1	–	–	19.9	7.4	–	–

Table 2
Calculated reaction energy values (ΔE and ΔG, kcal/mol) for reactions 1–6.

Reaction main product	Reaction	B3LYP/6–311++G**				MP2(fc)/6–311++G**			
		Gas phase		CH_2Cl_2 solution		Gas phase		CH_2Cl_2 solution	
		ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
2c	1	91.9	91.4	5.5	5.0	101.3	101.2	14.1	13.6
2b	1	101.6	101.6	8.9	9.1	111.0	111.3	22.0	22.0
4a	2	−25.3	−25.9	−30.3	−30.5	−24.9	−25.1	−30.5	−30.3
4b	2	−15.7	−16.0	−20.0	−19.6	−20.0	−20.1	−25.2	−24.5
7a	3	−7.7	1.5						
7b	3	−8.6	1.5	–	–	–	–	–	–
8a	4	25.7	25.3	–	–	–	–	–	–
8b	4	16.2	16.1	–	–	–	–	–	–
9a	5	−25.3	−14.3	–	–	−30.5	−18.4	–	–
9b	5	−29.6	−19.2	–	–	−28.8	−16.4	–	–
10a	6	−19.3	−8.7	–	–	−23.5	−14.3	–	–
10b	6	−23.7	−12.7	–	–	−28.3	−17.1	–	–

dissociation reaction, forming the free anion and SO_2, are shown in Table 1. The magnitude of ΔG for the C–S bond dissociation for the isolated $(F_3C)_2CF–SO_2^{(-)}$ anion (calculated at the MP2(fc)/6–311++G** level of theory) amounts 19.8 kcal/mol. In the dichloromethane solution, only 7.4 kcal/mol is necessary for this purpose. Thus, in the presence of bases, the haloalkyl sulfinic acids will probably easy loose SO_2. The most pronounced disposition towards SO_2 loosing is demonstrated by salts **6a**,**b** (Table 1). The dissociation energy calculated for the isolated molecule **6b** is only ca. 6 kcal/mol.

Our consideration of the anionic conversions of **4a**,**b** does not take into account the counterion effect. Now we consider using the DFT level of theory possible reaction stages and intermediates for the **1a**,**b** transformations in the presence of the base (pyridine) (Scheme 5). The first stage for both the hydrogen halogenide elimination and the halogen rearrangement is a coordination of pyridine at the C–H hydrogen forming the corresponding pyridinium salt, **7a**,**b**. Within the gas phase approximation, such coordination is exothermic for both halogenides, **1a** and **1b** (Table 2). Taking entropy into account yields the free energy of the reaction close to zero, obviously due to formation of an aggregate from two separate molecules. However, based on the approximated quantum chemical considerations, it is usually difficult to estimate the entropy contribution. First of all, the geometry optimization is still carried out towards the total energy minimum, not the Gibbs free energy, because the optimization algorithm using the free energy as a criterion for optimization is *hitherto* unknown. Secondly, calculations are usually performed for isolated molecules. Since reactions are normally carried out in solutions, molecules are not isolated, but exist in the form of solvates. Desolvation is an endothermic process that decreases the real exothermic effect of reaction. Taking all above-mentioned conclusions into account, we can suggest that the formation of **7a**,**b** will probably be slightly exothermic and will not determine the



Scheme 5. Transformations of **1a,b** in presence of pyridine.

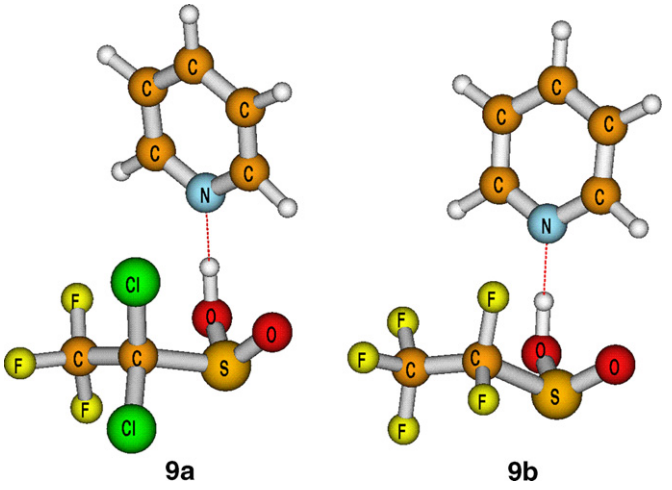


Fig. 5. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **9,b**.

total reaction rate. In both cases our gas phase calculations predict a covalent character for the C–H bond where as the N–H bond remains coordinative. Similarly to anions **4a**,**b**, the S–Hal distances in **7a**,**b** are noticeably elongated (2.112 and 1.627 Å, respectively):

$$CF_3{-}CHal(H){-}SO_2Hal + Py \rightarrow CF_3{-}CHal(H \cdot Py){-}SO_2Hal + \Delta E^3 \quad (3)$$

A deprotonation, following the coordination of pyridine to **1a**,**b** (Eqn. (4)) is an endothermic process, however, the thermodynamic reaction parameters are also effected by solvents and, probably, by the nature of a counterion. Since the reaction has been carried out in the relative low-polar dichloromethane, **4a**,**b** will probably exist in the form of close ion pairs. The structures **8a**,**b** with the lowest total energies have been located by geometry optimization at the B3LYP/6–311++G** level of theory (see Supplementary Material for details). In the both adducts, the pyridinium cation is coordinated at oxygen of the SO_2 group (Scheme 5). The predicted reaction energies ΔE^4 are endothermic (Table 2):

$$CF_3{-}CHal(H \cdot Py){-}SO_2Hal \rightarrow CF_3{-}CHal^{(-)}{-}SO_2Hal \cdot HPy^{(+)} + \Delta E^4 \quad (4)$$

As the last stage either the halogen migration proceeds yielding **9a**,**b** (Fig. 5), or the next pyridine molecule attacks nucleophilically the C(Hal) carbon atom forming inner salts **10a**,**b** (Fig. 6). As a result, reactions (5) and (6) are exothermic:

$$CF_3{-}C(Hal)H{-}SO_2Hal + Py \rightarrow CF_3{-}CHal_2{-}SO_2H \cdot Py + \Delta E^5 \quad (5)$$

$$CF_3{-}C(Hal)H{-}SO_2Hal + 2Py \rightarrow CF_3{-}C(Hal)Py^{(+)}{-}SO_2{}^{(-)} + HalH \cdot Py + \Delta E^6 \quad (6)$$

A comparison of the ΔE^5 and ΔE^6 values derived from the total energies at the B3LYP/6–311++G** level of theory (Table 2) indicates that reaction (5) is more preferable for the both halogenides **1a**,**b**. Geometry optimizations for **9a**,**b** and **10a**,**b** carried out at the more superior level of approximation (MP2/6–311++G**) make reaction (5) significantly more favoured for chloride **1a** (ΔE^5 = −30.5, ΔE^6 = −23.5 kcal/mol), whereas in case of **1b** both reaction energy values are very close (ΔE^5 = −28.8, ΔE^6 = −28.3 kcal/mol). Changing to ΔG values makes reaction (6) for **1b** even slightly more favourable (ΔG^5 = −16.4, ΔG^6 = −17.1 kcal/mol). Thus, the reaction pathway will strongly depend upon the reaction conditions. An elimination product **10b** can result from the higher activation energy inherent to **1b** in the isomerization reaction than that calculated for **1a**. Any case, the formation of the sulfene adduct with pyridine in case of **1b** can be considered as a result of a subtle balance of different effects and processes, which cannot simultaneously be taken into account using the currently available quantum chemistry methods. Nevertheless, such results do not exclude that **1b** under appropriate conditions might undergo isomerization, similarly to **1a**.

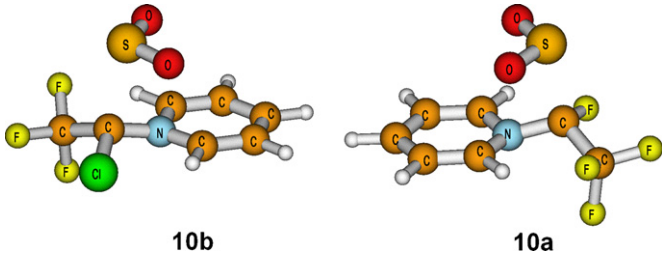


Fig. 6. MOLDEN plots of optimized (MP2(fc)/6–311++G**) structures **10,b**.

3. Conclusions

A convenient way of synthesis of the previously unknown 1-chloro-2,2,2-trifluoroethansulfonylchloride (**1a**) has been proposed. In the presence of basic amines **1a** undergoes easily chlorine migration, where as in case of low-basic 3-(trifluoromethyl) aniline only the corresponding sulfonylamide is formed. Two ways of transformation of **1a** as well as the structurally similar 1,2,2,2-tetrafluoroethansulfonylfluoride (**1b**) with pyridine have been investigated theoretically at the DFT and MP2(fc) levels of approximation. It has been found that **1a** preferably reacts with the halogen migration from sulfur to carbon. It is different in the case of 1,2,2,2-tetrafluoroethansulfonylfluoride that was previously demonstrated to undergo hydrogen halogenide elimination yielding in solution a stable adduct of the corresponding sulfene with pyridine. Both reactions begin with deprotonation, the corresponding anions indicate rather short C–S bonds and elongated S–Hal bonds and can be better represented as adducts of corresponding sulfenes with the halogenide anions. The further conversion can proceed as the elimination or halogen migration processes. The latter reaction proceeds intramolecularly with the relatively low activation energy and is in both cases an exothermic process. For the products, anions of the sulfinic acids, long C–SO_2 distances have been predicted. One can better describe these structures as adducts of the stable perhalogenated anions with the SO_2 molecule, and these should be disposed towards easy dissociation, similarly to other anions of haloalkyl sufinic acids. The elimination reaction is endothermic within the gas phase approximation and becomes exothermic only if the unstable sulfene is stabilized by complexation with pyridine. However, the latter should be considered as the adduct of a perhalogenated carbene, coordinated with an amine and SO_2. For 1-chloro-2,2,2-trifluoroethansulfonylchloride, the migration process is definitely more favoured whereas 1,2,2,2-tetrafluoroethansulfonylfluoride demonstrates similar MP2 reaction energies for both migration and elimination. Thus, the conversion of the latter in the presence of amines via the halogen migration cannot also be excluded.

4. Experimental

4.1. General

^{1}H NMR (500 MHz), ^{19}F (470 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance DRX 500 spectrometer.

TMS (^{1}H NMR and ^{13}C NMR spectroscopy), and $CFCl_3$ (^{19}F NMR spectroscopy) were used as internal standards. Infrared (IR) spectra were recorded on a UR-20 spectrometer in KBr or neat for 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**). Melting points were measured with a Buchi melting points apparatus and are uncorrected. Boiling point for 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**) is uncorrected.

Sodium 1,1-dichloro-2,2,2-trifluoroethanesulfinate and sodium 1-chloro-2,2,2-trifluoroethanesulfinate were synthesized as described in literature [5,6]. All experiments were carried out under inert atmosphere. Dichloromethane was distilled over phosphorous pentoxide under argon.

4.2. 1-Chloro-2,2,2-trifluoroethanesulfonyl chloride (1a)

To 5 g (3 ml, 37 mmol) of sulfuryl chloride in 10 ml dichloromethane 3.8 g (18.58 mmol) of sodium 1-chloro-2,2,2-trifluoroethanesulfinate was added in portions at 5 °C and the mixture was vigorously stirred for 10 min. The reaction mixture was allowed to warm to RT and then heated under stirring at 35 °C for 2 h. A precipitate was filtered off; distillation of the filtrate at atmospheric pressure provided a colourless liquid **(1a)**. Yield: 3.02 g (75%); b.p. = 135–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.48 (q, $^3J_{HF}$ = 5.5 Hz, 1H, CH). ^{19}F NMR (470 MHz, $CDCl_3$): δ = −67.84 (d, $^3J_{FH}$ = 5.5 Hz, 3F, CF_3). ^{13}C (125 MHz, $CDCl_3$): δ = 119.7 (dq, $^1J_{CF}$ = 283 Hz, $^2J_{CH}$ = 6.3 Hz, CF_3), 76.3 (dq, $^1J_{CH}$ = 163.5 Hz, $^2J_{CF}$ = 35.2 Hz, CH). IR (neat), ν(cm^{-1}): 1420, 1310, 1230, 1200, 1140, 900, 780, 700. Anal. calcd. for $C_2HCl_2F_3O_2S$: C 11.07; H 0.46; Cl 32.68; F 26.27; S 14.78. Found: C 11.05; H 0.5; Cl 32.71; F 26.08; S 14.74.

4.3. Pyridinium 1,1-dichloro-2,2,2-trifluoroethanesulfinat (2a)

To a solution of 1.1 g (5 mmol) of 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**) in 20 ml of dry dichloromethane a solution of 0.4 g, 0.41 ml (5 mmol) of dry pyridine in 10 ml of dry dichloromethane was added dropwise at 5 °C and under vigorous stirring. After 1 h stirring at this temperature hexane (10 ml) was added. The mixture was filtrated and hexane was added to the filtrate until crystallization begins. After 1 h **2a** was filtered as the colourless semisolid hydroscopic masse. Yield: 1.13 g (76.3%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (t, $^3J_{HH}$ = 6.8 Hz, 2H, $3H_{Py}$), 8.48 (t, $^3J_{HH}$ = 7.7 Hz, 1H, $4H_{Py}$), 8.95 (d, $^3J_{HH}$ = 5.5 Hz, 2H, $2H_{Py}$), 13.5(br s, 1H, NH). ^{19}F NMR (470 MHz, $CDCl_3$): δ = −72.53 (s, 3F, CF_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.43 (q, $^1J_{CF}$ = 283 Hz, **C**F_3), 96.49 (q, $^2J_{CF}$ = 29 Hz, CCl_2). IR (KBr), ν(cm^{-1}): 3010–2650, 1620, 1470, 1210, 1120, 1060, 910, 890, 760, 710.

4.4. Sodium 1,1-dichloro-2,2,2-trifluoroethanesulfinate

^{19}F NMR (470 MHz, CD_3COCD_3): δ = −71.53 (s, 3F, CF_3). ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 122.3 (q, $^1J_{CF}$ = 283 Hz, CF_3), 95.5 (q, $^2J_{CF}$ = 30.2 Hz, CCl_2). IR (KBr), ν(cm^{-1}): 1210, 1120, 1060, 910, 890, 760, 710.

4.5. 4-[(1-Chloro-2,2,2-trifluoroethyl)sulfonyl]morpholine (3a)

To a solution of 1.74 g (1.75 ml, 20 mmol) of morpholine in 15 ml of dichloromethane at 5 °C under stirring was added dropwise 2.17 g (10 mmol) of 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**) in 20 ml of dichloromethane. Formation up to 15% morpholinium salt of 1,1-dichloro-2,2,2-trifluoroethanesulfinic acid was detected with the ^{19}F NMR spectroscopy. A reaction mixture was washed with water; the organic layer was separated, dried with $MgSO_4$ and evaporated under reduced pressure. A residue (**3a**) was crystallized from hexane. Yield: 2.14 g (80%), m.p. = 111–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.06 (q, $^3J_{HF}$ = 6.5 Hz, CH), 3.76 (m, 4H, CH_2OCH_2), 3.53 (m, 4H, CH_2NCH_2). ^{19}F NMR (470 MHz, $CDCl_3$): δ = −68.94 (d, $^3J_{FH}$ = 6.5 Hz, 3F, CF_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.0 (q, $^1J_{CF}$ = 281 Hz, CF_3), 68.26 (q, $^2J_{CF}$ = 34 Hz, CHCl), 66.91 (s, CH_2O), 47.47 (s, CH_2N). IR (KBr), ν(cm^{-1}): 2990–2920, 1690, 1480, 1340, 1290, 1190, 1180, 1170, 1060, 1040, 765,720. Anal. calcd. for $C_6H_9ClF_3NO_3S$: C 26.93; H 3.39; Cl 13.25; F 21.29; N 5.23; S 11.98. Found: C 27.07; H 3.60; Cl 13.38; F 21.01; N 5.24; S 12.04.

4.6. 1-Chloro-2,2,2-trifluoroethanesulfonamide (3b)

30 ml of dry dichloromethane was saturated at 0 °C with dry ammonia. 4.34 g (20 mmol) of sulfonylchloride **1a** was added dropwise at 0 °C under stirring and continuous bubbling of dry ammonia. Full conversion of **1a** was controlled by the ^{19}F NMR spectroscopy. Formation up to 20% of 1,1-dichloro-2,2,2-trifluoroethanesulfinate ammonium salt was detected by NMR spectroscopy. A reaction mixture was allowed to warm to room temperature and then saturated with a gaseous HCl. The precipitate was filtered off; the solvent was evaporated under vacuum. The residue (**3b)** was crystallized from hexane. Yield: 3.16 g (80%) as colourless hygroscopic crystals, m.p. = 86–87 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.29 (q, $^3J_{HF}$ = 6.8 Hz, CH), 8.11 (s, 2H, NH_2). ^{19}F NMR (470 MHz, DMSO-d_6): δ = −67.34 (d, $^3J_{FH}$ = 6.8 Hz, 3F, CF_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 121.52 (q, $^1J_{CF}$ = 280.4 Hz, CF_3), 67.52 (dq, $^1J_{CH}$ = 163.5 Hz, $^2J_{CF}$ = 32.07 Hz, CHCl). IR (KBr), ν(cm^{-1}): 3310–3060, 2910, 1695, 1470, 1340, 1290, 1200, 1160, 1150, 1040, 1010, 780, 720. Anal. calcd. for $C_2H_3ClF_3NO_2S$: C 12.16; H 1.53; Cl 17.95; F 28.85; N 7.09; S 16.23. Found: C 12.20; H 1.60; Cl 17.92; F 28.58; N 6.92; S 16.14.

4.7. 1-Chloro-2,2,2-trifluoro-N-[3-(trifluoromethyl)phenyl]ethanesulfonamide (3c)

To a solution of 2.17 g (10 mmol) of 1-chloro-2,2,2-trifluoroethanesulfonyl chloride (**1a**) in 10 ml of dichloromethane at 5 °C under stirring was added dropwise a solution 3.22 g (20 mmol) of 3-(trifluoromethyl)aniline in 10 ml of dichloromethane. A precipitate of 3-(trifluoromethyl)aniline chlorohydrate was filtered off, a filtrate was evaporated under reduced pressure, a residue was crystallized from hexane. Yield of (**3c**) 2.74 g (80%) as colourless crystals with m.p. = 73–74 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.05 (q, $^3J_{HF}$ = 5.7 Hz, 1H, CH), 7.48 (br s, 1H, NH), 7.54–7.58 (m, 4H, H_{apoM}.). ^{19}F NMR (470 MHz, $CDCl_3$): δ = −63.40 (s, 3F, CF_{3Ar}), −68.12 (d, $^3J_{FH}$ = 5.7 Hz, 3F, CF_3CHCl). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.44 (s, C_{Ar}), 132.63 (q, $^2J_{CF}$ = 34 Hz, $C_{Ar.}$), 130.72 (s, C_{Ar}), 125.75 (s, C_{Ar}), 124.0 (q, $^3J_{CF}$ = 3.8 Hz, C_{Ar}), 123.44 (q, $^1J_{CF}$ = 272 Hz, CF_{3Ar}), 120.82 (q, $^1J_{CF}$ = 282 Hz, CF_{3CHCl}), 119.39 (q, $^3J_{CF}$ = 6.0 Hz, C_{Ar}), 67.25 (q, $^2J_{CF}$ = 34 Hz, C_{CHCl}). IR (KBr), ν(cm^{-1}): 3010, 1695, 1470, 1340, 1285, 1190, 1030, 785, 720, 665, 480. Anal. calcd. for $C_9H_6ClF_6NO_2S$: C 31.64; H 1.77; Cl 10.38; F 33.36; N 4.10; S 9.38. Found: C 31.73; H 1.87; Cl 10.26; F 33.18; N 4.10; S 9.16.

5. Details of calculations

The structures of the studied compounds were fully optimized with the GAUSSIAN-03 set of programs [19] at the DFT (B3LYP [20]) and MP2(fc) level of theory (using frozen core approximation). In the former case a three-parameter hybrid functional B3LYP, including correlation fuctionals from Lee et al. [21] and VWN5 [22]. In both cases, geometry optimizations were carried out using medium-size 6–311++G** basis sets. As default within the GAUSSIAN packet the mentioned basis sets are defined as the proper 6–311G Pople basis sets [23] for hydrogen and the second period atoms (C, N, O, F) and the (12s,9p) McLean-Chandler basis

set [24] for sulfur and chlorine, expanded with the appropriate polarization and diffuse Gaussian functions. Calculations of vibration frequencies were performed at the both levels of approximation for all optimized structures. The only exception were structures **2a**, **13a**,**b**, **14** and **15a**,**b**, of especially large size, for which the vibration frequencies were calculated only using the MP2/6–311G** approach. The first and second derivatives were computed analytically. Zero and one imaginary frequency for the structure indicated the local minimum and transition state, respectively. GAUSSIAN-03 default setting (temperature 298.150 K, pressure 1 atm) was used for thermochemistry calculations. The calculated energy values were corrected by addition of zero point energy (ZPE) values (for calculation of ΔE magnitudes) or thermal correction to Gibbs free energy (TCGFE) values (for calculation of ΔG magnitudes). For some cases, the geometries were re-optimized using the empirical procedure CPCM (COSMO) [10] and modelling the situation in dichloromethane. The atomic charges were calculated using the NBO packet [25]. All structures within the paper are pictured using the MOLDEN [26] visualization program set.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.11.001.

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