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PAPER

Interaction of acetonitrile with trifluoromethanesulfonic acid: unexpected formation of a wide variety of structures†

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Interaction of acetonitrile with trifluoromethanesulfonic acid has been studied by multinuclear NMR and ESI-MS. It has been found that the interaction results in formation of a great variety of different cations and neutral compounds which is controlled by the ratio of CH_3CN to TfOH. In the presence of an excess of the acid (molar ratio 1 : 8–14) diprotonated *N*-acetylacetamidine **1** is formed as the major product, which eventually transforms into protonated acetamidine **3** and acetic acid **4**. At molar ratio of (1 : 1–2) diprotonated 2,4-dimethyl-6-methylidene-3*H*-1,3,5-triazine **12**, tautomer of the diprotonated trimethyl-s-triazine **11**, becomes the main product at an early stage of the reaction and diprotonated 1-(dimethyl-1,3,5-triazin-2-yl)prop-1-en-2-ol **15** at a later stage. In the case of a large excess of acetonitrile (4–20 : 1) trication **17** is formed as a result of the interaction between **11** and **12** along with some oligomers $[(CH_3CN)_3]_n$ (n = 4–12).

Introduction

Acetonitrile is a common solvent in organic chemistry and trifluoromethanesulfonic acid (TfOH) is often used to acidify acetonitrile solutions. However, although the chemical behaviour of nitriles in acids has been studied for many years,[1] data on the interaction of the simplest nitrile, acetonitrile, with TfOH are limited. It is generally assumed that these substances mix, in ambient conditions, without any reaction,[2] though on occasion some unspecified chemical reactions were observed[3] (*cf.* ref. 4 and 5). The authors of the paper[6] had suggested that the interaction of CH_3CN with TfOH resulted in formation of rather stable acetonitrilium triflate, but later it was found that such interaction resulted in formation of protonated trimethyl-s-triazine.[7,8] We have found that the interaction of CH_3CN with TfOH gives rise to a large number of other products. The purpose of this paper is to determine the structures of these products and to discuss the mechanisms of their formation.

We have studied the interaction of acetonitrile with trifluoromethanesulfonic acid (TfOH) at different ratios using multinuclear NMR and ESI-MS. Structure elucidation and NMR signal assignment for the products presented on Schemes 1, 4, and 6 were performed on the basis of 2D NMR correlation spectra ^1H–^1H (NOESY, ROESY), ^1H–^{13}C (HSQC, HMBC), and ^1H–^{15}N (HMBC).

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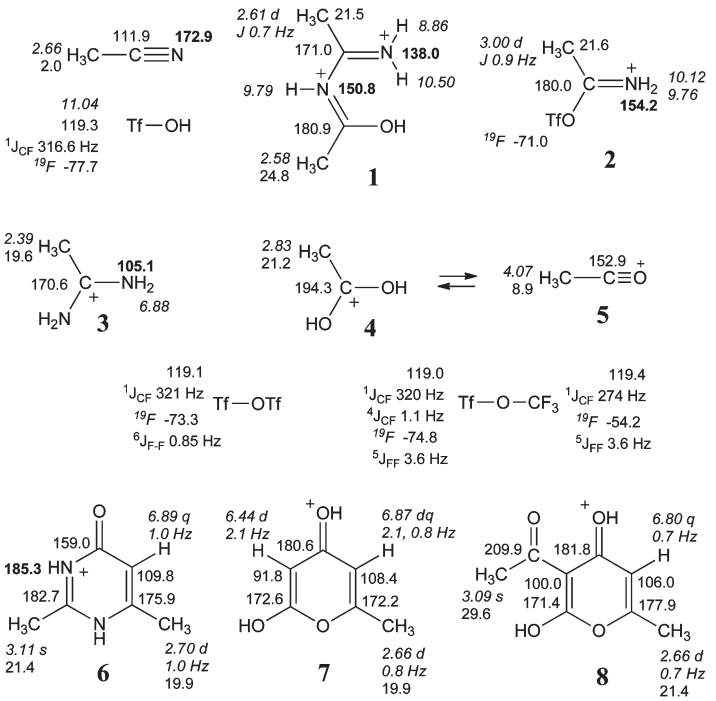
Results and discussion

All reaction mixtures in this study contain both neutral and protonated acetonitrile as indicated by the ^{15}N chemical shifts 246 and 144 ppm,[9] respectively. For the mixtures under investigation the ^{15}N chemical shift changes from 240 to 173 ppm when the initial CH_3CN : TfOH ratio varies from 4 : 1 to 1 : 14.

The products formed upon the interaction of CH_3CN with TfOH (molar ratio 1 : 14) are given in Scheme 1. At the early stages of the reaction the main product is dication **1**, *cf.* ref. 1 and 10. By NOESY data, this dication exists in the s-*cis*-form, apparently due to formation of the intramolecular hydrogen bond. The ^1H NMR signal of the OH group of **1** is not observable obviously due to a rapid proton exchange with TfOH. Along with **1**, cation **2** is also observed (Fig. 1, see also Table 1 in ESI†), *cf.* ref. 5 and 11. The ^1H NMR spectrum of **2** is considerably different from the spectrum of protonated acetamide [δ 2.62 ppm (CH_3), 8.12 ppm (NH), 8.32 ppm (NH), *cf.* ref. 12] and similar to that of cation **9**[13] bearing a OTf group (Scheme 2), the ^{19}F chemical shift being equal to that of cation **9**.

In the course of the reaction the content of cations **1** and **2** decreases with time and the other species, **3**, **4**, and **5**, appear (Fig. 1). According to DOSY data (Fig. 2) hydrodynamic volumes of structures **3**, **4**, and **5** are roughly equal, while that of structure **1** is doubled. The chemical shifts of **3**, **4**, and **5** are close to those of acetamidinium cation,[14] protonated acetic acid and acetyl cation,[15] respectively. According to 2D NMR spectra both **4** and **5** have one set of correlations corresponding to the CH_3–C– fragment and no nitrogen atoms. Cross-peaks corresponding to chemical exchange between **4** and **5** are observed in



Scheme 1 NMR data for CH_3CN, TfOH (molar ratio 1 : 14) and for the products of their interaction.‡

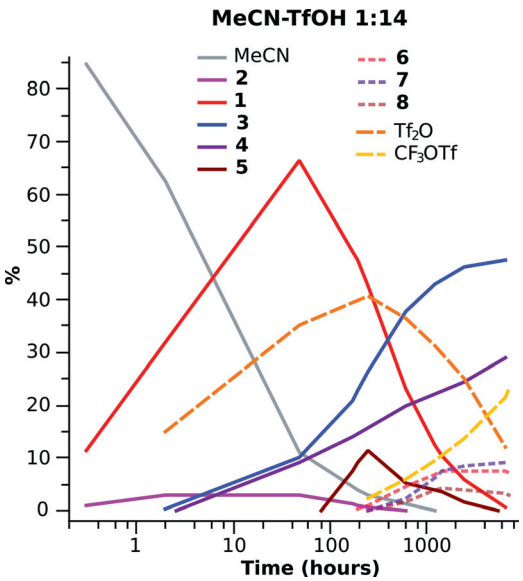
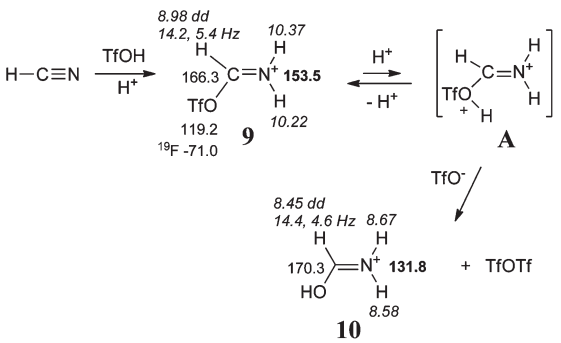


Fig. 1 Progress of the reaction of CH_3CN with TfOH (mol. ratio 1 : 14) with time.

the NOESY spectrum. Such exchange is typical for the equilibrium between protonated acetic acid and acetyl cation.[16] So, we have concluded that **3** is an acetamidinium cation, **4** is a protonated acetic acid and **5** is an acetyl cation.

Almost from the very beginning of the reaction a signal for Tf_2O appears in the ^{19}F NMR spectra. Its identification has been made from the observation of a long-range spin–spin coupling constant ^{19}F–^{19}F (J = 0.85 Hz in the ^{13}C satellites) and was confirmed by comparison with the ^{19}F NMR spectrum of the mixture Tf_2O–TfOH. The content of Tf_2O in solution passes



Scheme 2 Interaction of HCN with TfOH.‡

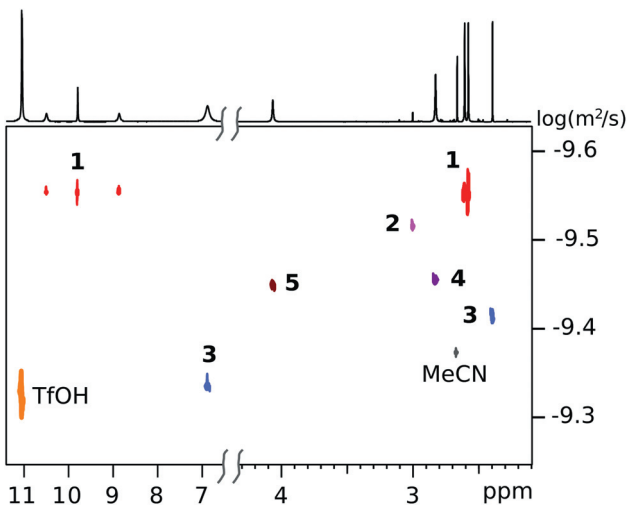
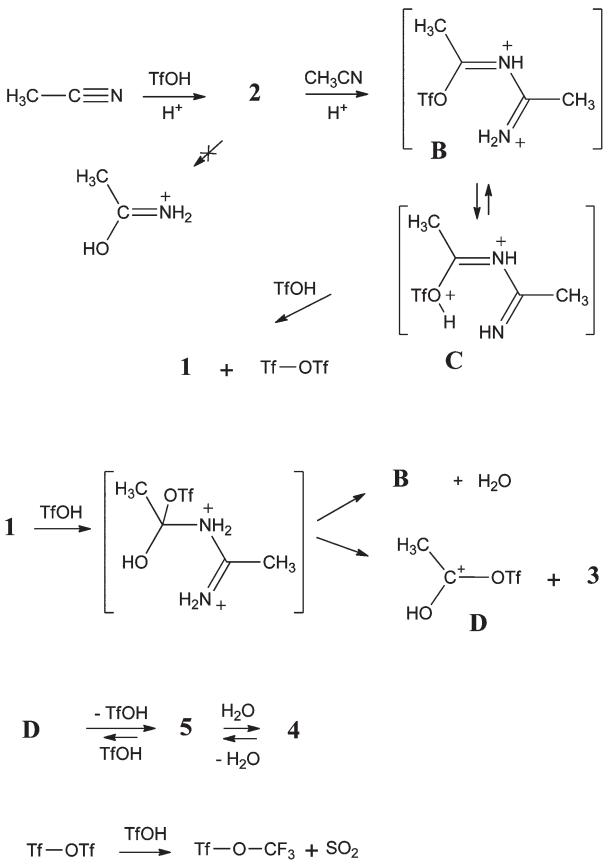


Fig. 2 2D DOSY spectrum of CH_3CN–TfOH mixture (mol. ratio 1 : 14) after 192 h.



Scheme 3 Mechanism of the reaction between CH_3CN and TfOH (molar ratio 1 : 14).

through a maximum and then decreases. When the reaction mixture is kept for a long time an additional species appears, its structure is tentatively assigned as **6** on the basis of its 2D NMR data. Further ageing and heating leads to the appearance of two more species, identified as **7** and **8**.

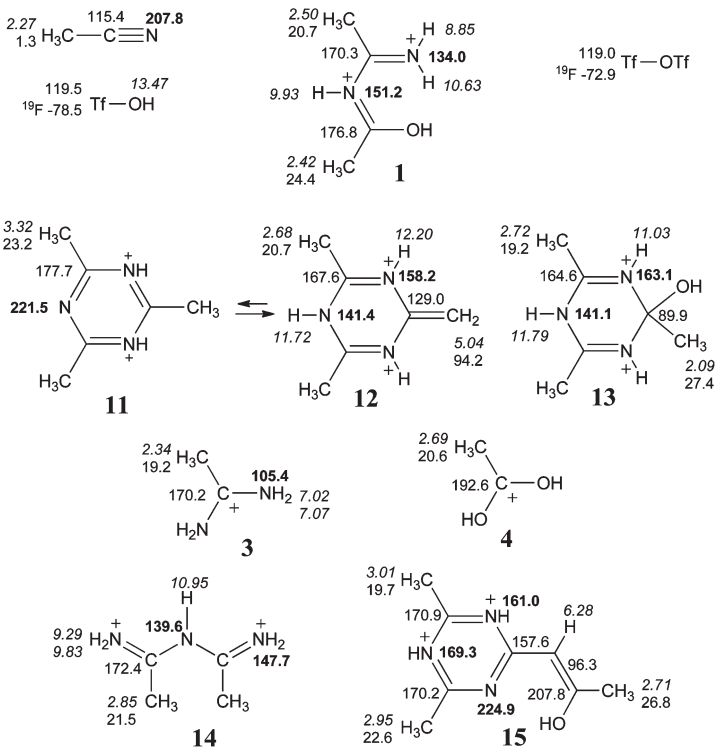
The suggested mechanism is given in Scheme 3. At first cation **2** is formed (*cf.* ref. 1). The interaction of this cation with acetonitrile gives intermediate **B**, subsequently transforming into dication **1**, with the source of the OH group being TfOH itself while undergoing dehydration to Tf_2O. Thus, acetonitrile formally plays the role of a dehydrating reagent, *cf.* ref. 17. An analogous process was observed earlier upon the interaction of HCN with TfOH[13] without indication of Tf_2O formation, but now we have found that Tf_2O is formed according to Scheme 2. The transformation of **9** into protonated formamide **10** is very slow ($t_{1/2}$ is approx. 30 days at ambient temperature). This is quite natural as it has to proceed through unstable intermediate **A**, bearing an extra positive charge. Analogous conversion of **2** into the protonated acetamide is also very slow, much slower than its conversion into **1**, and we have not managed to detect this reaction. On the contrary, conversion of intermediate **B** into **1** is more favourable as it can proceed *via* intramolecular tautomerization into **C**, bearing no extra charge. Addition of TfOH to dication **1** followed by β-scission of the N–C bond results in formation of amidinium cation **3** and intermediate **D**. The latter transforms into acetyl cation **5**. The conclusion of intermediate **D** formation was supported by the NOE from ^{19}F nuclei to the methyl group protons of cation **5** as detected by heteronuclear ^{19}F–^{1}H NOE difference experiments. The longitudinal magnetization is transferred from the irradiated ^{19}F to ^{1}H nuclei in **D** where these nuclei are spatially close to each other and transferred further *via* chemical exchange to cation **5**. An alternative mechanism of magnetization transfer, due to formation of rather strong associates of cation **5** with TfOH, is not justified, as diffusion of **5** according to DOSY spectra is not slowed down in comparison with the other species. Hydration of cation **5** gives cation **4**. TfOH apparently plays the role of water source, being partially transformed into Tf_2O. The latter partially transforms into CF_3OTf. This process is known.[18]

Species **7** and **8** are obviously formed as a result of the interaction of protonated acetic acid (cation **4**) with Tf_2O. This conclusion is confirmed by the following experiments. Thus, cation **4** formed from acetic acid in TfOH (AcOH–TfOH, molar ratio 1 : 7) is stable for 7 h at 110 °C, however, upon heating the mixture AcOH–TfOH–Tf_2O 1 : 7 : 0.5 (7 h at 110 °C) a reaction proceeds that results in formation of the mixture of **7** and **8** (molar ratio 5 : 1). Neutral precursors of cations **7** and **8**, triacetic acid lactone and dehydroacetic acid, are well known and can transform into each other in acidic media.[19] The neutral precursor of cation **6**, 2,4-dimethyl-1,6-dihydro-6-pyrimidone, is also known and can arise from acetamidine and various derivatives of acetic acid.[20]

The same products at similar ratios are formed in the systems CH_3CN–TfOH 1 : 10 and 1 : 8. However, when the ratio of CH_3CN to TfOH increases to 1 : 2 the composition of the products changes sharply (Scheme 4, Fig. 3, Table 2 in ESI†). According to literature data,[7] the main product observed upon neutralization of such mixture is trimethyl-s-triazine. The authors of that paper suggested that in the 1 : 2 mixture of CH_3CN–TfOH trimethyl-s-triazine is present in triprotonated form. According to our data, diprotonated form **11** can be identified in the solution (as reasoned below). **11** is in slow exchange, on the NMR time scale, with its tautomer **12**, the latter being more stable. The equilibrium mixture of **11** and **12** remains unchanged for a long time. The other products, **13**, **14**, and **15**, have also been detected by NMR spectroscopy. Relative sizes of cations **1**, **3**, **11**, **12**, and **13** are in accordance with the DOSY data (Fig. 4): the ratio of their hydrodynamic volumes estimated from the respective diffusion coefficients is 2 : 1 : 3 : 3 : 3.

In the ESI-MS spectra (at $m/z > 100$, see ESI†) we observed signals corresponding to products **11** (**12**), **15**, and additionally a weaker signal with m/z 208.107 corresponding to the molecular formula $(CH_3CN)_3(CH_2CO)_2+H^+$. Concentration of the respective cation in solution is too low to allow its unambiguous identification by NMR. By analogy to **15**, we suggest structure **16** for this cation (Scheme 5).

The suggested mechanism of the reactions proceeding in the system CH_3CN–TfOH 1 : 2 is given in Scheme 5. The first step consists of the interaction of dication **1**, formed according to Scheme 3, with acetonitrile resulting in formation of intermediate **E**. The majority of this intermediate undergoes cyclization into dication **13**, which transforms into dications **12** and **11** as a result of dehydration. The rest of **E** undergoes scission into cations **5** and **14**, the former transforming almost quantitatively into its hydrated form, cation **4**. When acetonitrile is exhausted, formation of intermediate **E** becomes impossible and dication **1**



Scheme 4 Chemical shifts of CH_3CN (in a molar ratio of 1 : 2 with TfOH) and of the products of their interaction.‡ The respective signals of **11** are averaged over the triazine ring due to proton exchange.

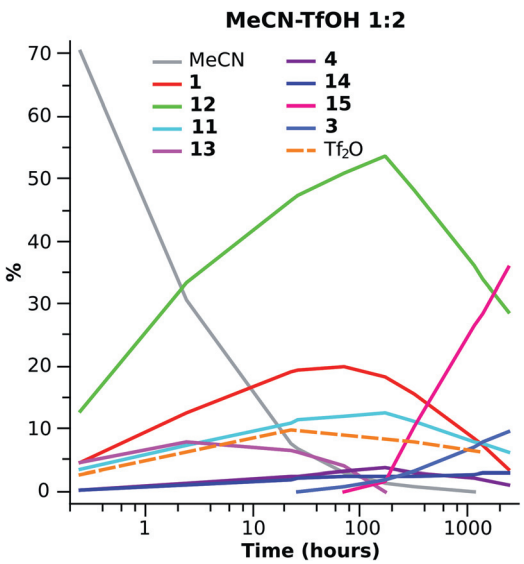


Fig. 3 Progress of the reaction of CH_3CN with TfOH (mol. ratio 1 : 2) with time.

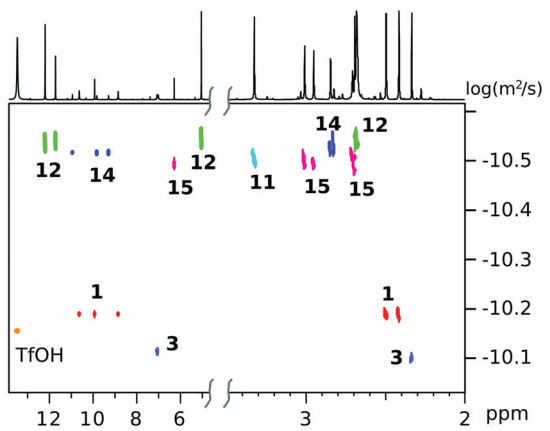
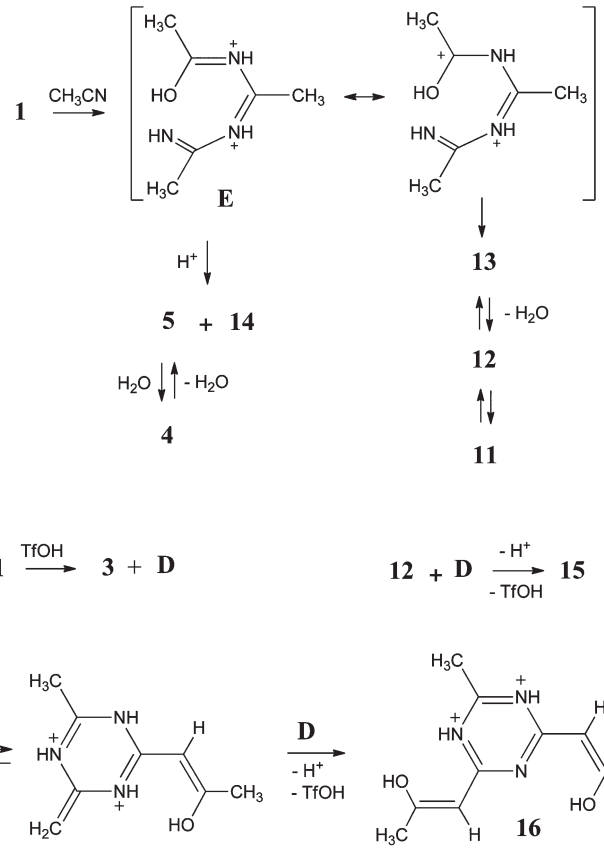


Fig. 4 2D DOSY spectrum of CH_3CN–TfOH mixture (mol. ratio 1 : 2) after 316 h.

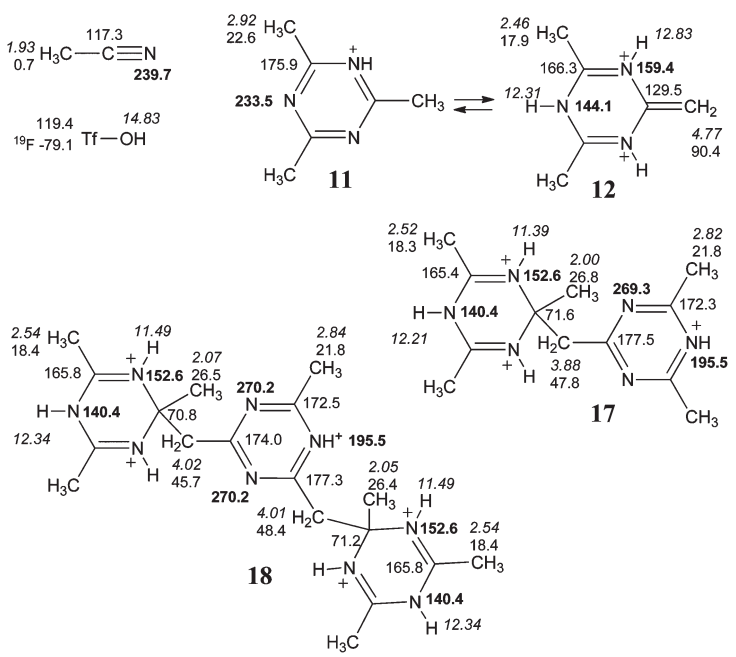
continues to react according to the other mechanism, which is analogous to Scheme 3, resulting in cation **3** and intermediate **D**. The latter adds to *exo*-double bond of dication **12** producing dication **15**. This dication can add one more fragment of **D** giving **16**.

Scheme 5 is consistent with the data on deuterium distribution in products formed in the system CD_3CN–TfOH. CD_3 groups of deuterated **1**, **3** and **14** are not involved in isotope exchange with TfOH protons, in contrast to those of deuterated analogs of **4**, **5** (*cf.* ref. 21), **11**, **12**, **13**, and **15**. Equilibrium distribution of deuterium is observed at all the positions of cations **11**, **12**, **13**, and **15**. For cations **11** and **12** it follows from their tautomerization. Obviously an analogous process is also possible for dication **15**. All the positions of the deuterated dication **13** are involved in isotope exchange with TfOH, probably *via* dication **12**.

When the ratio CH_3CN to TfOH is 1 : 1 only **11** and **12** are formed in the beginning of the reaction (see ESI†). In 24 h the reaction mixture becomes viscous, so that high-resolution NMR spectra are unavailable. Upon increase of the acetonitrile content in the mixture with TfOH to 4 : 1 ratio the interaction of these



Scheme 5 Mechanism of the reaction between CH_3CN and TfOH (molar ratio 1 : 2).



Scheme 6 Chemical shifts of CH_3CN, TfOH (molar ratio 4 : 1) and of the products of their interaction.‡

components results in formation of cations **11**, **12**, and **17** (Scheme 6, Fig. 5, Table 3 in the ESI†). The same products are formed upon increase of the ratio to 20 : 1, see ESI.† Trication **17** obviously results from an electrophilic attack at the *exo*-methylene bond of dication **12** by its aromatic tautomeric form **11** (Scheme 7). It is quite natural to suggest that the triazinium

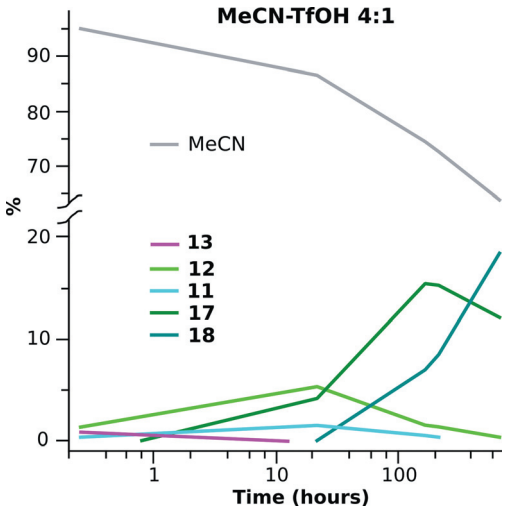
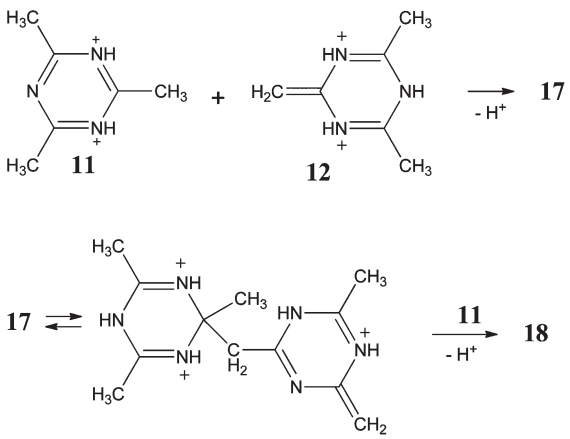


Fig. 5 Progress of the reaction of CH_3CN with TfOH (mol. ratio 4 : 1) with time.



Scheme 7 Mechanism of the reaction between CH_3CN and TfOH (molar ratio 4 : 1).

fragment of **17** can produce tautomeric forms having *exo*-methylene bonds and these forms can add more fragments of **11** by analogy to Scheme 7. As a result, the extent of oligomerization can increase. Indeed, the set of NMR signals corresponding to cation **18** is observed.

Upon keeping the reaction mixture for a longer time, a growth of broadened signals with chemical shifts very close to that of **18** is observed. This may indicate the formation of further similar structures with even higher oligomerization degree.

In the ESI-MS spectra (see ESI†) signals corresponding to products **11**, **12** and **17** are observed. There are also strong signals corresponding to **18**, $[(CH_3CN)_3]_3$. In addition, signals corresponding to other products with even higher degree of oligomerization are observed: $[(CH_3CN)_3]_n$ (n = 4, 5). There are also weak signals corresponding to structures with n = 6, 7, and (under conditions optimized for observation of large ions) signals of even larger oligomers (n is up to 12). Signals corresponding to oligomers with $n > 12$ do not appear in the ESI-MS spectra at all, and the amount of oligomers with $n > 4$ is rather low, indicating that there is no significant polymerization of acetonitrile. The concentration of all the cations larger than **18** is too low to be detected by NMR. In principle, linear as well as branched aggregates with $n > 3$ are probable.

When the ratio CH_3CN–TfOH is increased to 200 : 1, the protonated acetamide is formed as a sole product (*cf.* ref. 8) obviously as a result of hydrolysis of acetonitrile due to the presence of water traces.

On degree of trimethyl-s-triazine protonation

Although the proton signals of the NH groups in **11** are not observed, consideration of its NMR spectra, in a combination with the literary data, allows estimation of the degree of trimethyl-s-triazine protonation in media with various amounts of TfOH. ^{15}N chemical shifts strongly depend on the extent of protonation. A signal of the protonated nitrogen atom is at higher field than that of the neutral one, *e.g.* the ^{15}N chemical shift for pyridine is δ 306 ppm, while that for the pyridinium cation is δ 210 ppm. The ^{15}N chemical shift for neutral trimethyl-s-triazine is δ 267.2 ppm.[22] On the basis of these data it is reasonable to suggest that one of the nitrogen atoms of the aromatic ring of tri-cation **17** is protonated (δ 195.5 ppm), the two others are neutral (δ 269.3 ppm). The average value due to proton exchange of ^{15}N chemical shift for monoprotonated trimethyl-s-triazine is expected to be δ 245 ppm, while that for the diprotonated species is δ 220 ppm. So, in the 1 : 2 and 1 : 1 mixtures of CH_3CN–TfOH the diprotonated form of trimethyl-s-triazine is predominantly formed (the ^{15}N chemical shifts are 221.5 and 222.6 ppm, respectively), and in the 4 : 1 mixture of CH_3CN–TfOH a substantial part of trimethyl-s-triazine is monoprotonated (the ^{15}N chemical shift is 233.5 ppm).

Conclusions

Interaction of the two simple compounds, CH_3CN and TfOH, results in formation of a great variety of complicated structures, the composition of the reaction products being a function of the ratio of CH_3CN to TfOH.

Experimental

General methods and materials

NMR and ESI-MS spectra were obtained at the Chemical Service Centre of the Siberian Branch of the Russian Academy of Sciences. Multinuclear NMR spectra (^1H, ^2H, ^{13}C, ^{15}N, ^{19}F) were obtained on Bruker AV-600 (resonance frequency for ^1H 600.3 MHz), AV-400 (400.13 MHz), and AV-300 (300.13 MHz) spectrometers. Chemical shifts for ^1H, ^2H and ^{13}C measured relative to the internal standard CD_2Cl_2 (δ 5.33 ppm for ^1H and ^2H, 53.6 ppm for ^{13}C), for ^{15}N relative to external NH_3, for ^{19}F relative to external $CFCl_3$. For structure elucidation and NMR signal assignment 2D correlation spectra ^1H–^1H (NOESY, ROESY with mixing times τ_m = 0.4–0.7 s), ^1H–^{13}C (HSQC, HMBC), ^1H–^{15}N (HMBC), and heteronuclear ($^{19}F \rightarrow {}^1H$) NOE difference spectra were used. For separation of NMR subspectra corresponding to different cationic species and for measurement of diffusion coefficients diffusion oriented spectroscopy (DOSY)

with longitudinal eddy current delay (LED)[23] on ^{1}H and ^{19}F nuclei was used.

The ESI mass spectra were recorded for *m*/*z* 100–3000. For the mixture CH_3CN–TfOH 4 : 1 additionally ESI mass spectra from *m*/*z* 200 to 10 000 were recorded. A hybrid QTOF (quadrupole-time-of-flight) mass spectrometer with an electrospray interface (micrOTOF-Q, Bruker Daltonics) was utilized. Nitrogen was used as a drying gas at 220 °C and at flow of 4 L min^{-1}. Nebulizer pressure was set to 1.0 bar. The capillary voltage was set at −4.0 kV in the positive scan mode. Sample solutions were infused into the ESI source by LC Agilent 1200 at FIA mode (Flow Injection Analysis, 2–5 μL at a flow rate of CH_3CN 0.1 mL min^{-1}).

CH_3CN Panreac (HPLC-gradient grade, 99.9%), CD_2Cl_2 was dried over molecular sieves 4 Å, TfOH reagent grade, 98% was purchased from Aldrich and used without further purification. All the mixtures under study contained 20% (v/v) of CD_2Cl_2 (for field-frequency lock). Special experiments showed that the usage of freshly distilled TfOH and adding CD_2Cl_2 to the reaction mixtures did not influence the products composition.

Preparation of acidic solutions

TfOH (50–670 mg, 0.33–4.5 mmol), CD_2Cl_2 (0.1 mL), and CH_3CN (13–270 mg, 0.32–6.6 mmol) put into NMR tube in such portions to obtain the ratio CH_3CN–TfOH needed (from 1 : 14 to 20 : 1). The tube closed and the three-layered mixture shook under cooling with cold water just before the NMR spectra registration. For ESI-MS determination a drop (approx. 5 mg) of the reaction mixture was solved in 1 mL of acetonitrile. The reaction mixture CH_3CN–TfOH 200 : 1 was boiled under argon for 5 h (*cf*. ref. 8).

Spectral data for identified species and the data on composition of mixtures are given in Schemes 1, 4, 6 and in the ESI.†

Acknowledgements

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Notes and references

‡ ^{1}H chemical shifts are given in italics, ^{13}C in ordinary font, ^{15}N in bold face, the chemical shifts of acetonitrile are in fact those of its mixture with the protonated form, the signals are averaged through rapid exchange of both forms on the NMR time scale.

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