

Trifluoromethyl Sulfur Pentafluoride (CF₃SF₅): A Review of the Recently Discovered Super-Greenhouse Gas in the Atmosphere

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Abstract: Trifluoromethyl sulfur pentafluoride (CF₃SF₅) is considered to be the most potent greenhouse gas present in the Earth's atmosphere. Its global warming potential is estimated to be 18 000 times that of carbon dioxide. CF₃SF₅ is resistant to photolysis and to reactions with common atmospheric and industrial ions, however it has been observed to react with positive ions in the ionosphere and undergo both electron attachment and protonation. Its lifetime in the atmosphere is estimated to be on the order of 1000 years. Levels prior to the 1960s are estimated to be zero, providing strong evidence that it is solely of anthropogenic origin. At a current atmospheric concentration of approximately 0.12 to 0.16 parts per trillion, CF₃SF₅ does not contribute significantly to total radiative forcing, but because of its atmospheric lifetime and stability, it is still of considerable importance with regards to Earth's future climate.

INTRODUCTION

Although global warming has been an issue of contention in the past, it is now generally agreed upon by the scientific community that the observed increased global temperatures can be linked to anthropogenic activities. Global surface temperature has increased 0.5 °C within the past century [1]. Although this may seem to be an insignificant increase, even slight changes in global temperatures can have dramatic effects such as sea level rise, wildlife habitat alteration, increases in disease rates, etc. It is estimated that at current rates of increase in greenhouse gas levels, a 0.3 to 0.9 °C increase in surface temperature may be observed by the end of the 21st century [2]. Recently, there has been a discovery of a previously unidentified greenhouse gas present in the atmosphere that is orders of magnitude more potent at inducing the greenhouse effect than is CO₂. This compound, trifluoromethyl sulfur pentafluoride (CF₃SF₅), is considered to be one of several super greenhouse gases, and because of its recent detection in the atmosphere, there is a relatively limited amount of literature available on CF₃SF₅. This review will present what is currently known regarding this molecule. Among the topics to be presented include the effects of CF₃SF₅ in the atmosphere, elimination mechanisms, lifetime and rate of increase, as well as information on possible sources of release into the atmosphere.

SUPER GREENHOUSE GASES

Greenhouse gases (GHGs) have different capacities to contribute to global warming. This is due to differences in absorption and re-radiation at specific wavelengths in the infrared (IR) spectrum and from residence times in the atmosphere [3]. The concept of the global warming potential (GWP) was introduced by the Intergovernmental Panel On

Climate Change (IPCC) to express the relative effectiveness of a given amount of a specific GHG, over a specified period of time to induce a positive radiative forcing [3]. This measure is based on the potency of carbon dioxide to induce global warming, given a GWP of 1, and then comparing all other GHGs to CO₂. Some common GHGs with their respective GWPs include methane (GWP=21) and nitrogen dioxide (GWP=310). Gases that have GWPs that are four to five times the magnitude of carbon dioxide are appropriately referred to as super greenhouse gases.

CF₃SF₅ is considered to be one of the several super greenhouse gases. On a per molecule basis, it is considered to be the most potent greenhouse gas present in Earth's atmosphere [4]. The most effective greenhouse gases absorb radiation in the infrared window, containing the wavelengths from approximately 700 to 1300 cm⁻¹ [5]. Due to CF₃SF₅'s strong absorptive power in this atmospheric window (60% of the wavelengths that are absorbed by CF₃SF₅ are contained within the 800-1300 cm⁻¹ range), CF₃SF₅ is an extremely efficient inducer of the greenhouse effect [4,6]. Furthermore, it has been calculated that CF₃SF₅ has a radiative force of 0.57 watt per square meter per part per billion [W m⁻² ppb⁻¹] [6]. Comparatively, some well known CFCs and HFCs have a radiative forcing per ppb ranging from 0.02 to 0.26 W m⁻² ppb⁻¹ [5]. This data, provided in Table 1, shows that CF₃SF₅ can be up to 25 to 30 times more potent at inducing the greenhouse effect than other chlorine and fluorine containing compounds that have been of interest in the past. By assuming that CF₃SF₅ has a similar atmospheric lifetime of SF₆, the 100-year global warming potential is estimated to be 18 000 times that of CO₂ [4,6].

CHEMISTRY IN THE ATMOSPHERE

Several investigations have been conducted to determine how CF₃SF₅ is destroyed in the atmosphere and thereby provide an estimate of its lifetime. These mechanisms include photolysis, reactions with several atmospheric and industrial

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compounds, electron attachment, and protonation reactions. Table 2 provides a summary of these data.

Table 1. Radiative Forcing of Selected Fluorinated Compounds [5]

Compound	Radiative Forcing (W m ⁻² ppb ⁻¹)
SF ₆	0.64
CF ₃ SF ₅	0.57
CFC 11 (CFCl ₃)	0.29
HFC 134a (CH ₂ FCF ₃)	0.17
HFC 152a (CH ₃ CHF ₂)	0.11

Oxidation

The troposphere is an important area for chemical reactions to occur, as it contains 85% of total atmospheric mass [7]. Oxidation is a primary route by which many trace gases are removed from the atmosphere, with the most abundant oxidizers being O₂ and O₃ [7]. However these molecules are generally unreactive towards non-radicals [7]. Organic compounds are oxidized in the atmosphere primarily through reactions with OH and O₃ (also to some extent NO₃) [5]. Oxidation with hydroxyl radicals tends to form stable water molecules *via* abstraction of a hydrogen atom in alkanes or through double bond attack in alkenes forming alcohols [5]. Ozone also attacks the double bond in alkenes. CF₃SF₅ contains neither the hydrogen atoms nor the double bonds that are the targets of OH and O₃ and therefore are unreactive to these oxidizers. No experimental data could be found, however oxidation modeling has been conducted with SF₆, which is molecularly similar to CF₃SF₅ [8]. It was calculated that SF₆ would have an atmospheric lifetime of 60000 years when removed exclusively by OH and O₃ [8], thereby providing evidence that the oxidation of CF₃SF₅ is not likely to occur.

Photolysis

Photolysis refers to reactions in which chemicals are altered by exposure to light, though it is usually UV photons that contain enough energy to break down molecules. Photolytic reactions play important roles in both the attenuation and activation of chemicals in the atmosphere. Gerstell *et al.* 2001 showed that the CF₃-SF₅ bond is able to withstand UV photo disassociation in the stratosphere [9]. They hypothesized that because CF₃SF₅ contains no double bonds or hydrogen atoms, photolysis should be considered the primary destructive pathway for CF₃SF₅ in the atmosphere. If this is the case, CF₃SF₅ is expected to have a lifetime of approximately 4050 years in the atmosphere [9]. No solar radiation of wavelengths shorter than 290 nm reaches the troposphere [10]; therefore it is not likely to be destroyed in this region *via* photolysis as well.

Reactions with Ions

Charged particles are generally not found with any significant concentration in the troposphere and stratosphere and therefore would play a minor, if any role in the degradation of CF₃SF₅ in these areas. The charged particle concentration near ground level is on the order of 10³ particles per cubic centimeter, however it is subject to a miniscule mixing ratio of approximately 1 part in 10¹⁶ [11]. This indicates that reactions with charged particles in the lower atmosphere will not likely destroy CF₃SF₅ molecules. Ions and electrons are most abundant at altitudes above 60 km, in the mesosphere and above because a majority of the Sun's ionizing radiation is absorbed at this altitude and above [11]. Within the upper mesosphere and lower thermosphere, is the ionosphere, a region where ions are produced by photoionization. Chemistry in the ionosphere may be of lesser importance compared to actions occurring lower in the atmosphere; however, charged particle reactions can still represent a natural sink for CF₃SF₅ given that it is resistant to oxidation and photolysis.

The ionosphere is divided into several discrete sections and for the purposes of this discussion only the D, E, and F

Table 2. Summary of Observed/Investigated Reactions with CF₃SF₅

Type	Reactants	Products	Reaction Rate (/10 ⁹ cm ³ s ⁻¹)	Usual Atmospheric Region of Occurrence	Source
Oxidation	OH, O ₂ , O ₃	No reaction	---	Troposphere and Stratosphere	[8]
Photolysis	UV Photons	No reaction	---	Stratosphere	[9]
Anions	O ₂ ⁻	SF ₅ ⁻ , CF ₃ ⁻ , and O ₂	0.36 – 0.55	Ionosphere (D region)	[12]
	CO ₃ ⁻ and NO ₃ ⁻	No reaction	<0.006	Ionosphere (D region)	[12]
Cations	O ₂ ⁺	CF ₃ ⁺ and SF ₃ ⁺	0.01	Ionosphere (E region)	[13, 14]
	NO ⁺	No reaction	---	Ionosphere (E region)	[14]
	N ⁺	CF ₃ ⁺ and SF ₃ ⁺	2.2	Ionosphere (F region)	[13, 14]
	O ⁺	CF ₃ ⁺ and SF ₃ ⁺	1.9	Ionosphere (F region)	[13, 14]
Electron Attachment	Electrons	SF ₅ ⁻ and CF ₃	77	Ionosphere	[15]
Protonation	Protons	CF ₃ , SF ₄ , HF, SF ₃ ⁺ , and CF ₃ ⁺	---	---	[16]

regions are of importance. The D region is located approximately 60 to 100 km in the atmosphere, contains some of the more complex molecular ions, and is also the only location where negative ions are observed in the ionosphere [11]. The primary negative ion is O_2^- , however HCO_3^- , CO_3^- , CO_4^- , NO_3^- , and Cl^- are also present at various heights in the ionosphere [11, 12]. CF_3SF_5 has been experimentally shown to react with O_2^- , yielding SF_5^- , CF_3^- , and O_2 . However, with measured rate constants ranging from 0.36 to $0.55 \times 10^{-9} \text{ cm}^3/\text{sec}$, it appears that O_2^- does not contribute to the atmospheric chemistry of CF_3SF_5 [12]. Arnold *et al.* 2003 observed no reaction between CF_3SF_5 and CO_3^- and NO_3^- [12].

The dominant ions located in the E region (100-150 km) are NO^+ and O_2^+ , but the E region also contains a relatively large concentration of molecular ions as well [11]. The dominant reaction mechanism between CF_3SF_5 and ions is most likely dissociative charge transfer, whereby CF_3SF_5 transfers an electron to the charged particle [13, 14]. Atturbury *et al.* 2001 showed that CF_3SF_5 can react with O_2^+ to form primarily CF_3^+ and SF_3^+ , but determined that the rate coefficient for this reaction was $0.01 \times 10^{-9} \text{ cm}^3/\text{sec}$, indicating that this reaction does not significantly destroy CF_3SF_5 molecules in the atmosphere [13]. Atturbury *et al.* 2001 also showed that CF_3SF_5 is unreactive with NO^+ [13]. Reactions with N_2^+ , CO^+ , H_2O , CO_2^+ , N_2O^+ were investigated, in which varying degrees of reactivity was observed. Although the reaction rate constants were all equal or greater than $1.1 \times 10^{-9} \text{ cm}^3/\text{sec}$, these species are known to exist in the upper atmosphere at very low concentrations and therefore is not likely that these ions will contribute significantly to the overall decomposition of CF_3SF_5 .

Dominant ions in the F region (>150 km) include O^+ and N^+ , while H^+ and He^+ are most abundant at the highest altitudes (i.e. >1000 km) [11]. The makeup of ions in the F region can be described as being comprised of primarily atomic ions [11]. Total charged particle (positive and negative ions and electrons) concentrations are only approximately a few hundred particles per cubic centimeter at 300 km in the F region [11]. It has been shown that CF_3SF_5 will disassociate in reactions with N^+ , O^+ , Ne^+ , Ar^+ , and F^+ under experimental conditions [13,14]. N^+ and O^+ are the dominant ions in the F region of the ionosphere, however because of the relatively low atmospheric mass that exists in this region, it is unlikely that CF_3SF_5 will undergo significant disassociation. Ne^+ , Ar^+ , and F^+ are considered trace ions in the ionosphere and are expected to have an even more subdued effect on CF_3SF_5 than N^+ and O^+ .

Electron Attachment and Protonation

Electron attachment reactions involve the attack of a free electron to a parent molecule forming an energetic and unstable intermediate ion that will then fragment. Kennedy and Mayhew 2001 present observations that CF_3SF_5 can be destroyed by fast dissociative electron attachment, yielding SF_5^- and CF_3^- with a reaction rate constant of $7.7 \times 10^{-8} \text{ cm}^3/\text{sec}$ [15]. Electron concentrations are greatest in the upper atmosphere; electrons range from $\sim 10^4$ to 10^6 particles per cm^3 at 100-250 km, the E and F regions of the ionosphere [11]. Given the relatively large reaction rate constant,

electron attachment reactions play an important role in the decomposition of CF_3SF_5 in the upper atmosphere.

Protonation refers to the addition of a proton to a parent molecule. As in electron attachment reactions, the formation of an unstable intermediary is formed and is subsequently dissociated in protonation reactions. The resulting products of this reaction are CF_3 , SF_4 and HF , including the formation of the following ions: SF_3^+ and CF_3^+ . Pepi *et al.* 2005 investigated these reactions with several proton sources, and of those studied, CO_2H^+ , N_2OH^+ , and COH^+ appear to be most potent at reacting with CF_3SF_5 [16]. As in many of the observed ion reactions, these molecules are not dominant in either the stratosphere or in the ionosphere, while H^+ are only present at very high altitudes (>1000 km).

ATMOSPHERIC LIFETIME

The only significant loss process for CF_3SF_5 in the atmosphere appears to be electron attachment reactions that can occur in the ionosphere. As discussed previously, it is estimated that CF_3SF_5 will have a lifetime of 60 000 years if solely destroyed by oxidation mechanisms in the stratosphere or 4050 years if degraded exclusively by photolysis. The lifetime of perfluorocompounds (fully fluorinated compounds) has been previously modeled [17]. These models indicate that for substances that are primarily inert, but subject to electron attachment, such as CF_3SF_5 and also SF_6 , atmospheric lifetime is estimated to range from 800 to 1000 years [17]. The electron attachment reaction rate for SF_6 in the atmosphere has been calculated to be approximately $310 \times 10^{-9} \text{ cm}^3/\text{sec}$, representing a rate that is close to the theoretical maximum [15, 17]. Given that the electron attachment rate of CF_3SF_5 is less, though relatively similar to that of SF_6 and that CF_3SF_5 is resistant to all other degradation reactions, it is estimated that the atmospheric lifetime of CF_3SF_5 is on the order of 1000 years. For comparison, the estimated lifetime of CO_2 , CH_4 , and N_2O are 50 to 100, 12, and 120 years, respectively. The lifetime of CF_3SF_5 is 10 to 100 times longer than these greenhouse gases that are causing significant problems today.

CURRENT RATE OF INCREASE IN THE ATMOSPHERE

The discovery of CF_3SF_5 as a component of the atmospheric gas mixture was very much an inadvertent one. Sturges *et al.*, 2000 reported that when analyzing for SF_6 in stratospheric gas samples, they noted a previously unidentified peak that eluded shortly after SF_6 in their gas chromatographic analyses. Subsequent investigations determined that these peaks corresponded to the presence of CF_3SF_5 [6].

After the identification of the presence CF_3SF_5 in stratospheric gas samples, efforts began to determine the concentration of this compound in the atmosphere. In January of 1999, air samples were pumped out of deep consolidated snow (firn) at Dome Concordia in eastern Antarctica [6]. These samples showed that the atmospheric concentration of CF_3SF_5 in the early 1960s were essentially zero; with measurable levels starting in the mid 1960s. Sturges *et al.* 2000 interpreted these data as emissions of CF_3SF_5 to have begun in the late 1950s [6]. After initial emissions began, a steady

increase in concentration can be observed into the 1990s. Current levels of CF₃SF₅ is approximately 0.12 to 0.18 parts per trillion (ppt), increasing approximately six percent per year based on analyses conducted on Antarctic firn [6, 18]. Sturges *et al.* reported a +/- 10 percent error to this predicted rate of increase [6].

Current concentrations of CF₃SF₅ in the atmosphere do not contribute to overall radiative forcing [6], however this may change as observed trends continue. For comparison, atmospheric concentrations of CH₄ and N₂O are 1750 parts per billion (ppb) and 310 ppb, respectively. It is estimated that anthropogenic releases of CH₄ must be reduced by 8% to current stabilize atmospheric levels, while releases of N₂O must be reduced by 50% [19]. Current concentration of atmospheric CO₂ is approximately 360 parts per million (ppm). Carbon dioxide, methane, and nitrogen dioxide, have contributed to 64%, 19%, and 6%, respectively, to global warming since the beginning of the Industrial Era [19]. Given that the atmospheric concentration of CF₃SF₅ is still very low, we have the unique opportunity to identify and mitigate sources of this molecule prior to it contributing to climate changes.

POSSIBLE ANTHROPOGENIC SOURCES

There are several possible uses of CF₃SF₅ in industry that may be contributing to the increased concentrations observed in the atmosphere. The estimate of zero concentration of CF₃SF₅ in the atmosphere prior to the 1960s indicates that the source of this molecule is exclusively anthropogenic. Santoro 2000 claims that he is aware of one definitive source of CF₃SF₅, a by-product of the manufacture of fluorochemicals [20]. It has been presented that the source of CF₃SF₅ in the atmosphere may originate from reactions of SF₆ with fluoropolymers used in electronic devices and in microchips [4, 12]. There has also been some speculation that CF₃SF₅ is associated with high voltage equipment created from SF₆ (a breakdown product of high voltage equipment) reacting with CF₃ to form the CF₃SF₅ molecule [15]. CF₃ is found as a breakdown product in fluoropolymers in this type of equipment. Furthermore, the rate of concentration increases of CF₃SF₅ tracks very closely to the trend observed in atmospheric SF₆ levels, indicating that these two molecules are connected.

Pepi *et al.* 2005 investigated the possibility of CF₃SF₅ through reactions of SF₆ in high voltage equipment and electrical devices [16]. In their experiments, they attempted to react SF₆ with various fluoropolymers containing CF₄, C₂F₆, and C₃F₈, stating that these reactions lend the possibility of forming CF₃SF₅. However, after mass spectrometric analysis of the resulting gas mixture, no detectable levels of CF₃SF₅ were found. The conclusion of the authors is that CF₃SF₅ is not produced from reactions of SF₆ and fluoropolymers used in high voltage equipment.

The source of CF₃SF₅ remains somewhat of a mystery. The hypothesis that CF₃SF₅ may be a by-product of electrical equipment processes seems to have failed based on the investigations conducted by Pepi *et al.* The only seemingly definitive source of CF₃SF₅ was through the formation of

fluoropolymers presented by Santoro 2000. No levels of production or chemical releases were provided, so it is unknown whether this process is the primary contributor to current atmospheric levels.

CONCLUSIONS

The scientific nuances underlying climate change mechanisms are still beginning to be understood. Currently, much of the focus on mitigating climate change has been focused on reducing the emissions of the major greenhouse gases such as CO₂, CH₄, and N₂O. The discovery of CF₃SF₅ in the atmosphere indicates that we need to keep in mind that trace gases have the potential to effect of global climate change. Although the current concentration of CF₃SF₅ remains at a level that is unlikely to measurably contribute to earth's warming, it is considered to be the most potent greenhouse gas in the atmosphere due to its inertness and long lifetime. The origin of its presence in the atmosphere is still unknown and still needs to be investigated if we are to combat its future influence on Earth's climate.

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