157 nm Pellicles for Photolithography: Mechanistic Investigation of the Deep UV Photolysis of Fluorocarbons.

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ABSTRACT

The advance of 157 nm as the next photolithographic wavelength has created a need to for transparent and radiation durable polymers for the use as pellicles. The most promising materials for the pellicles are fluorinated polymers, but the currently available fluorinated polymers undergo photodegradation and/or photodarkening upon exposure to 157 nm irradiation. To understand the mechanism of the photodegradation and photodarkening of fluorinated polymers, mechanistic studies on the photolysis of liquid model fluorocarbons such as, perfluoro butylethyl ether and perfluoro-2H-3-oxa-heptane, were performed employing UV, NMR, FTIR, GC, and GC/MS analysis. All hydrogen containing compounds showed decreased photostability compared to the fully perfluorinated compounds. Irradiation in the presence of atmospheric oxygen showed reduced photodarkening compared to deoxygenated samples. Irradiations were performed at 157 nm, 172 nm, 185 nm, and 254 nm and showed only minor wavelength dependence. Mechanisms for photodegradation of the fluorocarbons were proposed, where Rydberg excited states are involved.

Keywords: pellicles, fluorocarbon, hydrofluorocarbon, photochemistry, deep UV, VUV

1. INTRODUCTION

The semiconductor industry has used photolithography as the main tool in its march to 90 nm half-pitch. The emergence of 157 nm lithography is expected to continue the advance to dimensions less than 45 nm. The development of 157 nm lithography has offered significant challenges with materials involved in the technology. Many of the challenges with this technology come from the high energy (7.9 eV) of photons at 157 nm. For example, pellicle films that are designed to protect the photomask from the interfering particulate materials during the lithographic process, degrade rapidly under irradiation with 157 nm light. Materials used for 193 nm pellicles such as Teflon® AF or Cytop™ degrade rapidly at 157 nm.[1-3] An important challenge in 157 nm photolithography is development of pellicles that are transparent at a wavelength of 157 nm and that satisfy a number of stringent requirements, including photostability and persistence of transparency after many doses of 157 nm light.[4,5] A number of new fluoropolymers have been developed as candidate materials for soft pellicles, all of which lose transparency (photodarkening) upon irradiation at 157 nm.[1,5,6] Very little information concerning the photochemical mechanisms leading to the darkening at 157 nm is available.

One of the goals of the research reported here was to provide information that would provide insight concerning the mechanism of the photodegradation that leads to darkening of polymer pellicles during exposure to 157 nm irradiation and that would allow the design of new soft pellicle systems that would possess acceptable characteristics for 157 nm photolithography. A second goal was to invent experimental protocols and strategies for the investigation of photochemistry at 157 nm that would set standards for future investigations.

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A strategy for our initial investigations was to select a set of liquid model compounds possessing structures consistent with those present in pellicles proposed for use at 157 nm, and to investigate the wavelength dependence of the photolysis of these model compounds as neat liquids. The first phase of our report involves identifying the products produced by photolysis of the model compounds at various wavelengths of UV light (254 nm low pressure Hg lamp, 185 nm low pressure Hg lamp, 172 nm excimer lamp, 157 nm F_2 excimer laser). These experiments were designed to determine whether photolysis of small organic model fluorocarbon compounds would produce photoproducts upon UV irradiation and whether the photolysis at a variety of wavelengths produces the same primary products, as does photolysis at 157 nm. If this was the case, that is if the photochemistry of the model compounds was indeed essentially wavelength independent, exploratory studies of the products at 157 nm would be greatly facilitated since the equipment to investigate photolysis at 157 nm is very specialized and expensive, whereas, for example, photolysis at 185 nm can be achieved with commonly available and inexpensive equipment. It should be noted that although the model compounds selected for study in this report are "essentially transparent" at 157 nm, a certain small absorption at longer wavelengths would exist for all compounds because of "tailing" of the absorption spectra. Thus, the use of liquids and relatively long optical pathlengths for photolysis is expected to result in finite absorption which could initiate photochemistry.

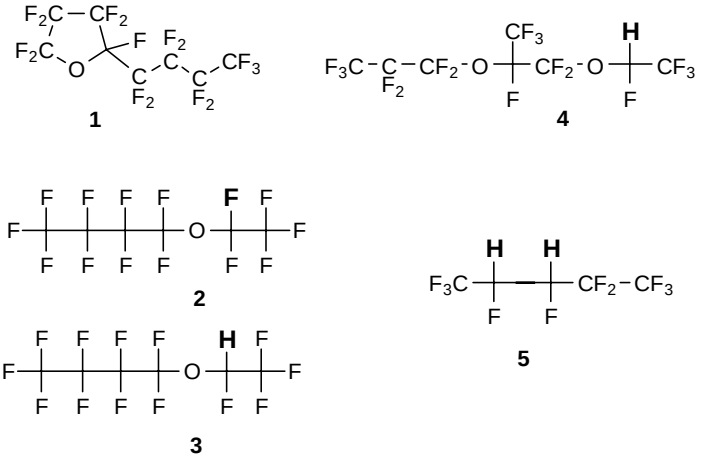


Chart 1: Structures of the model compounds.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Perfluoro-2-butyltetrahydrofuran (**1**) was purchased from Oakwood Fluorochem USA. Perfluoro butylethyl ether (**2**) and perfluoro-2H-3-oxa-heptane (**3**) were synthesized by Exfluoro Chem. Freon® E2 (**4**) and Vertrel® XF (**5**) were obtained from DuPont. All other reagents were obtained from Aldrich and used as received, unless noted otherwise.

2.2. Photolysis. Photolysis experiments at 185 nm and 254 nm were performed in a Rayonet Reactor (Southern New England Ultraviolet), which contains 16 low-pressure Hg lamps using suprasil quartz tubes (3 mm and 10 mm diameter) as sample containers. Deoxygenation of the samples was achieved by five freeze-pump-thaw cycles followed by flame sealing of the samples tube. Photolysis at 157 nm was performed using an Optex excimer laser (Lambda Physik) with a F_2 filling. The liquid samples were irradiated in a Harrick demountable liquid IR cell equipped with VUV laser grade CaF_2 windows. Photolysis at 172 nm was performed using a photoreactor equipped with a Xe-excimer lamp as described elsewhere.[8] Deoxygenation of the samples for 157 and 172 nm photolysis was achieved by nitrogen bubbling.

2.3. Actinometry. The light intensity of the Rayonet reactor was determined using a calibrated UV power meter (Model: C8026/H8025-185; Hamamadzu). The power at 185 nm at the sample tube position was approximately 0.57 mW/cm^2. Considering the setup geometry of our reactor, the photon exposure of our sample was estimated: 10 μmol of photons per mL sample in one hour (6 J/mL hour). Chemical actinometry to determine the light intensity at 172 nm and 185nm was performed as described by Braun et al. utilizing the photocleavege of water and scavenging of the

generated OH-radicals with methanol.[8] Using this chemical actinometer the light intensity at 185 nm was determined to be 7-9 μmol of photons per mL sample in one hour (5-6 J/mL hour).

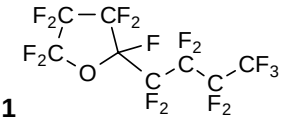
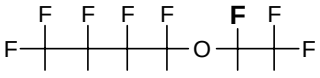
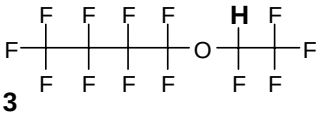
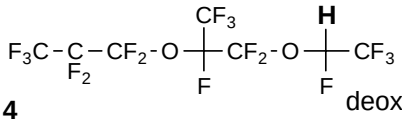
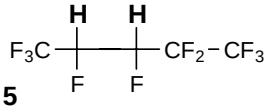
2.4. Spectroscopic Characterization. Spectroscopic characterization was performed with the neat samples. UV-Vis spectra were recorded using a Shimadzu UV-2401PC UV-Vis spectrophotometer. The VUV transmission based absorbance measurements of the samples were made using a Harrick Scientific Corp. demountable liquid cell (Model DLC-M13). The DLC-M13 was mounted in a VUV-Vase model VU-302 spectroscopic ellipsometer, which is capable of performing transmission measurements (J. A. Woolman Co., Inc., Lincoln, NE). The liquid specimen to be tested was held in a cell formed between parallel CaF_2 windows by insertion of a Teflon® ring between the windows. Teflon® rings of 6 to 2200 μm thickness were used, providing multiple optical path length through aliquots of the sample. The optical absorbance, A (cm^{-1}), per centimeter of specimen thickness is defined for purposes herein as the base 10 logarithm of the ratio of the transmission of the CaF_2 windows at the test wavelength divided by the transmission at that wavelength of the test sample (windows plus experimental specimen) divided by the thickness of the test specimen.[1] ^1H NMR and ^{19}F NMR measurements were conducted on Bruker NMR spectrometers at 400 MHz and 282.4 MHz, respectively. Sample tubes (containing $CDCl_3$ for locking) with coaxial inserts (containing the sample) were used in both ^1H NMR and ^{19}F NMR measurements. $CFCl_3$ was employed as an internal reference and calibrated as 0 ppm for the ^{19}F NMR experiments. The gas chromatography (GC) analyses were performed on a Varian 3900 gas chromatograph using a Varian Facter 4 capillary column or a WCOT fused silica column coating with CP-Sil 5 CB LOW BLEED/MS (25 m x 0.25 mm). Gas chromatography/mass spectrometry (GC/MS) was performed on a Varian Saturn 2100 GC/MS instrument using electron ionization. FTIR spectra were recorded on a NEXUS 870 FT-IR (Nicolet) using a Nicolet IR cell with CaF_2 windows.

3. RESULTS AND DISCUSSION

After an initial survey of potential candidates for study, the fluorocarbons (**1**-**5**, Chart 1) were selected as model compounds since they contain important structural units of the most promising pellicles such as Cytop™ and Teflon AF® [1] and because they could be obtained in high purity (i.e., high transparency in the UV and deep UV). The final set of selected model compounds were perfluoro-2-butyltetrahydrofuran (**1**), perfluoro butylethyl ether (**2**), perfluoro-2H-3-oxa-heptane (**3**), Freon® E2 (**4**), and Vertrel® XF (**5**), (structures of **1**- **5** are shown in Chart 1).

The selected fluorocarbons were photolyzed at 254 nm, 185 nm, 172 nm, and 157 nm in the presence and absence of oxygen. The relative photostabilities of the fluorocarbons **1**-**5** were determined by employing several sensitive analytical techniques (UV, NMR, FTIR, GC, and GC/MS). The results are summarized in Table 1 and are mostly based on GC and GC/MS analysis. The plus sign (+) indicates that significant new major signals assigned to photoproducts were observed. The minus sign (-) indicates that no significant major photoproducts were produced under our irradiation condition. +/- Sign means not clear under given condition. The results are qualitative and the term significant refers to clearly visible GC peaks with reasonable MS fragmentation patterns. From the data in Table 1 an important result is found: the model compounds that contain one or more hydrogen in their structures (*e.g.* **3**-**5**) are more rapidly undergoing photodegradation upon UV photolysis than fully perfluorinated model compounds (*e.g*. **1** and **2**).

The experimental results using UV, NMR, FTIR, GC, and GC/MS techniques will be presented in this paper in detail for **2** and **3** as representative examples. These compounds (perfluorinated ether, **2** and its analog **3**, which contains hydrogen instead of fluorine at the 2-positions) are specially designed in order to test the influence of hydrogen on the photostability of fluorocarbons in deep UV exposure. The photolysis of **2** and **3** were performed both in the presence and in the absence of molecular oxygen in order to investigate whether molecular oxygen is involved in the degradation pathway of perfluorinated or partially fluorinated organic molecules.

Model compounds		254 nm ~12 000 J	185 nm ~540 J	172 nm	157 nm ~48 J
 **1**	air	—	— **/+**		
	deoxygenated	—	—	—	— **/+**
 **2**	air	—	—		—
	deoxygenated	—	—	—	—
 **3**	air	+	+	+	+
	deoxygenated	+	+	+	+
 **4**	air	+	+	+	
	deoxygenated	+	+	+	+
 **5**	air	+	+	+	
	deoxygenated	+	+	+	+

+ photoproducts — no photoproducts — **/+** not sure

Table 1. Summary of relative photostabilities based on GC and GC/MS analysis of the selected model compounds under various irradiation wavelength under air saturated or deoxygenated condition.

In representative experiments, the neat liquid samples of **2** and **3** were placed into suprasil quartz tubes and irradiated at 185 nm for 90 hours in the absence (deoxygenated) and in the presence of oxygen (air). After photolysis, a volume decrease was observed for the air saturated samples (**2**: ~2%, **3**: 15%) and quartz tubes containing **3** were etched upon photolysis, suggestive of the formation of HF. No measurable volume decrease was observed for the deoxygenated samples, but a color change of samples from clear to light yellow after photolysis at 185 nm of **3**. However, quartz tubes from the photolysis of deoxygenated samples of **2** and **3** showed no sign of etching. Similar results were observed for photolysis at 254 nm of compounds **2** and **3**.

The UV absorption spectra of **2** and **3** upon irradiation at 185 nm are shown in Figure 1. Before irradiation (a, d) the model compounds are practically transparent at the observed wavelength range. No change in absorbance was observed for **2** after irradiation at 185 nm for 90 hours (b) under air saturated condition. Conversely, under deoxygenated condition the fully perfluorinated compound **2** showed a significant absorption increase (photodarkening) upon 185 nm photolysis (c). An even stronger absorption increase was observed for **3**, the compound with one hydrogen atom, after irradiation under deoxygenated condition (f). The absorption extended into the visible spectral region and the yellow color was observable by eye. Also under air saturated condition, **3** showed some photodarkening (e). From the UV analysis it can be concluded that the presence of atmospheric oxygen reduces photodarkening. Furthermore, the fully fluorinated compound **2** shows less photodarkening than **3**.

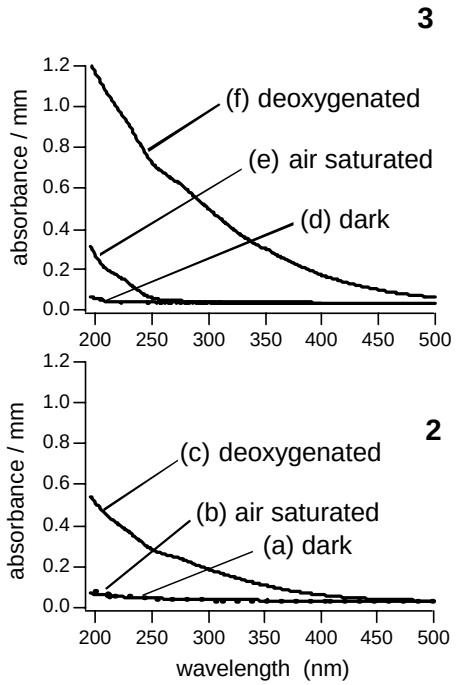


Figure 1. UV-Vis spectra of perfluoro butylethyl ether (**2**) (Spectra a-c) and perfluoro-2H-3-oxa-heptane (**3**) (Spectra d-f) upon 185 nm irradiation for 90 hours under air saturated (b, e) and deoxygenated (c, f) condition.

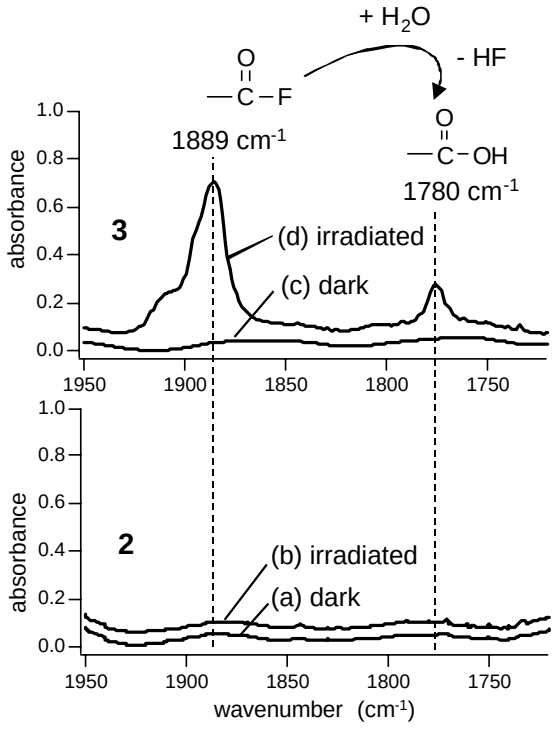


Figure 2. FTIR spectra of **2** (a, b) and **3** (c, d) before (a, c) and after 254 nm irradiation (b, d) under air saturated condition.

Compound **2** showed no evidence for significant product formation from other analyses of the samples photolyzed at the investigated irradiation wavelength (254 nm, 185 nm, 172 nm, and 157 nm), i.e., FTIR (Figure 2), NMR, and GC (Figure 4). However, peaks which were initially assigned to impurities in the samples disappeared as the result of photolysis.

A search for photoproducts of perfluoro-2H-3-oxa-heptane (**3**) produced upon UV irradiation was made using FTIR, ^{1}H NMR, ^{19}F NMR, GC, and GC/MS techniques. Two characteristic bands were observed from FTIR analysis of the photoproducts of **3** upon irradiation at both 254 nm and 185 nm under an air-saturated condition, as shown in spectrum d of Figure 2. These results provide evidence for the occurrence of a carboxylic acid and acid fluoride which have characteristic carbonyl stretching frequencies in the regions of ca 1780 cm^{-1} and 1890 cm^{-1}. The assignments are consistent with results previously reported in the literature.[9] A tentative mechanistic interpretation of the formation of these products is given in Figure 2, where the generated acid fluoride is hydrolyzed by water impurities present in the sample to form carboxylic acids. In addition, NMR analysis showed direct evidence for acyl fluoride and carboxylic acid formation after photolysis of **3** under air saturated condition. In ^{1}H NMR spectra a new broad peak at 10 ppm assigned to carboxylic acid (Figure 3e) and in ^{19}F NMR analysis a peak at +21.5 ppm assigned to acyl fluoride[10,11] were observed (Figure 3b).

GC/MS analysis of the photolyzed samples of **3** showed significant new peaks (Figure 4). MS analysis of the components and structure assignment is nontrivial, because of the similar fragmentation patterns of fluorocarbons. But two of the components were assigned with high confidence. Based on the mass fragmentation pattern and similarity with published spectra the carboxylic acids, perfluorobutanoic acid and perfluoropropionic acid, were identified as photoproducts after irradiation of air saturated samples of **3**.

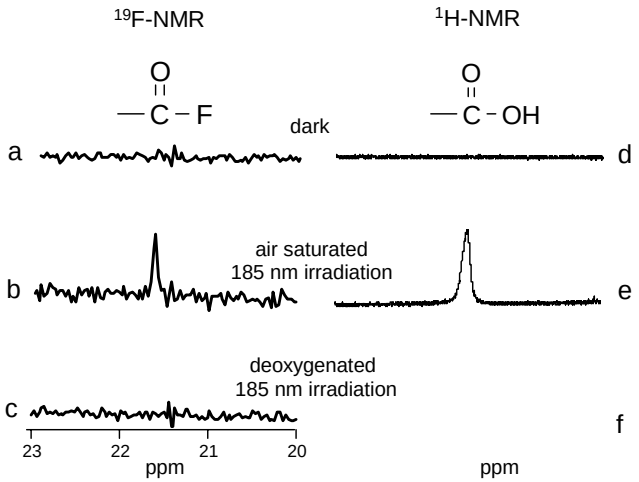


Figure 3. ^{19}F NMR (a-c) and ^{1}H NMR (d-f) **3** before (a, d) and after 185 nm irradiation under air saturated (b, e) and deoxygenated (c, f) condition.

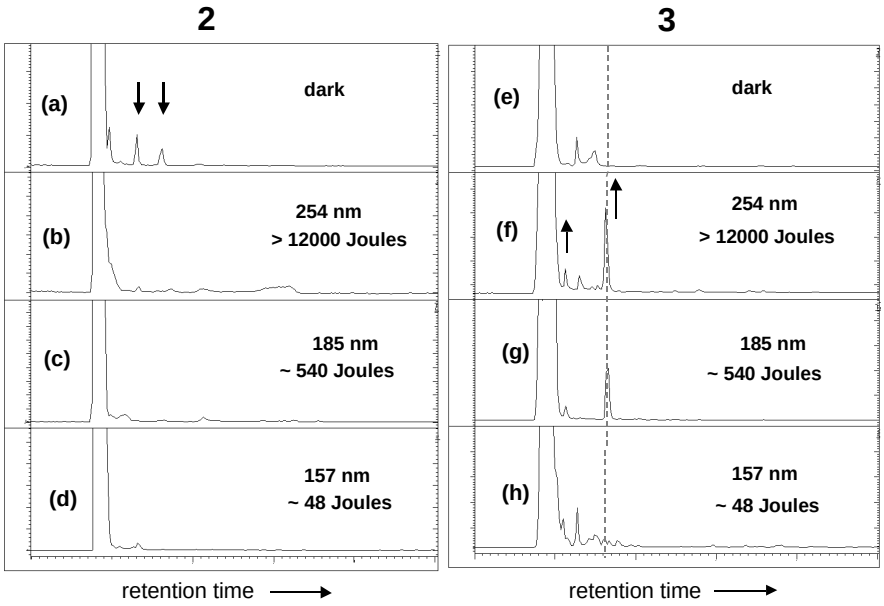
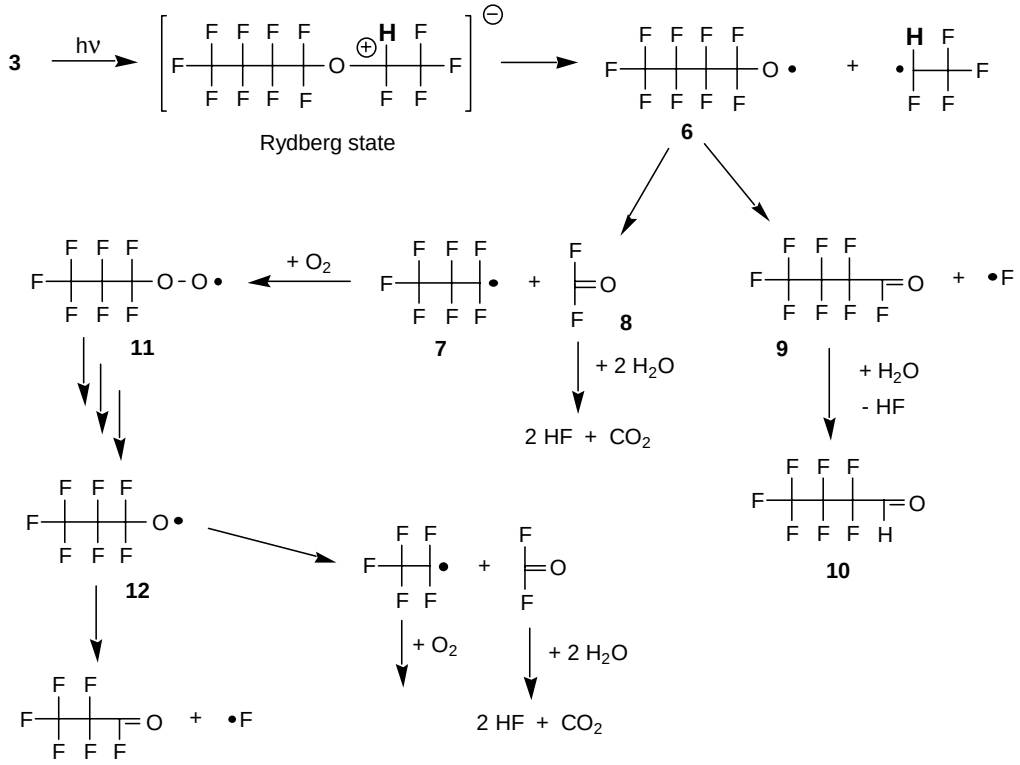


Figure 4. GC analysis of perfluoro butylethyl ether (**2**) and perfluoro-2H-3-oxa-heptane (**3**) upon irradiation at various wavelengths. The large peak at 1.6 to 1.9 min. corresponds to unreacted **2** and **3**.

From theoretical calculations,[12,13] the excited state produced by absorption of light is assumed to be a Rydberg state, which can be approximated as a state for which an electron has been removed from a sigma bonding orbital or a non-bonding orbital to a nearly ionized state. In this model the excited state is viewed as a radical cation with a closely affiliated loosely bound electron. Scheme 1 shows that the products can be readily rationalized in terms of this tentative model.[14] The weakest bond in **3** is the O-CHF bond based on theoretical calculations of similar compounds.[15-17] The resulting alkoxy radical (**6**) can undergo cleavage of the C-F or C-C bond producing fluorine radicals or carbon centered radicals (**7**) and acid fluorides (**8**, **9**). Acid fluorides were observed as photolysis products by FTIR and ^{19}F NMR (Figure 2 and 3). The acid fluorides hydrolyze in the presence of water impurities to produce carboxylic acids (**10**), which were directly observed by FTIR (Figure 2), ^{1}H NMR (Figure 3), and MS. The hydrolysis of the acid fluorides generates HF, which etched the suprasil quarts tubes. In the presence of atmospheric oxygen the

carbon centered radicals are scavanged generating peroxy radicals (**11**), which are known to generate alkoxy radicals (**12**) by several mechanisms.[18-20] The resulting alkoxy radical (**12**) can undergo fragmentations similar to **6**.



Scheme 1. Proposed photodegradation mechanism and photoproduct formation of perfluoro-2H-3-oxa-heptane (**3**).

4. CONCLUSION

To understand the mechanism of the photodegradation and photodarkening of polymer pellicles upon exposure to 157 nm irradiation, mechanistic studies on the photolysis of liquid model fluorocarbons **1**-**5** were performed. The hydrogen containing model compounds (**3**-**5**) showed decreased photostability compared to the fully perfluorinated compounds **1** and **2**. There was strong evidence for the formation of HF and acid fluoride as photoproducts after irradiation of the H-containing compounds **3**-**5** in the presence of atmospheric oxygen. Irradiation of deoxygenated samples **1**-**5** showed increased photodarkening compared to samples irradiated under air saturated condition. Therefore, it can be concluded that the presence of some atmospheric oxygen reduces photodarkening.

A preliminary mechanistic interpretation of the photochemical results (Scheme 1) can be made in terms of Rydberg excited states of the model compounds. Further theoretical calculations are required to determine the validity of this assumption.[12,21]

An important result of our investigation is recognizing the essential wavelength independence of the photolysis of the model compounds. This result establishes the possibility that exploratory experiments of the photochemistry of materials which absorb strongly in the deep UV may be examined with the much more convenient equipment that is available in the near UV. The wavelength independence of the condensed phase photochemistry of organic compounds in the visible and near UV regions of the spectrum has been known for many decades (Kasha' rule).[22] The results reported here indicate that this generalization may tentatively be expanded to the deep UV.

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