Synthesis of Trifluoromethanesulfonic Acid from CHF$_3$

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Abstract:
Trifluoromethane is transformed to trifluoromethanesulfonic acid (TFMSA) at low temperature in a liquid-phase reaction in a strong acid such as fuming sulfuric acid as well as in a strong base solution such as t-BuOK/DMF.

Introduction
Trifluoromethanesulfonic acid (TFMSA), also known as triflic acid, is a strong acid with high thermal stability and resistance to oxidation and reduction.1 It is widely used as a catalyst in the polymer, fuel, pharmaceutical, and sugar industries. There are also recent indications that it would be a superior electropolymerating agent. The current commercial process for producing TFMSA involves the electrochemical fluorination of CH$_3$SO$_2$Cl, is expensive.2 Alternative routes involve expensive raw materials such as CF$_3$S-S-CF$_3$ which is oxidized with K$_2$S$_2$O$_8$ or H$_2$O$_2$ to TFMSA.3 Cost intensive, low-yield processes have been reported for the synthesis of TFMSA starting from CF$_3$Br and CF$_3$I using stoichiometric amount of a reducing agent such as Zn.4

CHF$_3$ is a byproduct of the fluorochemical industry and is available in large quantities at a very low price. Prakash et al. have recently reported a novel method for synthesizing trimethyl(trifluoromethyl) silane (CF$_3$-TMS) from CHF$_3$;5 however, there is no report of synthesizing TFMSA directly from CHF$_3$. Here, we will show that CHF$_3$ can be functionalized to TFMSA in highly acidic as well as highly basic media. Our initial approach was based on recent studies by Sen et al.6 and by us,7 which have shown that CH$_4$ can be sulfonated with SO$_3$ in fuming sulfuric acid to produce MSA in high yield, using K$_2$S$_2$O$_8$, CaO$_2$, and urea—H$_2$O$_2$ and RhCl$_3$ combinations as free radical initiators.8 Since the C—H bond energy of CHF$_3$ is similar to that of CH$_4$, we reasoned that CHF$_3$ might be activated for sulfonation in a manner similar to that for CH$_4$.

In a typical reaction (Scheme 1), CHF$_3$ (650 psig) is reacted with SO$_3$ (21 mmol) in fuming sulfuric acid (5.67 g) for 12 h in the presence of a small amount of initiator, urea—H$_2$O$_2$ (0.4 mmol) and a promoter RhCl$_3$ (0.1 mmol) at 65 °C. The reaction mixture was analyzed by $^{19}$F NMR to identify and quantify CF$_3$SO$_3$H (chemical shift is −15.6 with respect to trifluorotoluene). D$_2$O was used as the NMR solvent in a capillary. Only, 2.5% of the initial SO$_3$ was converted to CF$_3$SO$_3$H using the urea—H$_2$O$_2$ and RhCl$_3$ combination. Over 400 reactions were performed to increase the yield without success.

The problem of low yield is understood on the basis of this proposed mechanism similar to that previously proposed for methane activation (reactions 1–4).7 The initiator abstracts a hydrogen atom from CHF$_3$ to generate CF$_3$• which then reacts with SO$_3$ to form CF$_3$SO$_3$•. This species then can react with CHF$_3$ to form the product, TFMSA, and another CF$_3$• radical. Termination of the radical chain can occur via the reaction of two CF$_3$• radicals to generate C$_2$F$_6$, as shown in reaction 4. The observation of C$_2$F$_6$ in the headspace suggests that chain termination occurs rapidly, thereby limiting the production of TFMSA.

When the reaction was performed with SO$_2$Cl$_2$ (21 mmol) instead of SO$_3$, about 3% of SO$_2$Cl$_2$ converted to

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Scheme 1. Direct reaction of CHF₃ with SO₃ in fuming sulfuric acid

\[
\text{CHF}_3 + \text{SO}_3 \xrightarrow{\text{Urea-H}_2\text{O}_2, \text{RhCl}_3} \rightarrow \text{CHF}_3\text{SO}_3\text{H}
\]

Scheme 2. Direct reaction of CHF₃ with SO₂Cl₂ in fuming sulfuric acid

\[
\text{CHF}_3 + \text{SO}_2\text{Cl}_2 \xrightarrow{\text{Urea-H}_2\text{O}_2, \text{RhCl}_3} \rightarrow \text{CF}_3\text{SO}_2\text{Cl} + \text{HCl}
\]

Scheme 3. Direct reaction of CHF₃ with Ph⁻S⁻S⁻Ph in DMF

\[
\text{CHF}_3 + \text{Ph-S-Ph} + \text{t-BuOK} \xrightarrow{30^\circ\text{C}, 12\text{ h}} \rightarrow \text{CF}_3\text{Ph} + \text{PhSK} + \text{t-BuOH} \text{DMF}
\]

CF₃SOCl₂, which could then be transformed to CF₃SO₂H by reaction with water (Scheme 2). Analysis of the reactor headspace showed the presence of C₂F₆ and CF₃Cl. These products are most likely formed via chain-termination processes involving the reaction of CF₃• radicals with each other radical or with a chlorine atom. The reaction, 2CHF₃ = C₂F₆ + H₂ is not thermodynamically favourable; however, the presence of an oxygen source derived from the radical initiator makes the reaction favourable, i.e., 2CHF₃ + 1/2O₂ = C₂F₆ + H₂O.

The low yield obtained in an acidic medium motivated us to consider CHF₃ activation in a highly basic medium. This approach was stimulated by the recent work of Prakash et al. on the synthesis of CF₃-TMS. The hydrogen on CHF₃ is acidic and can be removed by reaction with a strong base such as t-BuOK in DMF. Thus, CHF₃ was reacted with Ph⁻S⁻S⁻Ph in DMF⁸ in the presence of t-BuOK. CF₃⁻S⁻Ph (δ = +19.9) was obtained in moderate yield (Scheme 3). This product was then oxidized with a mixture of HCl and H₂O₂ to CF₃SO₂H (δ = -15.8). The main byproduct was CF₃SO₂Ph (δ = -11.9).

Table 1 shows the effect of different process parameters on the conversion of CHF₃ to CF₃⁻S⁻Ph by the reaction of CHF₃ and Ph⁻S⁻S⁻Ph in the presence of t-BuOK as the base (Scheme 3). Since DMF is unique in its ability to stabilize CF₃⁻, it was used as the solvent.⁸ Increasing the CHF₃ pressure from 50 psig to 450 psig increased the conversion of CHF₃. However, the selectivity to CF₃SPh decreased with increasing CHF₃ pressure. It was observed that the temperature has a predominant role on the conversion and selectivity. The maximum conversion (53%) and selectivity to CF₃SPh (16%) were obtained at 30 °C (Table 2, entries 5–7). Another parameter affecting the progress of the reaction is the mole ratio of t-BuOK to Ph⁻S⁻S⁻Ph (Table 2, entries 8–11). The maximum conversion and selectivity were obtained using a molar ratio at 1:5.

In the second step the CF₃SPh was oxidized to CF₃SO₂H using a mixture of HCl and H₂O₂ (Scheme 4). This “chlorine/water” oxidation (2HCl + H₂O₂ → Cl₂ + 2H₂O) was performed at 53 °C for 6 h using 1.12 mmol of CF₃SPh in water (total 10 mL). A phase-transfer catalyst (PTC) such as tetrabutylammonium chloride (TBAC), 0.05 g was used to enhance the rate of the biphasic reaction.⁹

Table 2 shows the effect of different molar ratios of HCl to H₂O₂ on the oxidation of CF₃SPh to CF₃SO₂H⁹

Table 1. Effect of different parameters on the CF₃SPh synthesis

<table>
<thead>
<tr>
<th>entry</th>
<th>parameter</th>
<th>conv of CHF₃, %</th>
<th>selectivity to CF₃SPh, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHF₃, 50 psig</td>
<td>2</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>250 psig</td>
<td>9</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>350 psig</td>
<td>12</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>450 psig</td>
<td>14</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>temp, 30 °C</td>
<td>16</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>46 °C</td>
<td>12</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>55 °C</td>
<td>11</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>t-BuOK:PhSSPh:1:1</td>
<td>7</td>
<td>42</td>
</tr>
<tr>
<td>9</td>
<td>1:1.5</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>10</td>
<td>1:2</td>
<td>13</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>1:5</td>
<td>16</td>
<td>53</td>
</tr>
</tbody>
</table>

* Standard reaction conditions (unless otherwise stated): CHF₃, 350 psig (0.08 mol); t-BuOK, 1.6 g (0.0143 mol); PhSSPh, 3.42 g (0.0214 mol); temperature, 46 °C; time, 16 h.

Table 2: Effect of molar ratio of HCl to H₂O₂ on the oxidation of CF₃SPh to CF₃SO₂H⁹

<table>
<thead>
<tr>
<th>entry</th>
<th>molar ratio of HCl/H₂O₂</th>
<th>conv of CF₃SPh, %</th>
<th>selectivity to CF₃SO₂H, %</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2:1</td>
<td>46</td>
<td>6</td>
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<tr>
<td>2</td>
<td>3:1</td>
<td>53</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>5:1</td>
<td>59</td>
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</tr>
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<td>4</td>
<td>5:2</td>
<td>66</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>7:3</td>
<td>73</td>
<td>16</td>
</tr>
</tbody>
</table>

* Reaction conditions: CF₃SPh, 1.12 mmol; temperature, 53 °C; time, 6 h; solvent, water, 10 mL; TBAC, 0.05 g.

Scheme 4. Direct oxidation of CF₃SPh with HCl and H₂O₂

\[
\text{CF}_3\text{S-Ph} \xrightarrow{\text{HCl/H}_2\text{O}_2} \rightarrow \text{CF}_3\text{SO}_3\text{H}
\]

Scheme 5. Direct reaction of CHF₃ with S and subsequent oxidation

\[
\text{CHF}_3 \xrightarrow{(i) \text{S, t-BuOK} \text{DMF}} \rightarrow \text{CF}_3\text{S-Ph} \xrightarrow{(ii) \text{HCl/H}_2\text{O}_2 \text{Water}} \rightarrow \text{CF}_3\text{SO}_3\text{H}
\]

(8) DMF is used as a solvent as it is known in the literature that it helps to stabilize the CF₃⁻ anion in solution by complex formation, see Russel, I.; Roques, N. *Tetrahedron*, 1998, 54, 13771.

difficult to identify. They are possibly of the general formula CF₃Sn. However, when the mixture was oxidized with HCl and H₂O₂, all the peaks disappeared and a new peak corresponding to CF₃SO₃H appeared, although in low yield (1.5% based on CHF₃).

In conclusion, we have developed a low-temperature reaction protocol to activate CHF₃ in acidic as well as in basic medium. The yields of triflic acid in both media are low. In acidic medium the low conversion may be due to the coupling of two CF₃ radicals to form C₂F₆, a process that is believed to be enhanced by the presence of an oxidant, the radical initiator. In basic medium CHF₃ can be transformed to CF₃SO₃H via a two-step process. The work presented here offers new opportunities for the conversion of CHF₃ to useful products.

**CAUTION:** Most of the compounds mentioned in this work are toxic and highly odorous; therefore, the entire work should be done inside a well-maintained hood.

**Acknowledgment**

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