REACTIONS OF SULFUR FLUORIDES AND BENZENES IN A LOW TEMPERATURE PLASMA

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Abstract
Sulfur fluorides SF₆, ClSF₅ and CF₃SF₅ were reacted with C₆H₆, C₆H₅Br and C₆H₅Cl in a low temperature radio-frequency plasma. Due to the stepwise dissociation of sulfur fluorides, the fluorination of benzenes was observed. In all reaction products C₆H₅SF₅ was found in minor quantities, and BrC₆H₄SF₅ or ClC₆H₄SF₅ along with numerous halogenated benzenes when C₆H₅Br or C₆H₅Cl were used as reactants, respectively.

Introduction

The introduction of a pentafluorosulfanyl group, SF₅, into organic molecules can substantially change their properties, which makes compounds containing the SF₅ group potentially useful in a number of applications.¹⁻⁶ Incorporating the pentafluorosulfanyl group instead of the trifluoromethyl group into high temperature polyimides may cause these polymers to show enhanced properties such as a lower dielectric constant, greater solubility, increased hydrophobicity, less colour and improved tensile properties.³ In the field of energetic materials the potential application of SF₅ containing compounds includes the reduction of shock sensitivity of energetic materials in which the nitro group has been replaced by the pentafluorosulfanyl group.⁶ The use of pentafluorosulfanylbenzenes has been inhibited by their low yields of production and for this reason many attempts have been made to improve the yields of syntheses and make the compounds available on a large scale.

The first to prepare C₆H₅SF₅ was Sheppard⁷ in 1960. He isolated several pentafluorosulfanylbenzenes by fluorination of aromatic disulfides with AgF₂ in CFC 113 at 393 K. Pentafluorosulfanylbenzenes were later prepared by various reactions: by the reaction of S₂F₁₀ with benzene⁸ at 453 K, by the reaction of SF₅C≡CH with 1,3-butadiene,⁹ by the reaction of SF₅C≡CH with SF₅Cl,¹⁰ by fluorination of aromatic disulfides in concentrated sulfuric acid,¹¹ by fluorination of aromatic disulfides with elemental fluorine in CH₃CN¹² (C₆H₅SF₅, 38.5% yield) and by fluorination of

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diphenyl disulfide by XeF$_2^{13,14}$ ($C_6H_5SF_5$, 25% yield). The disadvantage of these methods is the low yield of pentafluorosulfanylbenzenes and the presence of impurities which are difficult to separate from the main product.

Even though different approaches to synthesis have been used, there were so far no reports on reactions in a plasma, which would yield pentafluorosulfanylbenzenes. However, trifluoromethylbenzene, $C_6H_5CF_3$ was found to form in a low temperature plasma of gases $C_6H_5Br$ and $C_2F_6^{15}$ By using reactive CF$_3$ radicals generated in a low temperature plasma from $C_2F_6$ gas, numerous organometallic compounds were also prepared.$^{16}$ Similary, SF$_5$ radicals generated in a plasma would be expected to react with benzenes to produce pentafluorosulfanylbenzenes. The present work was aimed at the plasma chemistry of the sulfur fluorides SF$_6$, CF$_3$SF$_5$, ClSF$_5$ and benzenes, with special emphasis on the formation of pentafluorosulfanylbenzenes in the plasma.

**Experimental**

**Reagents.** Benzene (analytical grade) was obtained from Kemika, $C_6H_5Br$ (99%) and $C_6H_5Cl$ (99.9%) from Aldrich. SF$_6$ (99.75%) from Aldrich and CF$_3$SF$_5$ from Flura Corporation were used as received. ClSF$_5$ was prepared by the reaction of SF$_4$, Cl$_2$ and dry CsF in a stainless steel pressure reaction vessel which was gradually heated to 448 K during a 3 hour period and then kept at this temperature for 2 hours.$^{17}$ $C_6H_5SF_5$ which was used as a standard sample, was prepared by two different methods.$^{7,14}$

**Apparatus.** The source of radio-frequency power was an IEVT VGK 200/1 high frequency generator operating at 27 MHz and at 300 W maximum power. The power dissipated in the plasma reactors was measured by a Zetagi HP 201 SWR through-line wattmeter.

Reactions were carried out in a bell jar type quartz reactor described elsewhere$^{18}$ and in a stainless steel reactor.$^{19}$ The quartz reactor was a 70 mm o.d., 250 mm long quartz tube, connected on one side by two inlet tubes to gas cylinders with flow regulators, and on the other side to a cold trap held at 77 K, which was evacuated by a diffusion pump. The plasma was inductively coupled through a helical coil, which consisted of seven
turns of 4 mm o.d. copper tubing. The pressure inside the reactor was monitored by an ILM Labor Pirani vacuummeter and the power dissipated in the reactor was 15 W.

Stainless steel reactor was an in house constructed modified GEC reference cell of 200 mm i.d. and 284 mm in height. Gases were supplied to the reactor from gas cylinders and the flow was controlled by MKS 1359 CJ Mass Flow Controllers. The pressure in the reactor was measured by an MKS Baratron pressure meter (0-100 Pa) and by an in-house Alpert gauge high vacuum and ultra high vacuum meter. The plasma in the reactor was inductively coupled through a silica window by a five-turn planar coil of 3 mm diameter and the power dissipated in the reactor was 25 W.

**Methods.** *Reactions in a low temperature plasma.* Prior to reactions in a low temperature plasma, the system (all quartz or stainless steel) was evacuated to $10^{-3}$ Pa and a Dewar flask with liquid nitrogen was placed around the trap. The flow rates of gases were adjusted to the required values. After the flow and pressure stabilized, the plasma was initiated. Reaction products were trapped in the 77 K trap and were subsequently separated on a vacuum line into two fractions: low boiling and high boiling fractions. Low boiling fraction was analysed by FTIR while high boiling fraction was analyzed by GC–MS and by GC–FTIR. Chromatographically separated compounds were identified by comparing the mass spectra and IR spectra of individual components to NIST library mass spectra and to Aldrich library FTIR spectra, respectively.

In the quartz reactor sulfur fluorides SF$_6$ and CF$_3$SF$_5$ were reacted with C$_6$H$_6$, C$_6$H$_5$Br and C$_6$H$_5$Cl at a total flow rate of 1 mL min$^{-1}$ to 11.3 mL min$^{-1}$ in individual experiments. Reactions of SF$_6$, CF$_3$SF$_5$ and ClSF$_5$ with benzene were performed in the stainless steel reactor at a total flow rate of 7 mL min$^{-1}$ and argon was added at a flow rate of 1 mL min$^{-1}$ to the stainless steel reactor only to facilitate the excitation of species in the plasma. In the quartz reactor the pressure during reactions was kept at 5 Pa, while in the stainless steel reactor the pressure was varied from 1.4 Pa to 14 Pa in individual experiments. The pressure and the radio-frequency power were kept low due to the extensive polymerization of aromatics that occurred at higher applied pressure and radio-frequency power, especially when benzene was used as reactant.
Degree of dissociation–decomposition of SF₆ in plasma. For the production of pentafluorosulfanylbenzenes a high dissociation–decomposition of sulfur fluorides in the plasma, which means a high concentrations of SF₅ radicals, is essential. Therefore, the degree of dissociation-decomposition of SF₆ in the stainless steel reactor was determined by the online Dupont instruments quadrupole mass spectrometer 21-440 Residual Gas Analyzer (RGA) which was connected to one of the reactor windows and operated at an ionization energy of 70 eV. Scans from m/z 1 to m/z 200 were completed in 15 seconds. Reaction mixtures were sampled through a 0.05 mm orifice. A separate oil diffusion pump maintained the vacuum in the mass spectrometer at 10⁻⁴ Pa. The degree of dissociation–decomposition of SF₆ gas in a low temperature plasma in a particular stainless steel reactor was determined by the difference mass spectrum which was obtained by recording the mass spectra of SF₆ gas in the stainless steel reactor by the online spectrometer when the discharge was on and at essentially the same conditions when the discharge was off, and substracting the spectra. Difference mass spectra offer an estimation of the lower and upper limits of the degree of dissociation of the gas in the plasma.

Analyses. The direct GC-MS analysis of reaction products trapped at 77 K was carried out on an AutoSpec mass spectrometer (Micromass, Manchester, UK) coupled with an HP 5890 series gas II. chromatograph (Hewlett-Packard, Valdbron, Ge). An HP-5MS 30 m x 0.25 mm fused silica capillary column was used. Splitless injection (splitless duration 60 s) was carried out with an injector temperature of 523 K. The column was held at 323 K during injection and then programmed to the temperature of 473 K at 20 K min⁻¹, and to 523 K at 15 K min⁻¹. The final column temperature of 573 K was reached at 10 K min⁻¹. Helium at a flow rate of 1 mL min⁻¹ was used as carrier gas. The ionization energy was 70 eV and source electron current was 150 µA. Data were acquired in the magnet scan mode using a scan from m/z 50 to m/z 500 with a scan time of 0.8 s. GC-FTIR analyses were performed on a Model 8700 gas chromatograph coupled with a GC-IR interface to a 1710 FTIR spectrometer (all components from Perkin-Elmer). A Perkin-Elmer bonded methyl 5% phenyl silicone 10 m x 0.53 mm fused silica capillary column with 5 µm film thickness was used. Liquid
samples of 1-2 μl were injected into a packed column injector heated to 523 K. The column was held at 313 K for 5 minutes after injection, then programmed to 493 K at 10 K min⁻¹ and held at 493 K for 2-20 minutes. Helium was used as carrier gas. Components were detected by FID or TCD. Throughout the analyses the transfer line to the FTIR spectrometer and the gold coated light-pipe were heated to 513 K. Spectra were taken at 8 cm⁻¹ resolution.

Results and discussion

Determination of dissociation–decomposition rate in a plasma of SF₆ gas. The concentration of SF₅⁺ radicals in a plasma is closely related to the dissociation–decomposition rate of sulfur fluoride gas.²⁸ The differences in the mass spectra obtained with and without operation of the discharge were used to estimate the degree of dissociation–decomposition of SF₆ in the discharge.²⁷ Figure 1 shows mass spectra of plasma gases sampled online from the reactor and measured by quadrupole mass spectrometer. The mass spectrum in Figure 1A presents dissociation of SF₆ in the reactor when the discharge is off. The predominance of SF₅⁺ followed by SF₃⁺ is evident. The mass spectrum observed when the discharge is turned on is shown in Figure 1B. The predominant ion observed at rf discharge conditions is SF₂⁺, which indicates the extensive further stepwise dissociation of sulfur fluoride species SF₅. In addition to the main ions SF₂⁺, SF₃⁺ and SF₅⁺ measurable contributions to the total ion current from other ions derived directly or indirectly from SF₆, namely SF₄⁺, SF⁺, F⁺ and the doubly charged ions SF₂²⁺ and SF₄²⁺, are evident. A reduction in the relative intensities of the ions SF₅⁺ and SF₃⁺ is observed. The differential mass spectrum in Figure 1C was formed by subtracting the intensity of ion current of products in Figure 1B from the intensity of ion current of products in Figure 1A.

The degree of dissociation of SF₆ in a stainless steel reactor at a SF₆ flow rate of 2.5
Figure 1. Mass spectra of neutral species in SF₆ gas sampled at a pressure of 1.4 Pa: A) SF₆ gas sampled from the cell without discharge, B) SF₆ gas sampled from the cell with discharge on, and C) difference of mass spectra B) and A) where negative values indicate a loss when the plasma is on. The isotope peaks for sulfur containing ions were removed to simplify the spectra.
Reactions of sulfur fluorides and benzenes. In a low temperature plasma sulfur fluorides \( \text{SF}_6 \) and \( \text{CF}_3\text{SF}_5 \) were allowed to react with \( \text{C}_6\text{H}_6 \), \( \text{C}_6\text{H}_5\text{Br} \) and \( \text{C}_6\text{H}_5\text{Cl} \) in the bell jar reactor (Table 1), and reactions of \( \text{SF}_6 \), \( \text{CF}_3\text{SF}_5 \) and \( \text{ClSF}_5 \) with benzene were performed in the stainless steel reactor (Table 2), while argon was added to the stainless steel reactor only to facilitate the excitation of species in the plasma.\(^{25}\)

The composition of low boiling volatile products was determined by GC-MS and GC-FTIR. The GC-MS ion current traces of the condensed extract of the organic compounds from the two reactors are presented in the chromatograms shown in Figures 2 and 3. Mainly halogenated aromatic compounds were identified. Identification of compounds was confirmed by the mass spectra library search and by comparison with pure standards. Some of unknown chromatographic peaks were elucidated by interpretation of the mass spectra of unknowns.\(^{29}\) Aromatic compounds usually exhibit intensive molecular ion and typical fragment ions, which allow interpretation of unknowns. As an illustration the mass spectrum of the target compound \( \text{C}_6\text{H}_5\text{SF}_5 \), formed in reaction between \( \text{CF}_3\text{SF}_5 \) and benzene in a low temperature plasma is shown in Figure 4.

Reactions in the all quartz bell jar reactor. Reaction with the quartz wall was observed in the bell jar reactor when \( \text{SF}_6 \) was used as the source of \( \text{SF}_5 \) radicals; other volatile products determined by IR spectroscopy were \( \text{SiF}_4 \), \( \text{SOF}_4 \) and \( \text{SO}_2\text{F}_2 \) besides unreacted \( \text{SF}_6 \). Less volatile products separated by condensation at 253 K were composed mainly of several classes of halogenated benzenes (Table 1), while pentafluorosulfanylbenzene was determined in traces by GC–MS analysis. \( \text{SF}_6 \) is an extremely stable molecule and its primary bond dissociation energy\(^{30}\) of 420 kJ mol\(^{-1}\) is higher than of other sulfur fluoride primary bond dissociation energies (\( \text{SF}_5 \), 222 kJ mol\(^{-1}\); \( \text{SF}_4 \), 352 kJ mol\(^{-1}\); \( \text{SF}_3 \), 264 kJ mol\(^{-1}\); \( \text{SF}_2 \), 384 kJ mol\(^{-1}\); SF, 340 kJ mol\(^{-1}\)).\(^{31}\) Therefore, the energy required to dissociate the \( \text{SF}_6 \) molecule also causes the further stepwise dissociation of sulfur species \( \text{SF}_5 \), and consequently the fluorination of

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Figure 2. Gas chromatogram of reaction products of CF$_3$SF$_5$ with C$_6$H$_5$Cl in a plasma in a quartz reactor (5 mL min$^{-1}$ of CF$_3$SF$_5$, 5 mL min$^{-1}$ of C$_6$H$_5$Cl), retention time in minutes of C$_6$H$_5$SF$_5$, 2:40; C$_6$H$_5$ClF, 2:38; ClC$_6$H$_4$CF$_3$, 2:54; C$_6$H$_5$Cl$_2$F, 4:38; C$_6$H$_4$Cl$_2$, 5:22; FC$_6$H$_4$SSCF$_3$, 6:25; ClC$_6$H$_5$SF$_5$, 6:30; ClC$_6$H$_4$SSCF$_3$, 10:13; ClC$_6$H$_4$SSCCl$_2$, 13:22; ClC$_6$H$_4$S$_3$CF$_3$, 13:41; FC$_6$H$_4$SC$_6$H$_4$Cl, 17:20; ClC$_6$H$_4$SC$_6$H$_4$Cl, 19:44.

Figure 3. Gas chromatogram of reaction products of CF$_3$SF$_5$ with C$_6$H$_6$ in a plasma in a stainless steel reactor (3 mL min$^{-1}$ of CF$_3$SF$_5$, 3 mL min$^{-1}$ of C$_6$H$_6$ and 1 mL min$^{-1}$ of Ar), retention time of C$_6$H$_5$SF$_5$ is 2:31; FC$_6$H$_5$CF$_3$, 1:36; C$_6$H$_5$CF$_3$, 2:34; C$_6$H$_5$SF$_3$, 2:24; CH$_3$C$_6$H$_4$C$_2$H$_5$, 3:18; C$_6$H$_5$SSCF$_3$, 4:07; C$_{12}$H$_7$F, 4:57; C$_6$H$_5$C$_6$H$_4$C$_6$H$_5$, 5:48; C$_6$H$_5$C$_6$H$_5$, 6:27.
aromatic species is likely to occur. Benzene excited in a plasma undergoes two main reactions: monomolecular decomposition and bimolecular reaction with neutral molecules.\textsuperscript{32} The latter reaction explains the relatively high amount of biphenyl and halogenated biphenyl derivatives in the reaction products.

A plasma containing sulfur fluorides and benzenes together has an extraordinarily complex reaction scheme.\textsuperscript{26} In the reaction products of CF\textsubscript{3}SF\textsubscript{5} with C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}H\textsubscript{5}Br, C\textsubscript{6}H\textsubscript{5}SF\textsubscript{5} (Figure 4) was found by GC – MS (Figure 2) in minor quantities estimated at less than 1\% of all products (Table 1). When C\textsubscript{6}H\textsubscript{5}Cl was used as reactant, besides C\textsubscript{6}H\textsubscript{5}SF\textsubscript{5}, the chlorinated compound ClC\textsubscript{6}H\textsubscript{4}SF\textsubscript{5} was also found (Figure 2). In a low temperature plasma the dissociation of CF\textsubscript{3}SF\textsubscript{5} follows different routes. Dissociation into CF\textsubscript{3} and SF\textsubscript{5} by rupture of the C – S bond (E\textsubscript{diss}< 272 kJ mol\textsuperscript{-1})\textsuperscript{33} may be the primary process which produces the radicals necessary for the final products C\textsubscript{6}H\textsubscript{5}CF\textsubscript{3} and C\textsubscript{6}H\textsubscript{5}SF\textsubscript{5} to be formed. The stepwise dissociation of the SF\textsubscript{5} group in CF\textsubscript{3}SF\textsubscript{5} is another probable pathway which may lead to the SCF\textsubscript{3} substituted benzenes found in all reactions where CF\textsubscript{3}SF\textsubscript{5} was a reactant. When using CF\textsubscript{3}SF\textsubscript{5} as reactant common

![Figure 4. Mass spectrum of C\textsubscript{6}H\textsubscript{5}SF\textsubscript{5} found in the reaction products of CF\textsubscript{3}SF\textsubscript{5} with C\textsubscript{6}H\textsubscript{6} in a plasma.](image-url)
features in the composition of the reaction products were minor amounts of halogenated benzenes and greater numbers of compounds found in comparison to reactions with SF$_6$ as reactant. The first may well be explained by different dissociation pathways of CF$_3$SF$_5$ which may not lead to fluorinating species.

Table 1. Reaction products obtained in the quartz bell jar reactor

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction products</th>
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<tbody>
<tr>
<td>SF$_6$ + C$_6$H$_6$</td>
<td>C$_6$H$_5$C$_6$H$_5$, C$_6$H$_5$C$_2$H$_2$C$_6$H$_5$, C$_6$H$_5$C$_4$HF, C$_6$H$_5$CH$_3$, C$_6$H$_5$C$_2$H$_5$, C$_6$H$_5$SF$_5$</td>
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<tr>
<td>SF$_6$ + C$_6$H$_5$Br</td>
<td>C$_6$H$_5$C$_6$H$_5$, C$_6$H$_5$C$_6$H$_4$F, BrC$_6$H$_4$C$_6$H$_4$F, BrC$_6$H$_4$C$_6$H$_3$Br$_2$, C$_6$H$_4$BrF, C$_6$H$_4$BrF$_2$, C$_6$H$_4$BrF, C$_6$H$_3$Br$_2$F, C$_6$H$_4$Br$_2$, C$_6$H$_3$CF$_3$, C$_6$H$_5$SF$_5$</td>
</tr>
<tr>
<td>SF$_6$ + C$_6$H$_5$Cl</td>
<td>C$_6$H$_5$C$_6$H$_5$, C$_6$H$_4$ClSH, ClC$_6$H$_4$SC$_6$H$_4$Cl, ClC$_6$H$_4$SSC$_6$H$_4$Cl, C$_6$H$_5$SF$_5$, C$_6$H$_4$ClSF$_5$</td>
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<tr>
<td>CF$_3$SF$_5$ + C$_6$H$_6$</td>
<td>C$_6$H$_5$C$_6$H$_5$, C$_6$H$_5$SC$_6$H$_5$, C$_6$H$_5$C$_6$H$_4$F, C$_6$H$_5$CF$_3$, C$_6$H$_5$SCF$_3$, C$_6$H$_5$SSCF$_3$, C$_6$H$_5$SSSC$_6$H$_5$, C$_6$H$_5$CF$_2$C$_6$H$_5$, C$_6$H$_5$SF$_5$</td>
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<tr>
<td>CF$_3$SF$_5$ + C$_6$H$_5$Br</td>
<td>C$_6$H$_5$F, C$_6$H$_4$F, C$_6$H$_3$F, C$_6$H$_4$Br, C$_6$H$_4$BrF, C$_6$H$_3$BrF$_2$, C$_6$H$_3$Br$_2$F, C$_6$H$_4$BrCF$_3$, C$_6$H$_3$Br$_2$CF$_3$, C$_6$H$_3$SF$_5$, C$_6$H$_4$BrSF$_5$, FC$_6$H$_4$SSCF$_3$, BrC$_6$H$_4$SSCF$_3$, BrC$_6$H$_4$SCF$_3$, FC$_6$H$_4$SC$_6$H$_4$F, BrC$_6$H$_4$SC$_6$H$_4$F, BrC$_6$H$_4$SF$_5$, BrC$_6$H$_4$SC$_6$H$_4$SF$_5$, S$_6$, S$_8$</td>
</tr>
<tr>
<td>CF$_3$SF$_5$ + C$_6$H$_5$Cl</td>
<td>C$_6$H$_5$Cl, C$_6$H$_5$Cl$_2$, C$_6$H$_4$Cl, ClC$_6$H$_4$CF$_3$, FC$_6$H$_4$SCF$_3$, ClC$_6$H$_4$SSCF$_3$, ClC$_6$H$_4$SSSC$_6$H$_5$, C$_6$H$_5$SF$_5$, ClC$_6$H$_4$SF$_5$, ClC$_6$H$_4$SSC$_6$H$_5$Cl, ClC$_6$H$_4$SSCCl$_2$F, ClC$_6$H$_4$SSCFCF$_3$, FC$_6$H$_4$SC$_6$H$_4$Cl, ClC$_6$H$_4$SC$_6$H$_4$Cl</td>
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The greater number of compounds found in reaction mixtures containing CF$_3$SF$_5$ is the consequence of the relatively high stability of the CF$_3$ radical which is reflected in the formation of numerous trifluoromethylated compounds. Nevertheless, the reaction of CF$_3$SF$_5$ and C$_6$H$_6$ produces product with by far the most simple gas chromatogram out of nine, as only one halogen, fluorine, is introduced by the reactants. The

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concentrations of C₆H₅SF₅, C₆H₅CF₃ and biphenyl in the reaction products (Figure 3) were much higher when CF₃SF₅ was one of reactants. When ClSF₅ was used, the number of reaction products increased considerably, due to the chlorination of aromatic species, but the quantity of C₆H₅SF₅ was very low.

Reactions in the stainless steel reactor. The reactions of SF₆ and benzene in the stainless steel reactor at different flow rates of C₆H₆, 1 mL min⁻¹ of Ar and 3 mL min⁻¹ of SF₆ showed that a higher flow rate of C₆H₆ causes fewer products to form and in lower quantities. More volatile products i.e. SiF₄, SOF₄ and SO₂F₂, along with unreacted SF₆ were observed in traces; they originate from reactions of sulfur fluorides with the quartz windows of the stainless steel reactor.

Table 2. Reaction products obtained in the stainless steel reactor

<table>
<thead>
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<th>Reactants</th>
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<tbody>
<tr>
<td>SF₆ + C₆H₆</td>
<td>C₆H₅C₆H₅, C₆H₅C₂H₂C₆H₅, C₆H₅C₆H₄F, C₆H₅CH₂C₆H₅, C₆H₅CH₃, C₆H₅C₂H₃, C₆H₅SF₃, S₈, C₆H₅SF₅</td>
</tr>
<tr>
<td>CF₃SF₅ + C₆H₆</td>
<td>C₆H₅C₆H₅, C₆H₅C₆H₄F, C₆H₅CF₃, C₆H₅SCF₃, C₆H₄F₂, C₆H₃F₂CF₃, C₆H₅SF₅</td>
</tr>
<tr>
<td>ClSF₅ + C₆H₆</td>
<td>C₆H₃C₆H₅, ClC₆H₄SC₆H₄Cl, C₆H₄F₂, C₆H₄FCl, C₆H₅Cl, C₆H₃F₂Cl, C₆H₄ClC₆H₉, C₆H₅SO₂Cl, C₆H₅SF₅</td>
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</table>

Again, pentafluorosulfanylbenzene appeared in traces in all reaction products. An interesting feature is the appearance of FC₆H₄SF₅ in the reaction products at a C₆H₆ flow rate of 3.5 mL min⁻¹, along with large quantities of biphenyl. Though the concentration of C₆H₅SF₅ in the reaction products proved to depend on the reagents used and on the flow rates of reactants, no attempt was made to improve the yield of C₆H₅SF₅ by optimisation of the experimental conditions. However, it is very likely that the yield would increase dramatically by the use of S₂F₁₀, the most clean source of SF₅ radicals, but this was avoided in the present study due to its extremely high toxicity.³⁴
Conclusions

Dissociation–decomposition of SF6 gas in a low temperature plasma was determined to be in the range of 50% to 60%. Products of reactions of the sulfur fluorides SF6, CF3SF5 and ClSF5 with C6H5, C6H5Br and C6H5Cl in a low temperature plasma consisted mainly of halogenated benzenes. Pentafluorosulfanylbenzene was found in all cases in minor quantities but for the preparation of pentafluorosulfanylbenzenes conventional methods are preferred.

Acknowledgement

The authors are grateful to the Ministry of Education, Science and Sport of Slovenia for providing funding.

References and Notes

Povzetek
Žveplovi fluoridi SF$_6$, ClSF$_5$ in CF$_3$SF$_5$ v nizkotemperaturni radiofrekvenčni plazmi reagirajo s C$_6$H$_6$, C$_6$H$_5$Br in C$_6$H$_5$Cl. Zaradi postopne disociacije žveplovi fluoridi pride do fluoriranja benzenov. V vseh reakcijskih produktih je bil do kazan C$_6$H$_5$SF$_5$ v manjših količinah, v nekaterih tudi BrC$_6$H$_5$SF$_5$ ali ClC$_6$H$_5$SF$_5$, skupaj s številnimi halogeniranimi benzeni, kadar sta bila uporabljena reaktanta C$_6$H$_5$Br ali C$_6$H$_5$Cl.

22. NIST mass spectral library, NIST, Gaithersburg, MD, USA, 2002.

Povzetek
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