Metal-free reduction of the greenhouse gas sulfur hexafluoride, formation of SF₅ containing ion pairs and the application in fluorinations

Magnus Rueping,*a,b Pavlo Nikolaienko,1a,b Yury Lebedev1a,b and Alina Adamsc

A protocol for the fast and selective two-electron reduction of the potent greenhouse gas sulfur hexafluoride (SF₆) by organic electron donors at ambient temperature has been developed. The reaction yields solid ion pairs consisting of donor dications and SF₅-anions which can be effectively used in fluorination reactions.

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 SF₆-activation under milder conditions were reported. These methods require transition metals as catalyst or reducing agent and the products of SF₆-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 SF₅-anion14 from sulphur hexafluoride which would potentially allow the formation of SF₅ containing organic molecules which are of considerable interest as well.15 Taking into account that strong reducing agents react with SF₆ we became interested in the use of organic electron donors.

Organic electron donors16 are easily accessible in 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 (Figure 1) were chosen as reducing agents. Next to the 2,2'- and 4,4'-bipyridine derivatives we were also interested in evaluating other electron donors including TMBI (Tetramethylbisimida-zolidine) 1d18 and TDAE (Tetrakis(dimethylaminomethylene) 1e.19

Introduction

Sulphur hexafluoride is a non-flammable, odourless and colourless gas of high density.1 The unique physical and chemical properties of SF₆ makes 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 SF₆ produced is used as insulator and fire suppression agent in high-voltage circuit breakers.2 Another application of SF₆ consists in its use as a blanketing, sound- and thermo-insulating agent in industry3 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, SF₆ is a potent greenhouse gas included to Kyoto Protocol.6,7 According to the World Meteorological Organization, the atmospheric lifetime of SF₆ is ca 3200 years and its global warming potential is 22450 times higher than that of CO₂.8 Therefore, beside the necessity to control the level of SF₆ emissions and development of more efficient trapping techniques,9 a methodology to decompose this gas is on demand. Thus, since 1980s several reports on the SF₆ activation followed by the total reduction to compounds containing futile sulfides and fluorides have been published.

*King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Thuwal, 23955-6900 Saudi Arabia. E-mail: magnus.rueping@kaust.edu.sa
a RWTH Aachen University, Institute of Organic Chemistry, Landoltweg 1, D-52074 Aachen
b RWTH Aachen University, Institut für Technische und Makromolekulare Chemie Worringerweg 1, D-52074 Aachen
c Abdullkah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC)
† These authors contributed equally to this work
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Interestingly, exposure of 1a and 1b in n-hexane or toluene to SF₆ at ambient temperature led to an immediate colour change. The deep-purple colour of the starting material disappeared completely within minutes and formation of a brown microcrystalline precipitate was observed (2a and 2b, Scheme 1).

The in situ $^{19}$F($^1$H) NMR analysis of the supernatant solution showed, except of the residual SF₆, 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 $^1$H- and $^{19}$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 restoration of aromaticity and formation of the corresponding 2,2'-bipyridinum dications 1a$^{1+}$ and 1b$^{1+}$. Ambient temperature $^{19}$F NMR spectra showed signals of F$^{-}$ along with the signals of the solvent decomposition by anhydrous fluoride anion (e.g. DF$_2$-$^2$). The $^{19}$F NMR spectra of the salts 2a and 2b in acetonitrile-$d_3$ and DMF-$d_3$ recorded at $-30\,^\circ\mathrm{C}$ revealed two broad singlets at $\delta = +60.5$ ppm and $\delta = -142.8$ ppm, respectively (Figure 2, top). These data are in an excellent agreement with the previously described signals of SF$_5^-$ and F$^{-}$ ions 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 SI) at 298 K shows the absence of SOF$_3$ and formation of SO$_2$F.$^{21}$ 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 (Figure 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$^{-}$). Noteworthy, the intensity of the signal at $\delta = +60.2$ ppm decays upon 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.

Previously, IR and Raman spectra of salts containing SF$_5^-$ have been reported. Yet, no Raman spectra for 2a, b samples could be measured 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$_6$ adopts a square-pyramidal geometry$^{144}$ of C$_4$V 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 (Figure 3).

Diocetylviologen (C$_6$V) 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 evidences for SF$_5^-$-anion in the $^{19}$F NMR spectra was observed. Taking into consideration the colour of the product and its paramagnetivity we assume that incomplete oxidation of viologen occurred and the corresponding radical cation C$_6$V$^+$ 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.
The fact that violagen C\textsubscript{6}V is not forming the SF\textsubscript{5}\textsuperscript{−} anion product can be rationalized by the value of its redox-potentials (Table 1). The first E\textsubscript{redox,1} is sufficient to activate SF\textsubscript{6} but the second one is too low for the reduction of the SF\textsubscript{5}− radical. Notably, E\textsubscript{1/2} is sufficient for the reduction of fluoride radicals\textsuperscript{23} and C\textsubscript{6}V should give a SF\textsubscript{5}−-containing product in 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\textsuperscript{−} (for 1a, b) an ion pair consisting of a dication, a F\textsuperscript{−} and SF\textsubscript{5}− anion [D\textsuperscript{3+}[F\textsuperscript{−},SF\textsubscript{5}−]] is formed, which can be detected.

During our NMR studies, we recorded \textsuperscript{19}F-NMR spectra of 2a and 2b in methanol-d\textsubscript{4}. Interestingly, we observed a septet signal which was assigned to the formation of CD\textsubscript{3}F (\delta = -276.0 ppm, sept, J\textsubscript{DF} = 7.1 Hz) (Scheme 3).\textsuperscript{24}

\begin{align*}
\text{SF}_6 & \quad \text{SET} \quad \text{SF}_5 \quad \text{D}^+ \quad \text{F}^- \\
\text{SF}_5 & \quad \text{SET} \quad \text{SF}_4 \quad \text{D}^+ \quad \text{F}^- \\
\text{SF}_4 & \quad \text{+} \quad \text{SF}_6 \quad \text{SF}_5 \quad \text{CD}_3\text{OH} \quad \text{CD}_2\text{F}
\end{align*}

This result can be explained by a decay of the formed [D\textsuperscript{3+}[F\textsuperscript{−},SF\textsubscript{5}−]] ion pair in solution and the formation of [D\textsuperscript{3+}[2F\textsuperscript{−}]] which is known as deoxy-fluorinating reagent.\textsuperscript{25}

Given that salts [D\textsuperscript{3+}[F\textsuperscript{−},SF\textsubscript{5}−]] can be considered as solid, safe and easy to handle storage of SF\textsubscript{6}, 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-difluoromethanes from benzyl aldehyde (Scheme 4b) and acid fluoride from the carboxylic acid (Scheme 4c).\textsuperscript{26}

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

<table>
<thead>
<tr>
<th>Organic Electron Donor</th>
<th>E\textsubscript{1/2} (V)</th>
<th>E\textsubscript{2/1} (V)</th>
<th>Reaction with SF\textsubscript{6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-1.12</td>
<td>-</td>
<td>observed</td>
</tr>
<tr>
<td>1b</td>
<td>-0.98</td>
<td>-0.71</td>
<td>observed</td>
</tr>
<tr>
<td>C\textsubscript{6}\textsuperscript{V} (1c)</td>
<td>-0.81</td>
<td>-0.37</td>
<td>observed</td>
</tr>
<tr>
<td>TMBI (1d)</td>
<td>-0.67</td>
<td>-</td>
<td>not observed</td>
</tr>
<tr>
<td>TDAE (1e)</td>
<td>-0.78; -0.46\textsuperscript{n}</td>
<td>-0.62\textsuperscript{n}</td>
<td>not observed</td>
</tr>
</tbody>
</table>

All measurements were done in acetonitrile vs Ag/Ag\textsuperscript{+}(CH\textsubscript{3}CN)-couple quasi-reference electrode with ferrocene (E\textsubscript{redox} = 0.073 V) as an internal standard. The values are recalculate and stated versus Satuated Calomel Electrode (vs SCE); i) two anodic peaks; ii) one cathodic peak.

Starting with donor 1a we carried out the measurements in acetonitrile and Ag/Ag\textsuperscript{+} reference electrode (for details see SI). According to literature data,\textsuperscript{16c} 1a shows one reversible two-electron oxidation wave with E\textsubscript{1/2} = -1.23 V vs SCE in DMF due to similarity of E\textsubscript{redox,1} for each SET-process. The same behaviour was observed for 1a in acetonitrile and redox potential was determined with E\textsubscript{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\textsubscript{1/2} = -0.98 V and E\textsubscript{2/1} = -0.71 V vs SCE. Following this observation, we also measured redox-potentials of diocetylviologen 1c, (E\textsubscript{1/2} = -0.81 V; E\textsubscript{2/1} = -0.37 V vs SCE); TMBI 1d (E\textsubscript{1/2} = -0.67 V vs SCE) and TDAE 1e (two anodic peaks (E\textsubscript{pa} = -0.78 V; E\textsubscript{pa} = -0.62 V vs SCE) and one cathodic (E\textsubscript{pc} = -0.46 V vs SCE) were observed. From these results, we conclude that the electron donor need to have a redox potential of about E\textsubscript{1/2} = -0.8 V vs SCE in order to activate SF\textsubscript{6}.

The oxidation path of the electron donors is known and it proceeds through SET-processes via formation of a radical cation. However, so far, mechanistic investigations of SF\textsubscript{6} reduction are rare and were mainly performed in a gaseous phase or with solvated electrons.\textsuperscript{22} Based on these studies and our observations we propose the following mechanism for the sulphur hexafluoride reduction: SET from the electron donor D to SF\textsubscript{6} results in formation of the donor-radical-cation and SF\textsubscript{5}−-radical-anion couple (Scheme 2). The dissociation pathway of the resulting anion-radical SF\textsubscript{5}− is not clear and can lead either to fluorine-radical and SF\textsubscript{5}− anion (path b) or fluoride-anion and SF\textsubscript{5}-radical (path a). However, the latter is considered to be more favourable.

![Figure 3 The IR spectra of 2b (upper line) and 1b/2b (See SI) (bottom line). Bands attributed to the [bis(bu)Pyr(propylene)]\textsuperscript{+} cation and to the SF\textsubscript{5}− anion are denoted with (a) and (b), respectively.](image)

![Scheme 2 Proposed mechanism for the SF\textsubscript{6} reduction. D \textsuperscript{−} organic e-donor.](image)

![Scheme 3 Organic electron donor mediated deoxyfluorination.](image)
Conclusions

In summary, we report the use of organic electron donors for the activation of the greenhouse gas, sulphur hexafluoride. Bipyridine-based organic electron donors were found to react fast and selectively with SF₆ at ambient temperature in non-polar aprotic solvents within minutes to yield solid ion pairs consisting of donor dications [D⁺], fluoride [F⁻] and [SF₆]⁻ anions. The presence of the [SF₆]⁻ 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, SF₆ is a readily available and stable precursor for the otherwise more difficult to handle deoxofluorinating reagent, sulphur hexafluoride. 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 SF₆ as well as demonstration to reuse and recycle the electron donors are currently part of our further research.

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Notes and references


