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New protic salts of aprotic polar solvents

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Abstract—Aprotic polar solvents such as DMF, acetonitrile or DMSO can be protonated to form stable triflate salts when treated with triflic acid. The reaction of the same solvents with *N*,*N*-bis(trifluoromethanesulfonyl)imide led to the isolation of the corresponding *N*,*N*-bis(trifluoromethanesulfonyl)imide salts.

Triflic acid, CF_3SO_3H,[1,2] and bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2NH$ or TFSI[3] are two of the strongest monoprotic acids known. TfOH was first synthesised in 1954[1] and is now prepared by different procedures such as electrochemical fluorination of methanesulfonyl chloride or fluoride.[4,5] The synthesis of TFSI was first described by DesMarteau in 1984.[6] According to gaseous phase acidity studies, TFSI is a stronger acid than TfOH.[2]

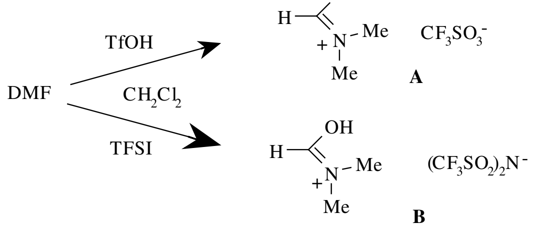
While working with TfOH and TFSI for the electrochemical synthesis of metallic triflates and triflimides in polar solvents,[7] we found that new nonmetallic compounds were formed in these reactions. This electrochemical synthesis of metallic triflates was run, for example, in TfOH/DMF in the presence of a rod of a metal M constituting the anode, which was oxidised into the corresponding metal cations M^{n+}. The cathodic process was the reduction of the acid to TfO^- and hydrogen, and the corresponding M^{n+} $(TfO^-)_n$ salts were formed in solution. The metallic salts were isolated and obtained in almost quantitative yields after partial solvent evaporation, filtration and washing of the precipitate. However, when the filtrate was analysed, a new compound could be isolated from the solution. This new compound did not contain any metal and in the view of the reaction components, we suggested the possibility of formation of a protonated triflate salt of DMF.

We therefore tested this hypothesis, in a direct reaction between DMF and TfOH, as shown in Scheme 1. Thus, when equimolar amounts of TFOH and distilled DMF were added to CH_2Cl_2 at room temperature and the solution stirred for 5 min, a white solid **A** was obtained in quantitative yield after solvent evaporation.

The ^1H NMR spectrum of **A** in $CDCl_3$ (0.6 M) at room temperature, as compared to that of DMF under the same conditions showed a shift of the $–NMe_2$ singlets from 2.88 and 2.96 to 3.14 and 3.31 ppm. The H of DMF/$CDCl_3$ at 8.02 appeared at 8.37 in **A**. The spectrum of **A** presented also a broad singlet around 13.85 ppm.

On the other hand, the ^{19}F NMR spectrum of **A** in $CDCl_3$ presented a singlet at −79.27 ppm. This signal is to be compared to that of triflic acid under the same conditions, which appears at −76.44 ppm.[8] For comparison, metallic triflate salts present their CF_3 singlet between −78.5 and −79.5 ppm.

The mass spectrometry of **A** under electrospray conditions indicated a cationic peak with *m*/*z* of 74.



Scheme 1.

Keywords: Triflic acid; Triflate; *N*,*N*-bis(trifluoromethanesulfonyl)-imide; DMF salt; DMSO salt; MeCN salt.

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Compound **A** was a stable solid, which was noncorrosive. Its elemental analysis corresponded to the 1:1 association TfOH–DMF.[9] On the view of these spectral and analytical data, and the fact that **A** is a defined solid, we suggested for **A** the structure of a protonated DMF salt, as shown in Scheme 1. The triflate salt of DMF has not been described before. Other analogous DMF salts are however known, such as the chlorinated Vilsmeyer salt.[10,11]

Similarly, when a reaction was carried out with equimolar amounts of TFSI and DMF in CH_2Cl_2 at room temperature, an oil **B** was obtained in quantitative yield after solvent evaporation. Compound **B** was also a stable and noncorrosive compound. The spectral data for **B** were close to those of **A**, as shown in Table 1. The ^{19}F NMR spectrum of **B** in $CDCl_3$ (0.6 M, rt; reference *p*-$ClC_6H_4CF_3$ at −63.0 ppm) presented a singlet at −79.41 ppm, whereas TFSI/$CDCl_3$ appeared at −75.5 ppm.[6a] Other metallic salts of TFSI presented their CF_3 singlet around −79.3 to −80 ppm.[7] By analogy with **A**, we propose for **B** the structure of the triflimide salt shown in Scheme 1.

The formation of stable triflate and triflimide salts of protonated DMF prompted us to prepare the corresponding salts with other polar solvents such as acetonitrile, DMSO or nitromethane. In the case of acetonitrile, oily organic salts were formed upon the reactions of equimolar quantities of MeCN and TfOH or TFSI in CH_2Cl_2, respectively, as indicated in Table 1.

In DMSO as well as in acetonitrile, the protonated triflate or triflimide salts were also formed quantitatively using the same procedure. However, we were not able to isolate a defined compound when we carried out the reaction with nitromethane. The chemical shift of the methyl group of $MeNO_2$ in an equimolar mixture of TFSI/CH_3NO_2 in $CDCl_3$ was similar to that of nitromethane alone. This should be an indication that the protonation of nitromethane by TFSI was not occurring in a large extent.

When TfOH or TFSI were added to a distilled THF solution a polymerisation of the solvent occurred. The reaction of TfOH or TFSI with diethyl ether led to solvent decomposition. For H_2O, an important increase of the chemical proton shift was observed in the presence of both acids.

A cyclic voltammetry study was carried out to evaluate the redox potential of TFSI in different polar solvents. These reduction potentials should be closely related to those of the corresponding organic salts formed in the medium. The cyclic voltammetry curves showed large and badly defined peaks. Figure 1 summarises the results of the position of the different peak potentials. According to these results, the reduction of TFSI was easier in CH_3NO_2 than in DMF or CH_3CN, indicating that nitromethane seemed to weekly interact with TFSI.

The ability of the solvent protonation by the super acids could be related to the donating numbers of Gutman, which evaluate the relative coordination of a ligand by protic or Lewis acids such as $SbCl_5$.[12] The donating numbers of Gutman, follow the order: nitromethane (2.7)<acetonitrile (14.1)<H_2O (18)<DMF (24.0)< DMSO (29.8). Our NMR and cyclic voltammetry data are in agreement with the donating numbers of Gutman and indicate that nitromethane is weekly protonated by TFSI or triflic acid in comparison with DMF or DMSO.

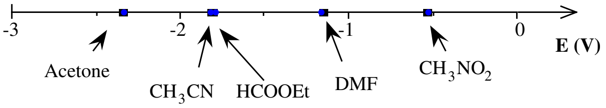
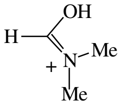
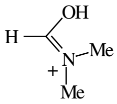
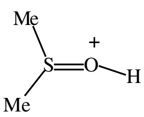
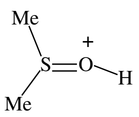


Figure 1. Reduction potentials of TFSI salts of organic solvents determined by cyclic voltammetry (E_{ref} = Ag/AgCl at 20 °C).

Table 1. Yields and NMR shifts of TFOH and TFSI salts of several solvents in $CDCl_3$ (0.6 M at 20 °C)

Solvent	Triflate salt			TFSI salt		
	Structure (% yield)	^1H NMR (ppm)	^{19}F NMR[a] (ppm)	Structure (% yield)	^1H NMR (ppm)	^{19}F NMR (ppm)
DMF	 $CF_3SO_3^-$ A (99%)	3.14 3.31 8.37 13.85	−79.27	 $(CF_3SO_2)_2N^-$ (84%) B	2.94 3.05 8.06	−79.41
DMSO	 $CF_3SO_3^-$ (99%)	3.08 10.18	−79.20	 $(CF_3SO_2)_2N^-$ (98%)	3.18 8.22	−79.23
MeCN	$Me-C\equiv\overset{+}{N}-H$ $CF_3SO_3^-$ (98%)	2.11 13.0	−78.81	$Me-C\equiv\overset{+}{N}-H$ $(CF_3SO_2)_2N^-$ (90%)	2.06 11.03	−76.81

[a] For comparison, ^{19}F NMR of TfOH alone in $CDCl_3$ at −76.44 ppm and of TFSI at −75.5 ppm.

In order to evaluate the reactivity of DMF-H^+ OTf^- and DMF-H^+ NTf_2^- as compared with analogous Vilsmeier's salts,[10,11] attempts to formylate guaïacol and anisole in the presence of the protic salts were carried out, without success.

In conclusion, TfOH and TFSI are corrosive and fuming strong acids. For the first time, we describe here their reactivity with common polar solvents with the formation of stable protic salts. The possibility to store or transport the super acids under a noncorrosive solid form (or an oily form)[13] by their combination with polar solvents might constitute an interesting and advantageous feature. A way of recovery of the acids is still under investigation.

Acknowledgements

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