REACTIONS OF SULFUR FLUORIDES AND BENZENES IN A LOW TEMPERATURE PLASMA

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Abstract

Sulfur fluorides SF_6, $ClSF_5$ and CF_3SF_5 were reacted with C_6H_6, C_6H_5Br and C_6H_5Cl 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 $C_6H_5SF_5$ was found in minor quantities, and $BrC_6H_4SF_5$ or $ClC_6H_4SF_5$ along with numerous halogenated benzenes when C_6H_5Br or C_6H_5Cl were used as reactants, respectively.

Introduction

The introduction of a pentafluorosulfanyl group, SF_5, into organic molecules can substantially change their properties, which makes compounds containing the SF_5 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 SF_5 containing compounds includes the reduction of shock sensitivity of energetic materials in which the nitro group has been replaced by the pentafluorosulfanyl group.[6] The use of pentafluorosulfanylbenzenes has been inhibited by their low yields of production and for this reason many attempts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 $C_6H_5SF_5$ was Sheppard[7] in 1960. He isolated several pentafluorosulfanylbenzenes by fluorination of aromatic disulfides with AgF_2 in CFC 113 at 393 K. Pentafluorosulfanylbenzenes were later prepared by various reactions: by the reaction of S_2F_{10} with benzene[8] at 453 K, by the reaction of $SF_5C{\equiv}CH$ with 1,3-butadiene,[9] by the reaction of $SF_5C{\equiv}CH$ with SF_5Cl,[10] by fluorination of aromatic disulfides in concentrated sulfuric acid,[11] by fluorination of aromatic disulfides with elemental fluorine in CH_3CN[12] ($C_6H_5SF_5$, 38.5% yield) and by fluorination of 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 $CF_3^{\cdot}$ radicals generated in a low temperature plasma from C_2F_6 gas, numerous organometallic compounds were also prepared.[16] Similary, $SF_5^{\cdot}$ 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_3SF_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_3SF_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 caried 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[19,20] 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[21] 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[22] and to Aldrich library FTIR spectra, respectively.[23,24]

In the quartz reactor sulfur fluorides SF_6 and CF_3SF_5 were reacted with C_6H_6, C_6H_5Br and C_6H_5Cl at a total flow rate of 1 mL min^{-1} to 11.3 mL min^{-1} in individual experiments. Reactions of SF_6, CF_3SF_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.[25] 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,[26] especially when benzene was used as reactant.

Degree of dissociation–decomposition of SF_6 in plasma. For the production of pentafluorosulfanylbenzenes a high dissociation–decomposition of sulfur fluorides in the plasma, which means a high concentrations of $SF_5^{\cdot}$ radicals, is essential. Therefore, the degree of dissociation-decomposition of SF_6 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 SF_6 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 SF_6 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.[27] 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 disscusion

Determination of dissociation–decomposition rate in a plasma of SF_6 gas. The concentration of $SF_5^{\cdot}$ 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 SF_6 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 SF_6 in the reactor when the discharge is off. The predominance of SF_5^+ followed by SF_3^+ 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 SF_2^+, which indicates the extensive further stepwise dissociation of sulfur fluoride species $SF_5^{\cdot}$. In addition to the main ions SF_2^+, SF_3^+ and SF_5^+ measurable contributions to the total ion current from other ions derived directly or indirectly from SF_6, namely SF_4^+, SF^+, F^+ and the doubly charged ions SF_2^{2+} and SF_4^{2+}, are evident. A reduction in the relative intensities of the ions SF_5^+ and SF_3^+ 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 SF_6 in a stainless steel reactor at a SF_6 flow rate of 2.5

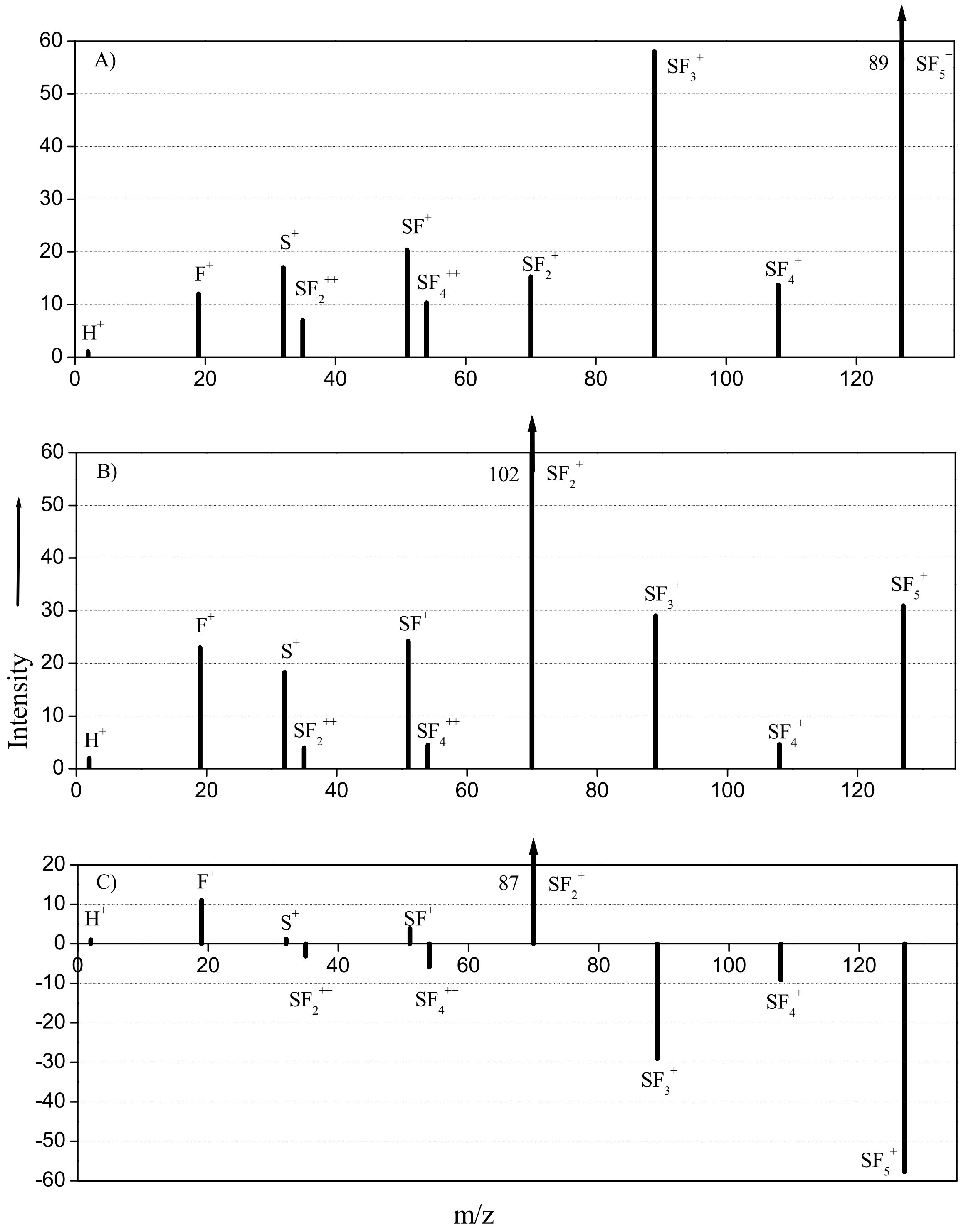

Figure 1. Mass spectra of neutral species in SF_6 gas sampled at a pressure of 1.4 Pa: A) SF_6 gas sampled from the cell without discharge, B) SF_6 gas sampled from the cell with discharge on, and C) difference of mass spectra B) and A) where negative values indicate a loss when the plasma is on. The isotope peaks for sulfur containing ions were removed to simplify the spectra.

mL min^{-1} and at a pressure of 1.4 Pa (Figure 1) was found to be in the range[27] from 50% to 60%.

Reactions of sulfur fluorides and benzenes. In a low temperature plasma sulfur fluorides SF_6 and CF_3SF_5 were allowed to react with C_6H_6, C_6H_5Br and C_6H_5Cl in the bell jar reactor (Table 1), and reactions of SF_6, CF_3SF_5 and $ClSF_5$ 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 $C_6H_5SF_5$, formed in reaction between CF_3SF_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 SF_6 was used as the source of $SF_5^{\cdot}$ radicals; other volatile products determined by IR spectroscopy were SiF_4, SOF_4 and SO_2F_2 besides unreacted 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. 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 (SF_5, 222 kJ mol^{-1}; SF_4, 352 kJ mol^{-1}; SF_3, 264 kJ mol^{-1}; SF_2, 384 kJ mol^{-1}; SF, 340 kJ mol^{-1}).[31] Therefore, the energy required to dissociate the SF_6 molecule also causes the further stepwise dissociation of sulfur species SF_5, and consequently the fluorination of

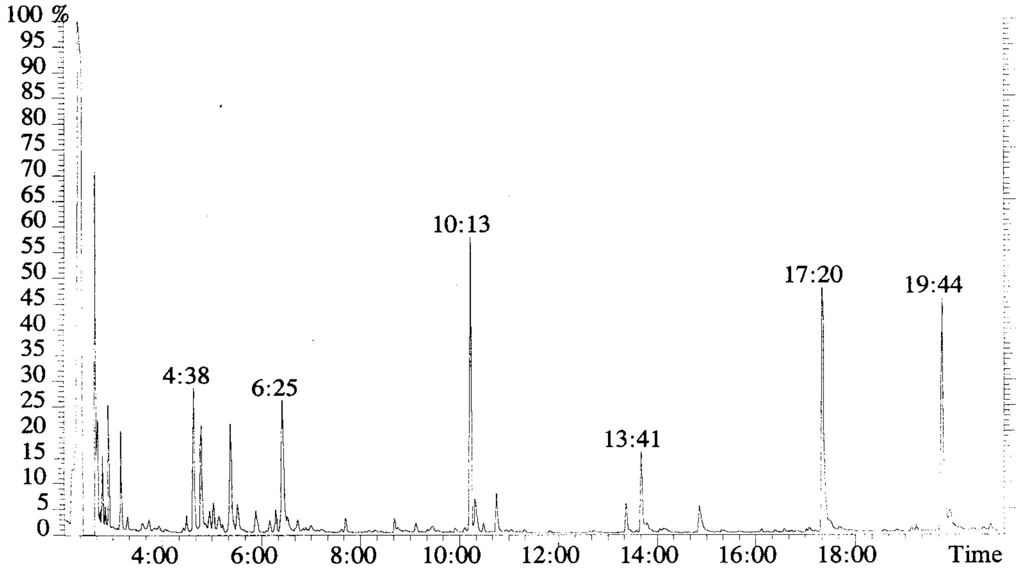

Figure 2. Gas chromatogram of reaction products of CF_3SF_5 with C_6H_5Cl in a plasma in a quartz reactor (5 mL min^{-1} of CF_3SF_5, 5 mL min^{-1} of C_6H_6Cl), retention time in minutes of $C_6H_5SF_5$, 2:40; C_6H_4ClF, 2:38; $ClC_6H_4CF_3$, 2:54; $C_6H_3Cl_2F$, 4:38; $C_6H_4Cl_2$, 5:22; $FC_6H_4SSCF_3$, 6:25; $ClC_6H_5SF_5$, 6:30; $ClC_6H_4SSCF_3$, 10:13; $ClC_6H_4SSCCl_2$, 13:22; $ClC_6H_4S_3CF_3$, 13:41; $FC_6H_4SC_6H_4Cl$, 17:20; $ClC_6H_4SC_6H_4Cl$, 19:44.

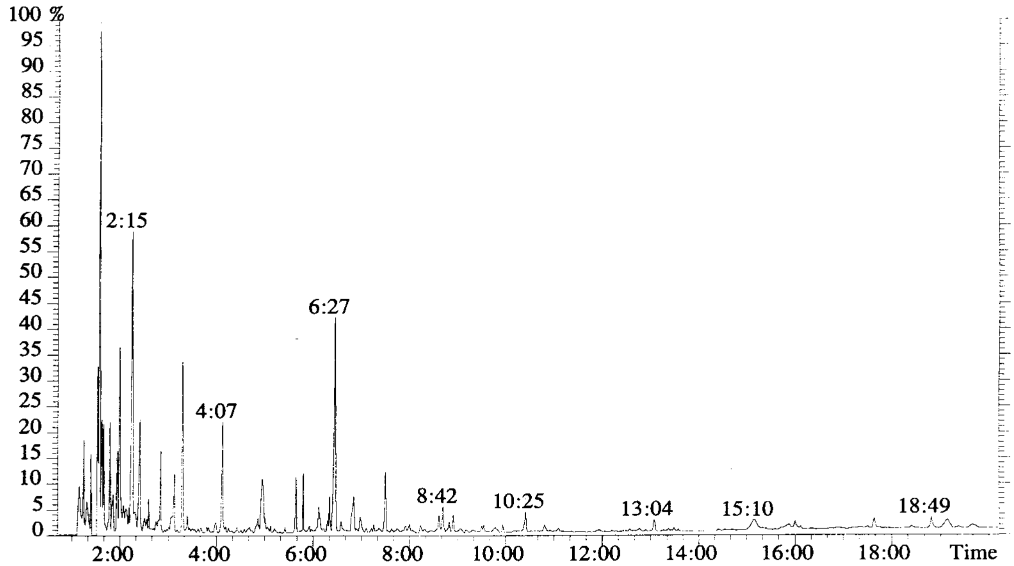

Figure 3. Gas chromatogram of reaction products of CF_3SF_5 with C_6H_6 in a plasma in a stainless steel reactor (3 mL min^{-1} of CF_3SF_5, 3 mL min^{-1} of C_6H_6 and 1 mL min^{-1} of Ar), retention time of $C_6H_5SF_5$ is 2:31; $FC_6H_5CF_3$, 1:36; $C_6H_5CF_3$, 2:34; $C_6H_5SF_3$, 2:24; $CH_3C_6H_4C_2H_5$, 3:18; $C_6H_5SSCF_3$, 4:07; $C_{12}H_7F$, 4:57; $C_4H_9C_6H_4C_4H_9$, 5:48; $C_6H_5C_6H_5$, 6:27.

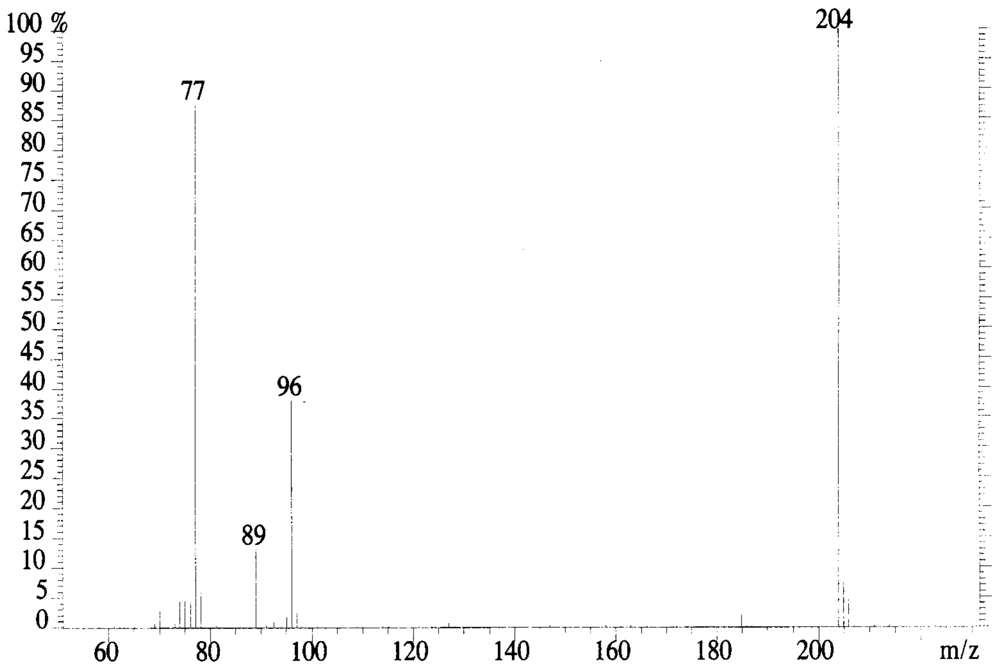

Figure 4. Mass spectrum of $C_6H_5SF_5$ found in the reaction products of CF_3SF_5 with C_6H_6 in a plasma.

aromatic species is likely to occur. Benzene excited in a plasma undergoes two main reactions: monomolecular decomposition and bimolecular reaction with neutral molecules.[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.[26] In the reaction products of CF_3SF_5 with C_6H_6 and C_6H_5Br, $C_6H_5SF_5$ (Figure 4) was found by GC – MS (Figure 2) in minor quantities estimated at less than 1% of all products (Table 1). When C_6H_5Cl was used as reactant, besides $C_6H_5SF_5$, the chlorinated compound $ClC_6H_4SF_5$ was also found (Figure 2). In a low temperature plasma the dissociation of CF_3SF_5 follows different routes. Dissociation into $CF_3^{\cdot}$ and $SF_5^{\cdot}$ by rupture of the C – S bond (E_{diss}< 272 kJ mol^{-1})[33] may be the primary process which produces the radicals necessary for the final products $C_6H_5CF_3$ and $C_6H_5SF_5$ to be formed. The stepwise dissociation of the SF_5 group in CF_3SF_5 is another probable pathway which may lead to the SCF_3 substituted benzenes found in all reactions where CF_3SF_5 was a reactant. When using CF_3SF_5 as reactant common 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_3SF_5 which may not lead to fluorinating species.

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

Reactants	Reaction products
$SF_6 + C_6H_6$	$C_6H_5C_6H_5$, $C_6H_5C_2H_2C_6H_5$, $C_6H_5C_6H_4F$, $C_6H_5CH_3$, $C_6H_5C_2H_5$, $C_6H_5SF_5$
$SF_6 + C_6H_5Br$	$C_6H_5C_6H_5$, $C_6H_5C_6H_4F$, $BrC_6H_4C_6H_4F$, $BrC_6H_4C_6H_3Br_2$, C_6H_4BrF, $C_6H_3BrF_2$, C_6H_4BrF, $C_6H_3Br_2F$, $C_6H_4Br_2$, $C_6H_5CF_3$, $C_6H_5SF_5$
$SF_6 + C_6H_5Cl$	$C_6H_5C_6H_5$, C_6H_4ClSH, $ClC_6H_4SC_6H_4Cl$, $ClC_6H_4SSC_6H_4Cl$, $C_6H_5SF_5$, $C_6H_4ClSF_5$
$CF_3SF_5 + C_6H_6$	$C_6H_5C_6H_5$, $C_6H_5SC_6H_5$, $C_6H_5C_6H_4F$, $C_6H_5CF_3$, $C_6H_5SCF_3$, $C_6H_5SSCF_3$, $C_6H_5SSC_6H_5$, $C_6H_5CF_2C_6H_5$, $C_6H_5SF_5$
$CF_3SF_5 + C_6H_5Br$	C_6H_5F, $C_6H_4F_2$, $C_6H_3F_3$, $C_6H_4Br_2$, C_6H_4BrF, $C_6H_3BrF_2$, $C_6H_3Br_2F$, $C_6H_5CF_3$, $C_6H_4BrCF_3$, $C_6H_3Br_2CF_3$, $C_6H_5SF_5$, $C_6H_4BrSF_5$, $FC_6H_4SSCF_3$, $BrC_6H_4SSCF_3$, $BrC_6H_4SCF_3$, $FC_6H_4SC_6H_4F$, $BrC_6H_4SC_6H_4F$, $BrC_6H_4SC_6H_4F$, $BrC_6H_4SSC_6H_4F$, $BrC_6H_4SC_6H_3BrF$, S_6, S_8
$CF_3SF_5 + C_6H_5Cl$	C_6H_4ClF, $C_6H_3Cl_2F$, $C_6H_4Cl_2$, $ClC_6H_4CF_3$, $FC_6H_4SSCF_3$, $ClC_6H_4SSCF_3$, $ClC_6H_4S_3CF_3$, $C_6H_5SF_5$, $ClC_6H_4SF_5$, $ClFC_6H_3SF_5$, $ClC_6H_4SSCCl_2F$, $ClC_6H_4SSCF_3$, $FC_6H_4SC_6H_4Cl$, $ClC_6H_4SC_6H_4Cl$

The greater number of compounds found in reaction mixtures containing CF_3SF_5 is the consequence of the relatively high stability of the $CF_3^{\cdot}$ radical which is reflected in the formation of numerous trifluoromethylated compounds. Nevertheless, the reaction of CF_3SF_5 and C_6H_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 concentrations of $C_6H_5SF_5$, $C_6H_5CF_3$ and biphenyl in the reaction products (Figure 3) were much higher when CF_3SF_5 was one of reactants. When $ClSF_5$ was used, the number of reaction products increased considerably, due to the chlorination of aromatic species, but the quantity of $C_6H_5SF_5$ was very low.

Reactions in the stainless steel reactor. The reactions of SF_6 and benzene in the stainless steel reactor at different flow rates of C_6H_6, 1 mL min^{-1} of Ar and 3 mL min^{-1} of SF_6 showed that a higher flow rate of C_6H_6 causes fewer products to form and in lower quantities. More volatile products *i.e.* SiF_4, SOF_4 and SO_2F_2, along with unreacted SF_6 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

Reactants	Reaction products
$SF_6 + C_6H_6$	$C_6H_5C_6H_5$, $C_6H_5C_2H_2C_6H_5$, $C_6H_5C_6H_4F$, $C_6H_5CH_2C_6H_5$, $C_6H_5CH_3$, $C_6H_5C_2H_5$, $C_6H_5SF_3$, S_8, $C_6H_5SF_5$
$CF_3SF_5 + C_6H_6$	$C_6H_5C_6H_5$, $C_6H_5C_6H_4F$, $C_6H_5CF_3$, $C_6H_5SCF_3$, $C_6H_4F_2$, $C_6H_3F_2CF_3$, $C_6H_5SF_5$
$ClSF_5 + C_6H_6$	$C_6H_5C_6H_5$, $ClC_6H_4SC_6H_4Cl$, $C_6H_4F_2$, C_6H_4FCl, C_6H_5Cl, $C_6H_3F_2Cl$, $C_6H_4ClC_4H_9$, $C_6H_5SO_2Cl$, $C_6H_5SF_5$

Again, pentafluorosulfanylbenzene appeared in traces in all reaction products. An interesting feature is the appearance of $FC_6H_4SF_5$ in the reaction products at a C_6H_6 flow rate of 3.5 mL min^{-1}, along with large quantities of biphenyl. Though the concentration of $C_6H_5SF_5$ 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 $C_6H_5SF_5$ by optimisation of the experimental conditions. However, it is very likely that the yield would increase dramatically by the use of S_2F_{10}, the most clean source of $SF_5^{\cdot}$ radicals, but this was avoided in the present study due to its extremely high toxicity.[34]

Conclusions

Dissociation–decomposition of SF_6 gas in a low temperature plasma was determined to be in the range of 50% to 60%. Products of reactions of the sulfur fluorides SF_6, CF_3SF_5 and $ClSF_5$ with C_6H_5, C_6H_5Br and C_6H_5Cl 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.

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Povzetek

Žveplovi fluoridi SF_6, $ClSF_5$ in CF_3SF_5 v nizkotemperaturni radiofrekvenčni plazmi reagirajo s C_6H_6, C_6H_5Br in C_6H_5Cl. Zaradi postopne disociacije žveplovih fluoridov pride do fluoriranja benzenov. V vseh reakcijskih produktih je bil dokazan $C_6H_5SF_5$ v manjših količinah, v nekaterih tudi $BrC_6H_5SF_5$ ali $ClC_6H_5SF_5$, skupaj s številnimi halogeniranimi benzeni, kadar sta bila uporabljena reaktanta C_6H_5Br ali C_6H_5Cl.