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# Metal-free reduction of the greenhouse gas sulfur hexafluoride, formation of $SF_5$ containing ion pairs and the application in fluorinations†

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A protocol for the fast and selective two-electron reduction of the potent greenhouse gas sulfur hexafluoride ($SF_6$) by organic electron donors at ambient temperature has been developed. The reaction yields solid ion pairs consisting of donor dications and $SF_5$-anions which can be effectively used in fluorination reactions.

## Introduction

Sulphur hexafluoride is a non-flammable, odourless and colourless gas of high density.[1] The unique physical and chemical properties of $SF_6$ make it suitable in specialized electrical equipment, commercial products as well as in scientific and industrial processes. Due to its great arc-quenching ability, almost 80% of all $SF_6$ produced is used as an insulator and fire suppression agent in high-voltage circuit breakers.[2] Another application of $SF_6$ consists in its use as a blanketing, sound- and thermo-insulating agent in industry[3] and as a contrast agent for ultrasound imaging in medicine.[4] Furthermore, sulphur hexafluoride is applied in the determination of ventilation efficiency as well as in environmental modeling.[5]

However, despite the mentioned applications, $SF_6$ is a potent greenhouse gas included in the Kyoto Protocol.[6,7] According to the World Meteorological Organization, the atmospheric lifetime of $SF_6$ is *ca.* 3200 years and its global warming potential is 22 450 times higher than that of $CO_2$.[8] Therefore, besides the necessity to control the level of $SF_6$ emissions and the development of more efficient trapping techniques,[9] a methodology to decompose this gas is in demand. Thus, since 1980s several reports on $SF_6$ activation followed by the total reduction to compounds containing futile sulfides and fluorides have been published. Such procedures generally require harsher conditions or/and elemental alkali metals.[10] Polycrystalline silicon, tin oxide and organic polymer layers react with sulphur hexafluoride at high temperature.[11] More recently, protocols for the $SF_6$ activation under milder conditions were reported. These methods require transition metals as catalysts or reducing agents and the products of $SF_6$ decomposition are fluorides, sulfides or/and silicon and phosphorus fluoro-derivatives.[12a–f] In addition, the reduction with tetrakis(dimethylamino)ethylene under UV-light irradiation is described.[13]

## Results and discussion

Based on our interest in developing metal-free reactions, we wondered whether purely organic molecules without UV irradiation would be able either to decompose this greenhouse gas at room temperature or to selectively activate it in an efficient manner, allowing simultaneous use of the reduction products in fluorination procedures. In particular, we were also interested in the preparation of the $SF_5^-$ anion[14] from sulphur hexafluoride which would potentially allow the formation of $SF_5$ containing organic molecules which are of considerable interest as well.[13,15] Taking into account the fact that strong reducing agents react with $SF_6$ we became interested in the use of organic electron donors.

Organic electron donors[16] are easily accessible on the multigram scale and redox reactions can be performed in regular organic solvents with common laboratory glassware. Hence, 2,2′-bipyridyl based organic electron donors **1a**,[16c] **1b** and a member of viologens,[17] octyl-4,4′-bipyridine **1c** (Fig. 1) were chosen as reducing agents. Next to the 2,2′- and 4,4′-bipyridine derivatives we were also interested in evaluating other electron

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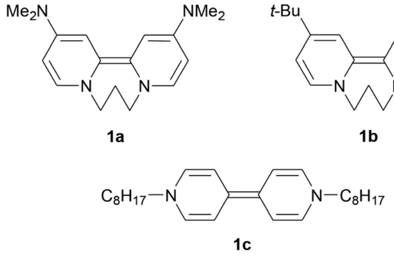


**Fig. 1** Selected donors **1a–c** for the $SF_6$-activation.

donors including TMBI (tetramethylbisimidazolidine) **1d**[18] and TDAE (tetrakis-dimethylaminoethylene) **1e.**[19]

Interestingly, exposure of **1a** and **1b** in *n*-hexane or toluene to $SF_6$ at ambient temperature led to an immediate colour change. The deep-purple colour of the starting material disappeared completely within minutes and the formation of a brown microcrystalline precipitate was observed (**2a** and **2b**, Scheme 1).

The *in situ* $^{19}F\{^1H\}$ NMR analysis of the supernatant solution showed, except for the residual $SF_6$, no fluorine containing materials. Subsequently, the solution was filtered off and the solvent was removed to dryness; however, no residue was obtained. The isolated products **2a** and **2b** were found to be poorly soluble in most common organic solvents. The $^1H$- and $^{13}C$ NMR spectra, recorded in acetonitrile-$d_3$, DMSO-$d_6$ and DMF-$d_7$, revealed products **2a** and **2b** as the reaction is driven by the restoration of aromaticity and formation of the corresponding 2,2′-bipyridynium dications **1a**$^{2+}$ and **1b**$^{2+}$. Ambient temperature $^{19}F$ NMR spectra showed signals of $F^-$ along with the signals arising from the solvent decomposition by an anhydrous fluoride anion (*e.g.* $DF_2^-$). The $^{19}F$ NMR spectra of the salts **2a** and **2b** in acetonitrile-$d_3$ and DMF-$d_7$ recorded at −30 °C revealed two broad singlets at $\delta = +60.5$ ppm and $\delta = -142.8$ ppm, respectively (Fig. 2, top). These data are in an excellent agreement with the previously described signals of $SF_5^-$ and $F^-$ anions in acetonitrile-$d_3$. Low temperature $^{19}F$ NMR measurement performed in liquid $SO_2$ with 1,2-difluorobenzene as an internal standard ($\delta = -138.8$ ppm) gave rise to the signal of fluoride ($\delta = -140$ ppm) and a singlet signal at $\delta = +72.2$ ppm corresponding to thionyl fluoride, $SOF_2$.[20] This result may be rationalized by the decomposition of $SF_5^-$ to $SF_4$ and $F^-$ and the following reaction of $SF_4$ with $SO_2$. Upon evaporation of sulphur dioxide and addition of acetonitrile-$d_3$ the $^{19}F$ NMR spectrum (see the ESI†) at 298 K shows the absence of $SOF_2$ and formation of $SO_2F^-$.[21] In order to establish the identity of the composition in solution and in bulk, solid state $^{19}F$-NMR spectroscopy analysis of **2b** was performed (Fig. 2, bottom). The spectrum gives rise to two broad singlet signals appearing at positions identical to those found in solution ($\delta = +60.2$ ppm $SF_5^-$; $\delta = -150$ ppm $F^-$). Noteworthily, the intensity of the signal at $\delta = +60.2$ ppm decays with time. Thus with 25 kHz rotational speed at ambient temperature after 24 h about 60% of the peak intensity vanished, whereas at 40 °C the signal disappeared completely after 12 h. These results are explained by the thermal instability of the $SF_5^-$ anion.

**Scheme 1** Reduction of $SF_6$ by organic electron donors.

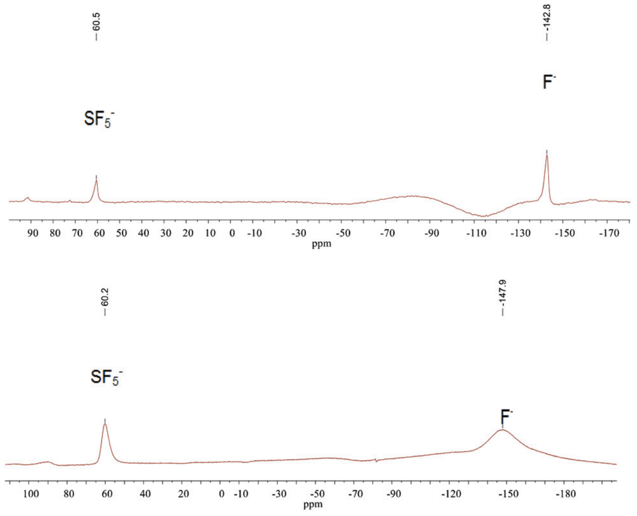


**Fig. 2** (Top) The $^{19}F$ NMR spectrum of the **2b** [{bis-(*t*-Bu)Py(propylene)}$^{2+}F^-$; $SF_5^-$] in acetonitrile-$d_3$ at −30 °C; (bottom) the solid state $^{19}F$ NMR spectrum of **2b** [{bis-(*t*-Bu)Py(propylene)}$^{2+}F^-$; $SF_5^-$] at a spinning rate of 30 kHz.

Previously, IR and Raman spectra of salts containing $SF_5^-$ have been reported. Yet, no Raman spectra for **2a** and **2b** samples could be recorded due to intensive fluorescence. However, IR spectroscopy provided us with an additional evidence for the presence of $SF_5^-$ anions. The $SF_5^-$ anion in $CsSF_5$ adopts a square-pyramidal geometry[14d] of $C_4V$ symmetry, giving rise to three characteristic absorbance maxima in the IR spectrum at 795, 525 and 469 cm$^{-1}$. These data are in excellent agreement with our results (Fig. 3).

Dioctylviologen ($C_8V$) **1c** also reacted with $SF_6$ to give a blue-green paramagnetic microcrystalline precipitate. However, only one signal of fluoride anions ($\delta = -160$ ppm) and no evidence for the $SF_5$ anion in the $^{19}F$ NMR spectra were observed. Taking into consideration the colour of the product and its paramagneticity we assume that incomplete oxidation of viologen occurred and the corresponding radical cation $C_8V^{\bullet +}$ was formed.[17a] Further experiments with other electron donors, such as TMBI **1d** and TADE **1e**, did not show any reaction.

In order to understand the correlation between the activity of the organic electron donors toward $SF_6$ activation and their redox potential, compounds **1a–e** were subjected to cyclic voltammetry (CV) studies. The results are presented in Table 1.

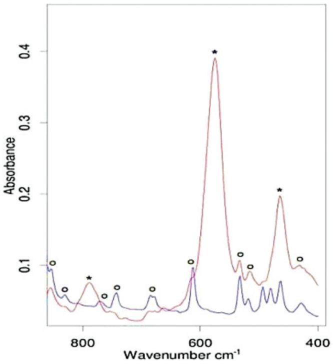


**Fig. 3** The IR spectra of **2b** (upper line) and [**1b**]2Br$^-$ (see the ESI†) (bottom line). Bands attributed to the {bis(*t*-Bu)Py(propylene)}$^{2+}$ dication and to the $SF_5^-$-anion are denoted with (o) and (*), respectively.

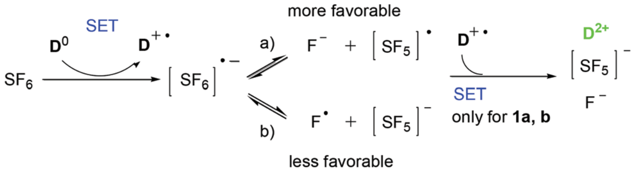
**Table 1** RedOx-potentials (*vs.* SCE) of donors **1a–e** measured by CV

| Organic electron donor | $E^1_{1/2}$ (V) | $E^2_{1/2}$ (V) | Reaction with $SF_6$ |
|---|---|---|---|
| **1a** | −1.12 | — | Observed |
| **1b** | −0.98 | −0.71 | Observed |
| $C_8$V (**1c**) | −0.81 | −0.37 | Observed |
| TMBI (**1d**) | −0.67 | — | Not observed |
| TDAE (**1e**) | −0.78; −0.62[a] | −0.46[b] | Not observed |

All measurements were done in acetonitrile *vs.* Ag/Ag$^+$($CH_3CN$)-couple quasi-reference electrode with ferrocene ($E_{redOx}$ = 0.073 V) as an internal standard. The values are recalculated and stated *versus* Saturated Calomel Electrode (*vs.* SCE). [a] Two anodic peaks. [b] One cathodic peak.

Starting with donor **1a** we carried out the measurements in acetonitrile and the Ag/Ag$^+$ reference electrode (for details see the ESI†). According to the literature data,[16c] **1a** shows one reversible two-electron oxidation wave with $E_{1/2}$ = −1.23 V *vs.* SCE in DMF due to the similarity of $E_{RedOx}$ for each SET-process. The same behaviour was observed for **1a** in acetonitrile and the redox potential was determined with $E_{1/2}$ = −1.12 V *vs.* SCE. The donor **1b** had not been measured before and two reversible one-electron waves were obtained with $E^1_{1/2}$ = −0.98 V and $E^2_{1/2}$ = −0.71 V *vs.* SCE. Following this observation, we also measured the redox-potentials of dioctylviologen **1c** ($E^1_{1/2}$ = −0.81 V; $E^2_{1/2}$ = −0.37 V *vs.* SCE); TMBI **1d** ($E^1_{1/2}$ = −0.67 V *vs.* SCE) and TDAE **1e**. Two anodic peaks ($E^1_{pa}$ = −0.78 V; $E^2_{pa}$ = −0.62 V *vs.* SCE) and one cathodic peak ($E_{pc}$ = −0.46 V *vs.* SCE) were observed. From these results, we conclude that the electron donor needs to have a redox potential of about $E_{1/2}$ = −0.8 V *vs.* SCE in order to activate $SF_6$.

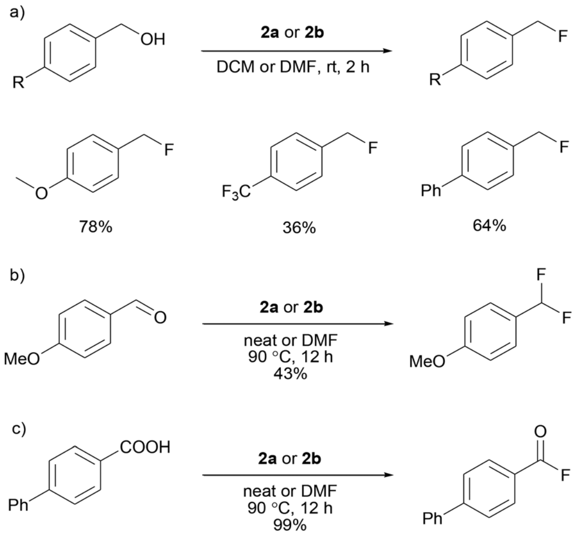
The oxidation path of the electron donors is known and it proceeds through SET processes *via* the formation of a radical cation. However, so far, mechanistic investigations of $SF_6$ reduction are rare and have been mainly performed in a gaseous phase or with solvated electrons.[22] Based on these studies and our observations we propose the following mechanism for the sulphur hexafluoride reduction: the SET process from the electron donor D to $SF_6$ results in the formation of the donor radical-cation and $SF_6^{\bullet-}$–radical-anion couple (Scheme 2). The dissociation pathway of the resulting anion-radical $SF_6^{\bullet-}$ is not clear and can lead either to the fluorine-radical and the $SF_5^-$ anion (path b) or the fluoride-anion and the $SF_5^\bullet$-radical (path a). However, the latter is considered to be more favourable.



**Scheme 2** Proposed mechanism for the $SF_6$ reduction. D – organic e-donor.

**Scheme 3** Organic electron donor mediated deoxyfluorination.

The fact that viologen $C_8$V does not form the $SF_5^-$ anion product can be rationalized by the value of its redox-potentials (Table 1). The first $E_{redOx}$ is sufficient to activate $SF_6$ but the second one is too low for the reduction of the $SF_5$-radical. Notably, $E^2_{1/2}$ is sufficient for the reduction of fluorine-radicals[23] and $C_8$V should give an $SF_5$-anion containing product in the case of path b. However, this is not observed, supporting the notion that path a is more probable. Finally, after the second SET from $D^{\bullet+}$ (for **1a**, **b**) an ion pair consisting of a dication, a $F^-$ and an $SF_5^-$ anion, [$D^{2+}$][$F^-$,$SF_5^-$], is formed, which can be detected.



**Scheme 4** Deoxyfluorination of benzylic alcohols, aldehydes and carboxylic acids with **2a** and **2b**.

During our NMR studies, we recorded the $^{19}$F-NMR spectra of **2a** and **2b** in methanol-d$_4$. Interestingly, we observed a septet signal which was assigned to the formation of $CD_3F$ ($\delta = -276.0$ ppm, sept, $J^2$(D,F) = 7.1 Hz) (Scheme 3).[24]

This result can be explained by a decay of the formed $[D^{2+}][F^-,SF_5^-]$ ion pair in solution and the formation of $[D^{2+}][2F^-]$ and sulphur tetrafluoride ($SF_4$), which is known as a deoxy-fluorinating reagent.[25]

Given that the salt $[D^{2+}][F^-,SF_5^-]$ can be considered as a solid, safe and easy to handle method of storage of $SF_4$, we decided to evaluate this new procedure by applying the method to the fluorination of benzyl alcohols, aldehydes and carboxylic acids. Our proof-of-concept studies are shown in Scheme 4. Generally, the reaction occurred with all three substrate classes and provided the benzyl fluorides from the corresponding alcohols (Scheme 4a), aryl-difluoromethane from benzyl aldehyde (Scheme 4b) and acid fluoride from the carboxylic acid (Scheme 4c).[26]

## Conclusions

In summary, we report the use of organic electron donors for the activation of the greenhouse gas, sulphur hexafluoride.[13] Bipyridine-based organic electron donors were found to react fast and selectively with $SF_6$ at ambient temperature in non-polar aprotic solvents within minutes to yield solid ion pairs consisting of donor dications $[D^{2+}]$ and fluoride $[F^-]$ and $[SF_5^-]$ anions. The presence of the $SF_5^-$ anion was confirmed by NMR- and IR-spectroscopy analysis. The salts can be isolated and also be applied as fluorinating reagents. This was demonstrated by the deoxofluorination of alcohols, aldehydes as well as carboxylic acids. Thus, $SF_6$ is a readily available and stable precursor for the otherwise more difficult to handle deoxofluorinating reagent, sulphur tetrafluoride. Given the simplicity of the procedure it can be used for both, the decomposition of one of the most potent greenhouse gases and at the same time the generation of a powerful fluorinating reagent. Further applications of this metal-free activation of $SF_6$ as well as demonstration to reuse and recycle the electron donors are currently part of our further research.

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