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Perfluoro-1,3-dioxolane and Perfluoro-oxetane: promising gases for electrical insulation

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Abstract. Perfluorinated cyclic ethers represent an interesting class of molecules to use as dielectric gases for electrical insulation. Measurements of the two compounds 4,4,5,5-Tetrachloro-2,2-difluoro-1,3-dioxolane ($c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, CAS 87075-01-2) and Octafluoro-1,4-dioxane ($c\text{-C}_4\text{F}_8\text{O}_2$, CAS 32981-22-9) in a Pulsed Townsend Experiment are presented, their ionization and attachment rate coefficients are obtained and their electron attachment cross sections are estimated. Both gases have a high critical electric field strength of about 3.5 and 1.3 times the one of SF_6 , respectively, which is presumably due to very high electron attachment cross sections in the range from 2 – 4 eV. In particular, for $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ the values appear to be very close to the S-wave scattering limit around 3 eV. Based on these results, we recommend the two analogous compounds Perfluoro-1,3-dioxolane ($c\text{-C}_3\text{F}_6\text{O}_2$, CAS 21297-65-4) and Perfluoro-oxetane ($c\text{-C}_3\text{F}_6\text{O}$, CAS 425-82-1) for further research for the use as insulation and refrigerant gases, since they are chemically comparable, presumably environmentally friendly, and have high vapor pressures.

1. Introduction

Over the last decades numerous efforts have attempted to identify alternative gases for gas-insulated switchgear and high voltage equipment, as replacement for the extremely potent greenhouse gas SF_6 which is today commonly used [6, 8, 31]. The requirements for such a gas are numerous: besides having a high vapor pressure and a high critical electric field, it should be low in toxicity, non-flammable, and chemically stable for decades inside the equipment vessel, while having zero ozone-depleting potential (ODP) and a low global warming potential (GWP) in case of leakage. The electric strength is loosely coupled with the electron affinity of the molecules, which is why the search is mostly focused on halogenated compounds. Restricting the halogens to fluorine only has the benefit of zero ODP and lower boiling points.

High voltage switchgear are commonly operated at 4–6 bar pressure, and require gases that do not liquefy at outdoor temperatures down to -25°C . Since only few fluorinated gases fulfill this condition, mixtures with "carrier gases" like N_2 or CO_2 are also considered as replacement for SF_6 . The maximum possible mole fraction for the fluorinated gas is then their partial pressure at the lowest required temperature.

We use a pulsed Townsend experiment to assess the electrical performance of gases. The gases are filled into a chamber with an electrode setup, which spans a homogeneous electric field. Electrons are released from the cathode by a UV laser pulse and drift in a towards the anode. At sufficiently high field strength, the elec-

trons ionize neutral gas molecules and grow exponentially in number. In electron-attaching gases, electrons can form negative ions upon collision with the neutral gas, and are thus removed from the avalanche. The displacement current of electrons and both negative and positive ions is measured and evaluated to yield the field-dependent ionization and attachment rate coefficients. Since the ionization rate increases with increasing field strength, a density-reduced critical electric field strength $(E/N)_{\text{crit}}$ can be defined for electron-attaching gases as the E/N value at which the ionization and attachment rate become equal. It marks the transition towards a self-sustained avalanche of electrons, which eventually, given enough time and space to grow, results in an electric breakdown of the gas.

According to a recently developed semi-empirical screening method [31], the two compounds perfluoro-1,3-dioxolane ($c\text{-C}_3\text{F}_6\text{O}_2$, CAS 21297-65-4, "R-CE216") and perfluoro-oxetane ($c\text{-C}_3\text{F}_6\text{O}$, CAS 425-82-1) are excellent candidates for insulating gases: the electric strength is predicted to be higher than that of SF_6 , while the boiling points are low (-22.1°C [27] and -38°C [1]). Samples could not yet be acquired, although there are synthesis routes for both of them, which yield stable and inert compounds. We could, however, obtain samples of two other cyclic fully halogenated ethers: in the 4,4,5,5-tetrachloro-2,2-difluoro-1,3-dioxolane ($c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, CAS 87075-01-2), four chlorine atoms take the place of fluorine, while 2,2,3,3,5,5,6,6-octafluoro-1,4-dioxane ($c\text{-C}_4\text{F}_8\text{O}_2$, CAS 32981-22-9) is a six-member ring instead of five.

The outline of this publication is as follows: a short

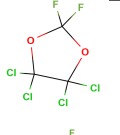
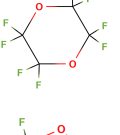
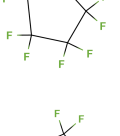
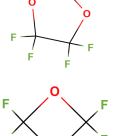
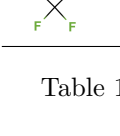
structure	compound	boiling point	$(E/N)_{\text{crit}}$
	c-C ₃ Cl ₄ F ₂ O ₂	87 - 91°C [44]	1200Td
	c-C ₄ F ₈ O ₂	22.5 - 23°C [44]	470Td
	c-C ₄ F ₈ O	0.6°C [44]	130Td for 0.6% gas in N ₂ [33]
	c-C ₃ F ₆ O ₂	-22.1°C [27]	?
	c-C ₃ F ₆ O	-38°C [1]	?

Table 1: Overview of cyclic halogenated ethers.

summary of the experiment and evaluation technique is followed by the results for the two measured compounds c-C₃Cl₄F₂O₂ and c-C₄F₈O₂. We compare their critical field strength and electron attachment cross section to those of SF₆. The sparse literature on what is known about c-C₃F₆O₂ and c-C₃F₆O is reviewed, and we discuss their potential suitability as insulation gases. As usual, we make our results publicly available on LXCat [35].

2. Methods

Both compounds c-C₃Cl₄F₂O₂ and c-C₄F₈O₂ were obtained from SynQuestLabs in small quantities and used without purification. The c-C₃Cl₄F₂O₂ is liquid and injected with a high-purity syringe through a septum.

The Pulsed Townsend experiment was presented in [28] and further developed in [40]. The base pressure of the vessel is 10⁻⁶ Pa, but since the quantities of the measured gases were rather small, impurities of up to 1% (air) can not be excluded for this measurement series. Due to the low vapor pressure of c-C₃Cl₄F₂O₂, a steady drop in pressure was observed while measuring, which we assume is due to adsorption to the chamber walls (few permille per minute).

The signals were first recorded at pressures of 100, 200 and 300 Pa for the pure c-C₄F₈O₂ and 80 Pa for the pure c-C₃Cl₄F₂O₂. c-C₄F₈O₂ and c-C₃Cl₄F₂O₂ were then diluted in steps with N₂ to assess the "synergy effect" of the gas mixtures (see section 3.3).

For c-C₄F₈O₂, the same procedure was repeated with CO₂ as buffer gas. For the most diluted mixtures pressures of 10 kPa for c-C₄F₈O₂:N₂,CO₂ and 6 kPa for c-C₃Cl₄F₂O₂:N₂ were reached.

The evaluation is described in detail in [38]. We choose a suitable ion-kinetic model (see figure 1), which we require to reproduce all measurements of the series at all pressures and mixing ratios. The rate coefficients appearing in the model are then fitted to the measurements based on simulations on GPUs.

3. Results

3.1. c-C₃Cl₄F₂O₂

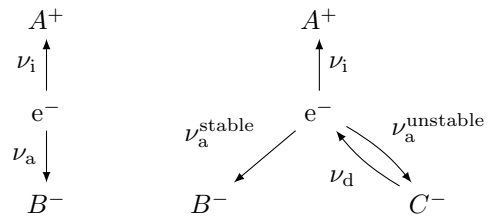


Figure 1: Symbolic representation of the kinetic models for c-C₃Cl₄F₂O₂ (left) and c-C₄F₈O₂ (right). ν_i denotes ionization rates, ν_a attachment rates to the ion species A and B. The detachment rate ν_d describes the process of a negative ion losing its electron in collisions with neutral molecules.

Simulations of a simple model (figure 1, left) consisting of only one positive and one negative ion reproduce well the measured waveforms in c-C₃Cl₄F₂O₂. The observation of different channels of ionization and attachment is only possible if there is sufficient difference in between the ion mobilities, which is not the case for this compound. The negative ion does not show electron detachment. Figure 2 shows the obtained ionization (red crosses) and attachment rate coefficient (blue circles), with which the critical field strength of c-C₃Cl₄F₂O₂ is established as 1200 Td. Compared to SF₆, the attachment rate coefficient is larger by an order of magnitude at 1200 Td, while the ionization rate coefficient is roughly halved. The density-normalized mobilities at 1200 Td are found as $\mu_N = 0.9 \cdot 10^{21} \text{ m}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for the positive ion and $1.36 \cdot 10^{21} \text{ m}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for the negative ion (unscaled, at experimental conditions and room temperature; confidence of few percent), and $\mu_e N = 2.6 \cdot 10^{23} \text{ m}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for the electrons (bulk mobility). The (bulk) density-normalized longitudinal diffusion coefficient is found as $ND_L = (0.95 \pm 0.1) \cdot 24 \text{ m}^2$.

We use an inverse method for estimating the attachment cross section, as described in [32]. The highly

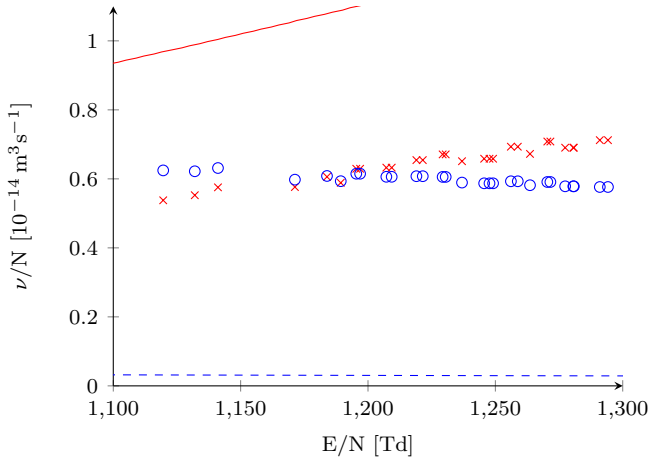


Figure 2: Ionization (red crosses) and attachment rate coefficient (blue circles) of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ compared to SF_6 (Bolsig+ simulation [24] using Biagi’s database [42]) total ionization (red line) and total attachment rate coefficient (blue dashed line). The critical field strength of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ is 1200 Td.

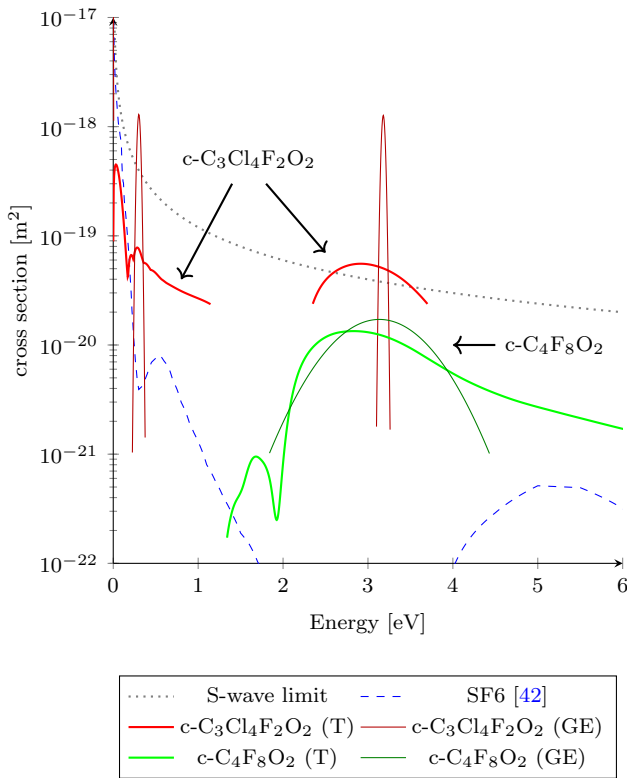


Figure 3: Attachment cross section of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ (red, dark red) and $c\text{-C}_4\text{F}_8\text{O}_2$ (green, dark green), obtained with a Tikhonov inversion (T) and gaussian expansion (GE), and compared to SF_6 (Biagi cross section set [42] from LXCat [35]) and the S-wave scattering limit.

diluted gas in a mixture with N_2 and CO_2 is measured up to 70 Td, from which the attachment rate of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ is obtained (and corrected for the attachment of CO_2). Under the approximation that the electron energy distribution function (eedf) is determined only by the background gas N_2 and CO_2 and not influenced by the admixed gas, the main peaks of the attachment cross section of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ can then be estimated from several measurements at different E/N . A Bolsig+ simulation [24] yields the eedf of N_2 and CO_2 for the E/N range up to 70 Td, using the cross section sets of Biagi [42] and Phelps [43], respectively, from LXCat [35]. For the regularization of the inverse problem we use two different methods: the well-known Tikhonov inversion (L-curve method), which penalizes the L2 norm of the solution, and a Gaussian expansion, which assumes that the attachment cross section is a superposition of Gaussian-shaped peaks.

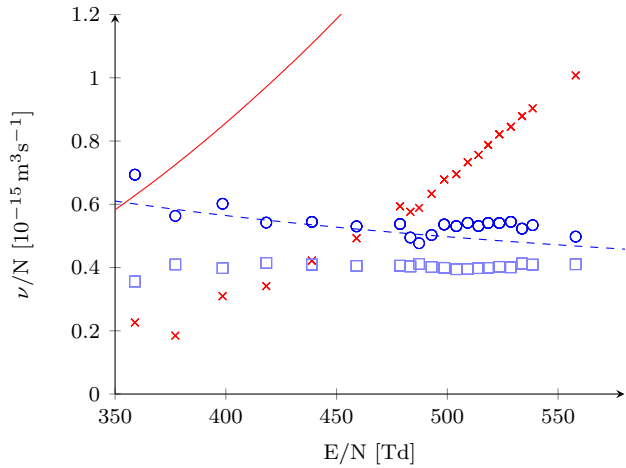
For $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, the poor signal quality and a lower than usual confidence in the mole fractions allowed only for a rough estimate, shown in figure 3. The Tikhonov inversion and Gaussian expansion agree on the peak positions of the cross section at around 0 eV, 0.5 eV and 3 eV, yet not on the width. The inverse problem is strongly underdetermined, and the attachment cross section cannot be refined further on basis of our measurements.

Ignorant of the S-wave scattering limit, the method finds higher values than physically possible around 3 eV. Compared to SF_6 , the attachment is orders of magnitudes smaller at thermal energies, but larger for electron energies above 0.2 eV.

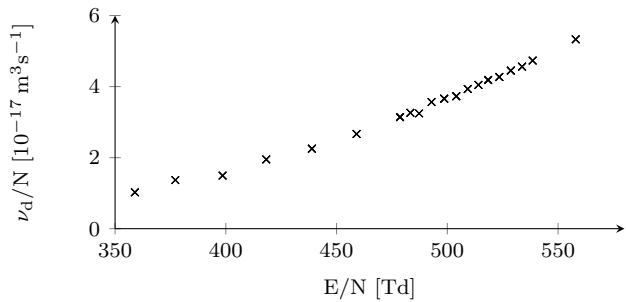
3.2. $c\text{-C}_4\text{F}_8\text{O}_2$

The avalanche in $c\text{-C}_4\text{F}_8\text{O}_2$ above 400 Td is dominated by two different negative ions, one of which (“ C^- ”) detaches at a fast rate ν_d , while the other (“ B^- ”) does not. Figure 1 shows a symbolic representation of the model on the right hand side. The rate coefficient ν_d/N , figure 4b, is independent of pressure, which suggests a collision-induced detachment and is common for ions of comparably low electron affinity. Figure 5 shows a typical measurement and fit result with the characteristic electron detachment feature around one μs .

We find a mobility of $1.2 \cdot 10^{21} \text{ m}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for both the negative stable ion B^- and positive ion. Due to its short lifetime, the mobility of the negative unstable ion C^- could not be determined, because the measured current is insensitive to this value. The electron mobility is $3.7 \cdot 10^{23} \text{ m}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ at 470 Td. The diffusion could not accurately be determined since electron detachment is the dominant cause for the spatial spread of electrons. We estimate it as $ND_L =$



(a) Ionization (red crosses) and two attachment rate coefficients of $c\text{-C}_4\text{F}_8\text{O}_2$ (dark circles: stable anion, bright squares: unstable anion); not taking the detaching ion into account yields a critical field strength of 470 Td. Compared to SF_6 (Bolsig+ simulation [24] using Biagi's database[37]), the ionization rate coefficient (red line) is lower, while the (total) attachment rate coefficient (blue dashed line) is comparable in magnitude to the attachment to the stable anion.



(b) Detachment rate coefficient of the detaching anion C^- .

Figure 4

$$(1.1 \pm 0.5) \cdot 10^{24}.$$

While electron detachment clearly lowers the insulation performance of a gas, the exact implication is not trivial, and was discussed e.g. in [38]. Although the attachment rate coefficient to the "unstable anion" is almost equal in size to that of the stable anion (figure 4a), the detachment rate coefficient is quite large, such that this ion contributes very little to the electric strength of the gas. Taking only the stable anion into account yields a critical electric field strength of 470 Td in figure 4a. Including the detaching ion would increase the value of the critical field strength by at most 20 Td.

Compared to SF_6 (Bolsig+ [24], Biagi's cross section set [42] on LXCat [35]), the ionization rate coefficient is lower by a factor of two. The total attachment rate coefficient of SF_6 , including all channels of parent ion

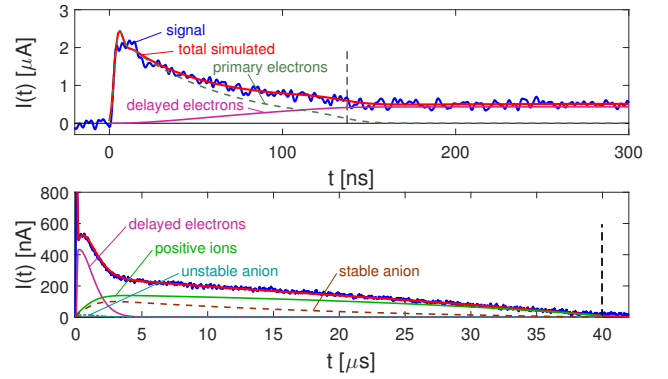


Figure 5: A Pulsed Townsend measurement and fit result in $c\text{-C}_4\text{F}_8\text{O}_2$ at 504 Td, a gap distance of 15 mm and a pressure of 310 Pa, on two different time-scales. The signal in the bottom figure is low-pass filtered. The partial contributions of electrons, "delayed electrons" (electrons that have detached off an anion), negative and positive ions is plotted color-coded. The dashed lines give the gap crossing time of electrons (upper plot) and ions. The observed peak at $1 \mu\text{s}$ is typical for detaching ions.

and dissociative attachment, is roughly equal to the attachment rate to the stable anion in $c\text{-C}_4\text{F}_8\text{O}_2$.

The evaluated attachment cross section (figure 3) does not distinguish between the two attachment rate coefficients to the two different ion species, since they cannot be separated below 70 Td. It shows a broad feature around 3 eV similar to $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, yet lower in magnitude. In contrast to $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, $c\text{-C}_4\text{F}_8\text{O}_2$ does not show attachment at thermal energies.

3.3. Synergism in mixtures with N_2 and CO_2

Disregarding their high boiling points, $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ and $c\text{-C}_4\text{F}_8\text{O}_2$ show exceptionally high critical field strength. We obtain $(E/N)_{\text{crit}}$ as 1200 Td for $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ and 470 Td for $c\text{-C}_4\text{F}_8\text{O}_2$, which is a factor of 3.5 and 1.3 higher than SF_6 . In mixtures with N_2 and CO_2 both gases show synergism (figure 6) in the sense that the mixture with low mole fraction of the fluorinated gas yields a higher $(E/N)_{\text{crit}}$ than what would be expected from a linear interpolation (see [7, 10]). However, the effect is less pronounced than for the $\text{SF}_6:\text{N}_2$ mixtures, as measured by Aschwanden [9]. The pressure of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ may have dropped by few percent when measuring in admixture with high concentration of N_2 due to adsorption to the chamber walls, such that the synergism might be slightly underestimated.

The $(E/N)_{\text{crit}}$ of the mixtures was obtained at different pressures, and from several measurements at different

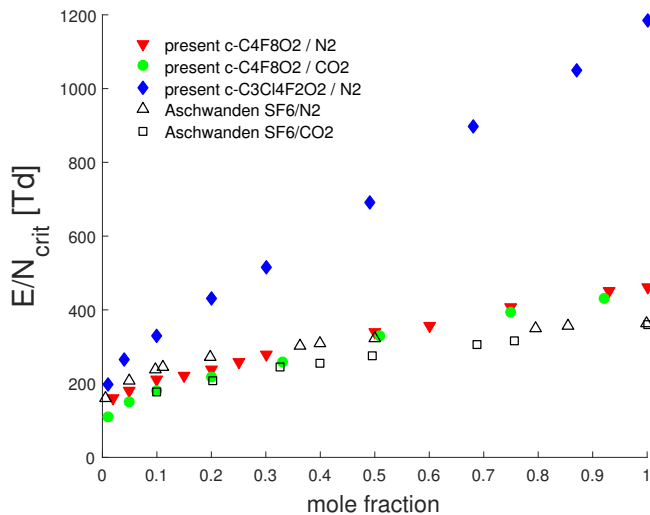


Figure 6: Synergy curve of $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ and $c\text{-C}_4\text{F}_8\text{O}_2$ in admixture with N_2 (crosses) and CO_2 (circles), i.e. the critical electric field plotted against different gas mixtures, and compared to the synergy curve of SF_6 from [9].

pressures we conclude that the $(E/N)_{\text{crit}}$ of both compounds is not pressure-dependent. Within the spread of the results, we see no evidence for a three-body attachment process in both gases. However, this might become observably only at higher pressures of the pure gases.

4. Discussion

Both measured compounds have excellent $(E/N)_{\text{crit}}$, which is a results of extremely high attachment rates as well as lower ionization rate, compared to the excellent insulation gas SF_6 . For $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, both the $(E/N)_{\text{crit}}$ and the attachment rate coefficient of $6 \cdot 10^{-15} \text{m}^3 \text{s}^{-1}$ at $(E/N)_{\text{crit}}$ present, to our knowledge, the highest ever measured values in any gas at the critical field strength, exceeding even the $\text{C}_4\text{F}_7\text{N}$ nitrile [39]. The lower ionization rate coefficient of both compounds suggest a superior electron moderation compared to SF_6 . Furthermore, the high electron attachment cross section at few eV is a highly interesting feature for insulating gases: close to breakdown strength of several hundred Td, average electron energies are several eV, which then overlaps well with the attachment cross section. The inverse method of obtaining the attachment cross section is ignorant of the physical S-wave scattering limit, and gives values that are higher and physically not possible around 3 eV. However, since the width of the resonance could not be determined as the comparison of Gaussian expansion and Tikhonov method shows, it is likely that the resonance is in fact broader and less high in

magnitude.

4.1. Comparison to $c\text{-C}_4\text{F}_8\text{O}$

In [33], yet another cyclic fluorinated ether was investigated: $c\text{-C}_4\text{F}_8\text{O}$ (CAS 773-14-8). The photocathode efficiency did not allow to measure the pure gas, but the $(E/N)_{\text{crit}}$ for a diluted mixture with 99.4% N_2 could be established as 130 Td. Contrary to the two compounds of this publication, strong three-body attachment to the parent ion was proposed to explain the dependence of $(E/N)_{\text{crit}}$ on the pressure. The attachment cross section (excluding three-body attachment) was found to be most prominent at 2 – 4 eV, similar to our findings, yet roughly two orders of magnitude lower.

For this gas, the negative ion yield was measured with an ion mass spectrometer [33, 41]. Besides a long lived negative parent ion, multiple channels of dissociative attachment were observed, mostly under formation of anions containing oxygen (with the exception of F^-).

4.2. Dissociative attachment and molecular strain

The inner strain of molecules might favor breakup upon electron impact, and effectively lower the energy threshold for dissociative attachment. This strain energy can be quite substantial, especially for fluorinated compounds: for the extreme case of $c\text{-C}_3\text{F}_6$, for which the bond-length of C-F is very small, the strain energy was estimated to 2.3 eV (54 kcal mol⁻¹) [11], which is twice the strain of the corresponding hydrocarbon cyclo-propane. Although fluorine atoms are slightly "larger" than hydrogen and therefore lead to higher strain, fluorination often stabilizes the corresponding hydrocarbon: $c\text{-C}_3\text{F}_6$ is, contrary to $c\text{-C}_3\text{H}_6$, highly inert and non-flammable. For the compounds in discussion the strain energies are unknown, yet the hydrocarbon dioxolane $c\text{-C}_3\text{H}_6\text{O}_2$ is known to be quite highly strained [3].

An increased dissociative attachment cross section, compared to non-strained molecules, might be a general feature of highly strained compounds, provided ions with high electron affinity can be formed in a dissociation process. The latter is certainly the case for the present oxygen-containing molecules: COF_2 is known to have a large electron affinity of 1.5 – 2.1 eV [21], and COF_3 even 3.6 – 4.4 eV [15, 19]. Consequently, both negative ions have rather low thresholds around 1.5 eV for dissociative electron attachment in the discharge of $c\text{-C}_4\text{F}_8\text{O}$ [41].

4.3. Review of $c\text{-C}_3\text{F}_6\text{O}_2$ and $c\text{-C}_3\text{F}_6\text{O}$

Our measurements motivate the investigation of Perfluoro-1,3-dioxolane $c\text{-C}_3\text{F}_6\text{O}_2$ (CAS 21297-65-4)

and Perfluoro-oxetane $c\text{-C}_3\text{F}_6\text{O}$ (CAS 425-82-1) for gaseous insulation applications. Both compounds have low boiling points and are presumably in a strained conformation. Judging from the results in $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$, $c\text{-C}_4\text{F}_8\text{O}_2$ and $c\text{-C}_4\text{F}_8\text{O}$, we expect good $(E/N)_{\text{crit}}$ and therefore insulation performance.

There are long-known synthesis routes with high yields for both compounds. Direct electro-fluorination of the hydrocarbon oxetane yields the perfluorinated oxetane $c\text{-C}_3\text{F}_6\text{O}$, this synthesis route was patented in 1948 [1]. For the $c\text{-C}_3\text{F}_6\text{O}_2$ multiple routes are known: reaction of $\text{CF}_2=\text{CF}_2$ with $\text{CF}_2(\text{OF})_2$ yields the desired compound and is described in [18], as well as UV irradiation of $c\text{-CF}_2\text{OCF}_2\text{CF}_2\text{OC}(\text{O})$ as disclosed in [4]. $c\text{-C}_3\text{F}_6\text{O}_2$ is furthermore a by-product in the synthesis of $c\text{-C}_4\text{F}_8\text{O}_2$ [5]. Despite this, we were unable to acquire samples of $c\text{-C}_3\text{F}_6\text{O}$ and $c\text{-C}_3\text{F}_6\text{O}_2$. $c\text{-C}_3\text{F}_6\text{O}_2$ is "inert to mineral acids and concentrated base solutions" [4], while the $c\text{-C}_3\text{F}_6\text{O}$ shows "a high degree of chemical inertness" [1]. Neither of these compounds have been tested for toxicity. The inertness suggests a rather low, if any, flammability. The $c\text{-C}_3\text{F}_6\text{O}_2$ and $c\text{-C}_3\text{F}_6\text{O}$ have boiling points of -22.1°C (given without source in [27]) and "approximately -38°C " (measured in [1]), respectively. In [16], a value of -29° is given for $c\text{-C}_3\text{F}_6\text{O}$, yet it is unclear whether this value was calculated or measured. Compared to other alternative gases in application such as the branched $\text{C}_4\text{F}_7\text{N}$ nitrile ($\approx -4^\circ\text{C}$) and $\text{C}_5\text{F}_{10}\text{O}$ ketone ($\approx 26^\circ\text{C}$) [36], they could therefore be used in much higher mole fraction in a mixture in application.

4.4. GWP estimation of $c\text{-C}_3\text{F}_6\text{O}$ and $c\text{-C}_3\text{F}_6\text{O}_2$

For a gas to have a low GWP, it should either have a low radiative forcing, or have a short lifetime in the atmosphere [29]. For the first, carbon-fluorine bond stretching vibrations are known to contribute strongly to IR adsorption of fluorinated compounds [25]. The lifetime, on the other hand, is mostly determined by chemical reactions with radicals in the upper atmosphere, or direct photolysis due to UV irradiation (disregarding several other less relevant mechanisms). Thus, for a fluorinated compound the two requirements of chemical inertness and low GWP contradict each other to a large extent.

For most gases, the determining factor is the reaction rate with OH radicals [12]. A popular empirical method for estimating this rate was presented by Atkinson et al. [12, 17], based on measured or calculated reaction rates of hydroxyl radicals with different chemical groups of the molecule. Since there is basically no reaction with the C-F bond, fully-fluorinated gases with carbon backbone, no reactive groups, and saturated bonds only are usually chemically inert and

have GWP values in the range of 5000 – 15000 [30] due to life-times of several hundred years.

The reaction rate of hydroxyl radicals with $c\text{-C}_3\text{F}_6\text{O}$ and the non-fully fluorinated compound $c\text{-C}_3\text{HF}_5\text{O}$ were measured in [14], yielding low rates and corresponding long life-times of over 330 years (lower limit) and 26 years. The authors state they assumed for $c\text{-C}_3\text{F}_6\text{O}$ that "there was a small possibility that OH might add to the ether linkage, particularly under conditions of significant ring strain", which turned out not to be the case.

Kazakov et al., who estimated life-times of fluorinated compounds for use as alternative refrigerants [29] based on hydroxyl reaction rates with Atkinson's method, point out that while the derived lifetimes agree fairly well within one order of magnitude for most gases, there is the exception of CF_3I . Due to a rather weak bond between the central carbon atom and the iodine atom, UV easily severs this bond, which makes UV irradiation the by far dominating factor for the lifetime. Not taking this channel into account leads to an overestimation of the lifetime by four orders of magnitude. A further example is the $\text{C}_6\text{F}_{12}\text{O}$ ketone (CAS 756-13-8), considered for application [34], which is destroyed exclusively by UV photolysis in the atmosphere [23], leading to a negligible GWP. Surprisingly, reaction with OH radicals was not observed, even though the Atkinson method suggests a high reactivity with the ketone group. In contrast to CF_3I and $\text{C}_6\text{F}_{12}\text{O}$, SF_5CF_3 despite its (relatively) weak S-C bond ($\approx 3.9\text{ eV}$ [25]) does not dissociate in the atmosphere via photolysis [22, 25], since it is transparent to UV light below 7 eV, while the highest (abundantly available, UV-b) photon energies are at 4.2 eV. Photodissociation is understood to require excited electronic states above the dissociation threshold [25], and SF_5CF_3 seems to lack those in between 3.9 eV and 7 eV.

For the $c\text{-C}_3\text{F}_6\text{O}_2$ and $c\text{-C}_3\text{F}_6\text{O}$ a high enough strain of these cyclic compounds could allow for easier breakup by photo irradiation, which is, in the language of photochemistry, an inverse Paterno-Büchi reaction. For the hydrocarbon oxetane $c\text{-C}_3\text{H}_6\text{O}$ this was studied in several publications:

Dissociation products are investigated under irradiation with UV photons (6.4 eV / 193 nm) in [26], and breakup into CH_2O and $\text{CH}_2=\text{CH}_2$ was found to be the main path. In an older publication [2] the activation energy for dissociation was estimated to be lower, as 2.6 eV (60 kcal mol $^{-1}$). In [13] the authors studied bond breaking for both the $c\text{-C}_3\text{H}_6\text{O}$ and 1,3-dioxolane, $c\text{-C}_3\text{H}_6\text{O}_2$, under infrared irradiation. In [20], a two-photon process was found to dissociate $c\text{-C}_4\text{H}_8\text{O}$ at photon energies of 4 eV (307 nm), which is typical UV-b energies in the atmosphere. Fitting with the find-

ings that CH_2O is the most common dissociation product [26], CF_2O is found as byproduct of the photochemical synthesis of $c\text{-C}_3\text{F}_6\text{O}_2$ as stated in [1]. CF_2O is also the main product of photo-dissociation of the C6 ketone [23].

The main dissociation path of $c\text{-C}_3\text{H}_6\text{O}$ does not require the cleavage of C-H bonds, which might be suppressed by the stronger C-F bond. The dissociation results might therefore hold for the fluorinated compounds in question.

CF_2O and $\text{CF}_2=\text{CF}_2$ are both reactive compounds, and thus have negligible GWP.

5. Conclusion

We propose the compounds Perfluoro-1,3-dioxolane $c\text{-C}_3\text{F}_6\text{O}_2$ (CAS 21297-65-4) and Perfluoro-oxetane $c\text{-C}_3\text{F}_6\text{O}$ (CAS 425-82-1) as candidates for alternative gases for electrical insulation, based on our results regarding $c\text{-C}_3\text{Cl}_4\text{F}_2\text{O}_2$ and $c\text{-C}_4\text{F}_8\text{O}_2$. Both $c\text{-C}_3\text{F}_6\text{O}_2$ and $c\text{-C}_3\text{F}_6\text{O}$ have low boiling points of -22.1°C and -38°C , making them applicable in high pressure switchgear. They are supposedly inert, which suggests low flammability and, being ethers, potentially low toxicity. While most inert fully fluorinated compounds have high global warming potential, we argue that their molecular strain could lead to easier breakup of the molecule under UV irradiation as observed for the hydrocarbon equivalent molecules, while possibly also favoring dissociative electron attachment.

The investigation of these four compounds in beam experiments with a mass spectrometer would allow a precise measurement of the dissociative attachment cross sections. At least for the two measured compounds the feature around 3 eV appears to be responsible for the high critical field strength. The UV absorption spectra of $c\text{-C}_3\text{F}_6\text{O}_2$ and $c\text{-C}_3\text{F}_6\text{O}$ in the relevant UV-b range, as well as the reaction rate of $c\text{-C}_3\text{F}_6\text{O}_2$ with hydroxyl radicals should be measured in order to estimate the GWP.

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