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Atmospheric Photooxidation of Fluoroacetates as a Source of Fluorocarboxylic Acids

M. B. BLANCO,[†] I. BEJAN,[‡,§] I. BARNES,[‡] P. WIESEN,[‡] AND MARIANO A. TERUEL*,[†]

Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina, Physikalische Chemie/FB-C, Bergische Universitaet Wuppertal, Wuppertal, Germany, and Faculty of Inorganic and Analytical Chemistry, "Al. I. Cuza" University of Iasi, Iasi, Romania

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A 1080 L environmental chamber with in situ FTIR spectroscopy detection was used to study the product distribution and the mechanism of the Cl-initiated photooxidation of a series of fluoroacetates. The gas-phase reactions of Cl atoms with ethyl trifluoroacetate ($CF_3C(O)OCH_2CH_3$), methyl trifluoroacetate ($CF_3C(O)OCH_3$), and methyl difluoroacetate ($CF_2HC(O)OCH_3$) were investigated at 296 ± 2 K and atmospheric pressure (~760 Torr) of synthetic air. The fate of the fluoroalkoxy radicals formed in the reaction with Cl atoms mainly occurs through (i) an H-atom abstraction by reaction with O_2, to produce the corresponding fluoroanhydride and (ii) an α-ester rearrangement via a five-membered ring intermediate to give the corresponding fluoroacetic acid. The yields of fluoroacids ($CF_2XC(O)OH$, with $X = H$, F) obtained were as follows: 78 ± 5, 23 ± 2, and 30 ± 5% for $CF_3C(O)OCH_2CH_3$, $CF_3C(O)OCH_3$, and $CF_2HC(O)OCH_3$, respectively. Yields of ≤20, ≤ 80, and ≤55% have been estimated for the anhydride formation from $CF_3C(O)OCH_2CH_3$, $CF_3C(O)OCH_3$, and $CF_2HC(O)OCH_3$, respectively. Formation of CF_2O, with yield of 13 ± 2% has been observed for the reaction of Cl with $CF_2HC(O)OCH_3$. The measured yields are rationalized in terms of mechanisms consisting of competitive reaction channels for the radicals formed in the oxidation, that is, reaction with O_2, α-ester rearrangement and a decomposition pathway. The stability of the five-membered transition state of the α-ester rearrangement is correlated with the acid yields observed for the different fluoroacetates. Atmospheric implications, especially with regard to the fluorocarboxylic acid formation, are discussed.

Introduction

In order to decrease the well-established harmful depleting effects of chlorofluorocarbons (CFCs) toward the Earth's ozone layer a significant amount of effort has gone into finding environmentally more benign alternatives to replace the CFCs. Oxygenated hydrocarbons, especially hydrofluoroethers (HFEs), have been developed as new alternatives to replace the CFCs in applications such as refrigerants, blowing, and cleaning agents (*1*). Obviously, the large-scale use of even such ozone friendly acceptable alternatives will result in releases of the compounds to the atmosphere in increasing amounts (*2, 3*). These fluorine-containing compounds, with zero ozone depletions potentials, have been shown to have shorter residence times in the troposphere than other replacements such as hydrofluorocarbons (HCFCs) or polyfluorocarbons (PFCs). The main fate of HFEs in the atmosphere is reaction with OH radicals and possibly with Cl atoms in marine environments and heavily industrialized urban areas with high levels of chloride-containing aerosol. In both cases the reactions proceed by H-atom abstraction followed by addition of O_2 to form a peroxy radical which reacts further to give eventually the corresponding hydrofluorinated esters (FESs) (*4–13*). Hence, for a complete assessment of the atmospheric chemistry and potential detrimental environmental impacts of HFEs it is also necessary to understand the atmospheric chemistry of FESs.

As for HFEs, FESs are removed from the troposphere mainly by reaction with OH radicals (*14, 15*) with also possible contributions from wet and dry deposition. Their degradation may contribute to the environmental burden of trifluoroacetic acid (or derivatives), HF and CO_2. Trifluoroacetic acid (TFA: $CF_3C(O)OH$) has been detected in surface waters (oceans, rivers, and lakes) and in fog, snow, and rainwater samples around the globe (*16–18*) and appears to be a ubiquitous persistent accumulating component of the hydrosphere. The available data suggest that trifluoroacetic acid is not a natural component of the fresh water environment (*19*). In order to evaluate the possible contribution of the photooxidation of FESs to TFA in the environment knowledge of the rate coefficients for the reactions of FESs with tropospheric oxidants such as OH radicals or Cl atoms, as well as the associated degradation pathways and product distributions, are required.

While there are many kinetic and mechanistic studies of the reactions of OH radicals and Cl atoms with a variety of hydrogenated esters, the database for haloesters is very limited. Furthermore, there is very little information available on the degradation mechanisms of fluorinated esters in the atmosphere and the resulting products (*13, 20*).

Reactions of the chlorine atom with organic compounds are now considered to be of potential importance in the marine troposphere where significant chlorine atom concentration may be present, especially in the early morning hours (*21, 22*). In general, the modes of attack of Cl and OH are fairly similar, however, Cl reacts more rapidly than OH with volatile organic compounds (VOCs) and oxygenated volatile organic compounds (OVOCs); this results in reaction times and OVOC conversions more compatible with the time constants of photoreactor experiments and the analysis precision of the detection systems applied. In this work we report the product distributions observed from the Cl-atom initiated oxidation of a series of fluoroacetates (ethyl trifluoroacetate ($CF_3C(O)OCH_2CH_3$), methyl trifluoroacetate ($CF_3C(O)OCH_3$), and methyl difluoroacetate ($CF_2HC(O)OCH_3$) performed at room temperature and atmospheric pressure in NO_x-free air:

$$Cl + CF_3C(O)OCH_2CH_3 \rightarrow products \qquad (1)$$

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* Corresponding author fax: +54 351 4334188; e-mail: mteruel@fcq.unc.edu.ar.

[†] Ciudad Universitaria.

[‡] Bergische Universitaet Wuppertal.

[§] University of Iasi.

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$$Cl + CF_3C(O)OCH_3 \rightarrow \text{products} \quad (2)$$

$$Cl + CF_2HC(O)OCH_3 \rightarrow \text{products} \quad (3)$$

The aim of the present work is to determine the fate of the fluoroalkoxy radicals formed in the Cl-initiated photodegradation of the fluoroacetates and appraise their possible contribution to the accumulation of fluorinated compounds such as trifluoroacetic acid in the environment. The study is part of ongoing work in our laboratories on haloesters and will help in the determination of the environmental suitability of such oxygenated VOCs as acceptable candidates to replace the harmful CFCs and their derivatives in industrial uses.

To our knowledge no other product studies on the fluoroesters investigated in this work have been reported in the literature.

Experimental Section

All the experiments were performed in a 1080 L quartz-glass reaction chamber at 296 ± 2 K and a total pressure of 760 ± 10 Torr synthetic air (760 Torr = 101.325 kPa). A detailed description of the reactor can be found elsewhere (*23*) and only a brief description is given here. A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40 W: 320−480 nm, λ_{max} = 360 nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of 5.91 ± 0.01 m for sensitive in situ long path absorption monitoring of reactants and products in the IR spectral range 4000−700 cm^{-1}. The White system was operated at 82 traverses, giving a total optical path length of 484.7 ± 0.8 m. The IR spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FT-IR spectrometer, equipped with a liquid nitrogen cooled mercury−cadmium−telluride (MCT) detector.

Chlorine atoms were generated by the photolysis of Cl_2 with the fluorescent lamps:

$$Cl_2 + hv \rightarrow 2Cl \quad (4)$$

Quantification of reactants and products was performed by comparison with calibrated reference spectra stored in the IR spectral database of the laboratories in Wuppertal and Córdoba.

The initial concentrations used in the experiments for the fluoroacetates and Cl_2 in ppm (1 ppm = 2.46×10^{13} molecules cm^{-3} at 298 K and 760 Torr of total pressure) were 0.34−0.78 for the fluoroacetates and around 4.6 ppm for Cl_2. The reactants were quantified at the following infrared absorption frequencies (in cm^{-1}): ethyl trifluoroacetate at 861 and 730; methyl trifluoroacetate at 840; methyl difluoroacetate at 1450; carbonyl fluoride at 774.3; difluoroacetic acid at 3578.9; trifluoroacetic acid at 3579.9 and 1206.9; carbon monoxide at 2169.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), ethyl trifluoroacetate (Aldrich, 99%), methyl trifluoroacetate (Aldrich, 99%), methyl difluoroacetate (Aldrich, 96%), and Cl_2 (Messer Griesheim, 99.8%).

Results and Discussion

To investigate the mechanism of the Cl-atom initiated oxidation of the fluoroacetates, mixtures of Cl_2/fluoroacetate/air were photolyzed with the fluorescent lamps. Reactants and products were analyzed by in situ FTIR spectroscopy whereby typically 64 interferograms were coadded per spectrum and generally 15 such spectra were collected over a period of approximately 15 min.

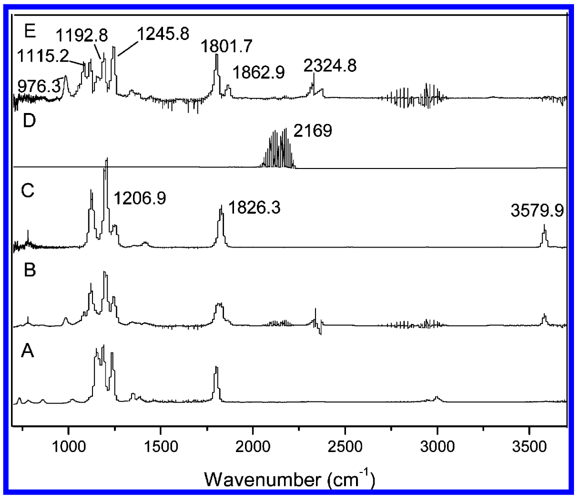

FIGURE 1. IR spectra (A) before and (B) after 335 s of irradiation of a mixture of $CF_3C(O)OCH_2CH_3$, Cl_2 and air. The consumption of $CF_3C(O)OCH_2CH_3$ was 95%. Panels C and D show reference spectra of $CF_3C(O)OH$ and CO, respectively. Panel E shows the residual spectrum obtained after subtraction of features belonging to $CF_3C(O)OH$ and CO from the spectrum in panel B.

Ethyl Trifluoroacetate (ETFA: $CF_3C(O)OCH_2CH_3$). Figure 1, panel (A), shows a spectrum of ethyl trifluoroacetate prior to irradiation and panel (B) shows the spectrum obtained after 335 s of irradiation and subtraction of the spectral features due to $CF_3C(O)OCH_2CH_3$. The consumption of $CF_3C(O)OCH_2CH_3$ in the experiments was typically around 95%. Panels (C) and (D) in Figure 1 show reference spectra of $CF_3C(O)OH$ and CO, respectively. Both $CF_3C(O)OH$ and CO were positively identified as reaction products. After subtraction of the spectral features attributable to $CF_3C(O)OH$ and CO from the spectrum in panel (B) the residual spectrum shown in Figure 1, panel (E), was obtained in which unidentified distinct bands centered at 1863, 1802, 1246, 1193, 1115, 1083, and 976 cm^{-1} are visible.

A plot of the concentration−time behavior of ETFA and the products is given in Supporting Information (SI) Figure S1.

There are also very weak absorptions at 3298, 1764, and 1448 cm^{-1} which are consistent with the formation of peroxy acetic acid ($CH_3C(O)OOH$).

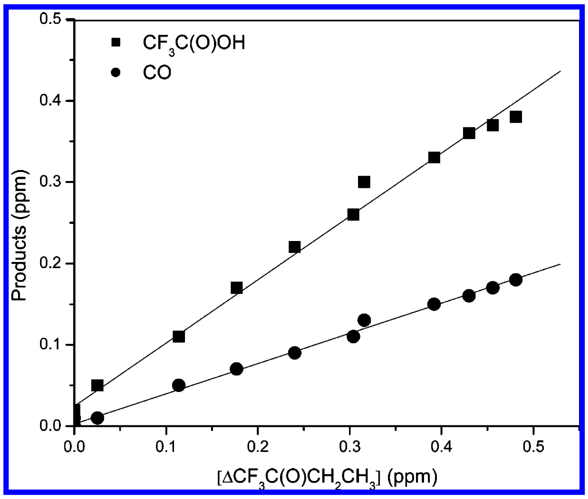

FIGURE 2. Plot of products yield obtained for the reaction of $CF_3C(O)OCH_2CH_3$ with Cl atoms.

TABLE 1. Oxidation Products from the Cl Atom Oxidation of the Fluoroacetates Studied in This Work and Their Formation Yields

fluoroacetate	products	yields (%)
$CF_3C(O)OCH_2CH_3$	CO	36 ± 3
	$CF_3C(O)OH$	78 ± 5
	$CF_3C(O)OC(O)CH_3$	$\leq 20^i$
$CF_3C(O)OCH_3$	CO	20 ± 2
	$CF_3C(O)OH$	23 ± 2
	$CF_3C(O)OCH(O)$	$\leq 80^i$
$CF_2HC(O)OCH_3$	CO	40 ± 3
	CF_2O	13 ± 2
	$CF_2HC(O)OH$	30 ± 5
	$CF_2HC(O)OCH(O)$	$\leq 55^i$

[i] Estimated upper limits for the yield based on the yields of the quantified products.

Yields of 78 ± 5 and 36 ± 3% have been obtained for the formation of $CF_3C(O)OH$ and CO respectively (Figure 2 and Table 1). The errors quoted are a combination of the 2σ statistical errors from the regression analysis together with the errors from the spectral subtraction procedure.

A simplified mechanism for the reaction of Cl with ETFA is shown in Figure 3. In this mechanism it has been assumed that the attack of the Cl atom occurs mainly at the $-CH_2-$ entity in the molecule (Figure 3, channel A). As will be shown below the observed products support this, however, kinetic studies on Cl with ethyl acetate (*24, 25*) and also a recent product study on Cl with ethyl acetate (*26*) indicate that for this compound some reaction occurs at the $-CH_3$ end of the ethyl fragment. Therefore, it cannot be completely excluded that some reaction with Cl is occurring at the $-CH_3$ group in $CF_3C(O)OCH_2CH_3$. Formation of CF_2O, that could be produced via a decomposition channel of the $CF_3C(O)OCO\cdot HCH_3$ radical was not observed. Therefore, the α-ester rearrangement shown in Figure 3, channel B represents the main reaction pathway. The high yield of $CF_3C(O)OH$ can be compared with the yield of around 53% reported recently by Orlando and Tyndall (*26*) for the reaction of Cl with $CH_3C(O)OCH_2CH_3$ and also the yields of 96 and 75% for acetic acid formation from the reaction of OH with $CH_3C(O)OCH_2CH_3$ by Tuazon et al. (*27*) and Picquet-Varrault et al. (*28*). Orlando and Tyndall (*26*) have observed the formation of acetic anhydride in the reaction of Cl with ethyl acetate with a yield of 26% which supports the tentative identification of the formation of $CF_3C(O)OC(O)CH_3$ from Cl with ETFA reported here.

The coproduct of $CF_3C(O)OH$, the $CH_3C(O)$ radical, will add O_2 to form the $CH_3C(O)OO$ peroxy radical. This radical can react with HO_2 to form peroxy acetic acid ($CH_3C(O)OOH$), evidence for which has been observed in the residual product spectrum, based on a comparison with a reference spectrum of the compound, or react with other peroxy radicals to form CO_2 and CH_3 radicals. Although CO_2 cannot be quantitatively determined in the system because of high background levels there were indications that its concentration was increasing during the course of the reaction. The CH_3 radical will be oxidized to formaldehyde (HCHO). Formaldehyde could not be detected in the reaction system; however, its reaction with Cl atoms is very fast and will be responsible for the CO formation observed in the experiments.

As stated above attack of Cl at the terminal $-CH_3$ group in ETFA cannot be completely excluded, if occurring, it could result in the formation of products such as $CF_3C(O)OCH_2CHO$ (trifluoroacetoxyacetaldehyde) and $CF_3C(O)OCHO$ (formic trifluoroacetic anhydride). Picquet-Varrault et al. (*28*) have reported the formation of acetoxyacetaldehyde ($CH_3C(O)OCH_2CHO$) in the reaction of OH with ethyl acetate and Orlando and Tyndall (*26*) in their study of Cl with ethyl acetate report that ≤25% could be occurring by attack at the ethyl CH_3 group. However, the high yield of $CF_3C(O)OH$ determined in this study for Cl with ETFA and positive indications for the formation of the anhydride $CF_3C(O)OC(O)CH_3$ suggest that attack of Cl at the $-CH_3$ group in ETFA will not be so important.

The two bands in the carbonyl region at 1863 and 1802 cm^{-1} as well as the absorption bands in the fingerprint region resemble very strongly those of an anhydride which in this case as shown in Figure 3, channel C will be trifluoroacetic acetic anhydride ($CF_3C(O)OC(O)CH_3$). Unfortunately, this anhydride is not commercially available for comparative and quantification purposes, however, the wavenumbers of the absorptions fall between those of the corresponding absorptions for $CH_3C(O)OC(O)CH_3$ and $CF_3C(O)OC(O)CF_3$ which is what one would expect for the mixed anhydride. The bands at 1863 and 1802 cm^{-1} are, therefore, tentatively assigned to the symmetric and antisymmetric vibrations of the carbonyl groups with the symmetric vibrations being much weaker as expected for this type of anhydride.

Methyl Trifluoroacetate (MTFA: $CF_3C(O)OCH_3$). $CF_3C(O)OH$ and CO were positively identified as products of the reaction of Cl atoms with methyl trifluoroacetate (SI Figure S2). Concentration−time profiles $CF_3C(O)OCH_3$ and the products show that both $CF_3C(O)OH$ and CO are primary reaction products (see SI Figure S3). Plots of product formation versus loss of $CF_3C(O)OCH_3$ are linear (SI Figure S4) and least-squares analyses of the slopes of the plots gives yields of 23 ± 2% and 20 ± 2% for $CF_3C(O)OH$ and CO, respectively (Table 1).

A simplified mechanism for the reaction of Cl atoms with $CF_3C(O)OCH_3$ is shown in SI Figure S5. The reaction of chlorine atoms with $CF_3C(O)OCH_3$ is believed to proceed wholly via an H-atom abstraction from the $-CH_3$ group to form $CF_3C(O)OCH_2$ radicals (SI Figure S5, channel A). These radicals are expected to add O_2 to give $CF_3C(O)OCH_2OO$ peroxy radicals. In the NO-free system employed in the present study it is expected that the self-reaction of the peroxy radicals will produce to a large extent $CF_3C(O)OCH_2O$ alkoxy radicals. However, a channel producing the molecular products formic trifluoroacetic anhydride ($CF_3C(O)OC(O)H$) and hydroxymethyl trifluoroacetate ($CF_3C(O)OCH_2OH$) is also possible (*29*):

$$2\ CF_3C(O)OCH_2OO \rightarrow CF_3C(O)OC(O)H + CF_3C(O)OCH_2OH + O_2$$

In addition, reaction with HO_2 could produce a hydroperoxide:

$$CF_3C(O)OCH_2OO + H_2O \rightarrow CF_3C(O)OCH_2OOH + O_2$$

As outlined in the mechanism in SI Figure S5 the alkoxy radicals produced by the self-reaction are expected to react with O_2 to form the anhydride $CF_3C(O)OC(O)H$ (SI Figure S5C) and also undergo a so-called α-ester rearrangement via a 5-membered ring (*27*) to form trifluoroacetic acid ($CF_3C(O)OH$) and HCO radicals which will react further with O_2 to give CO and HO_2 radicals (Figure S5, channel B). Decomposition via a O−C bond cleavage (not shown in SI Figure S5) is a third possibility:

$$CF_3C(O)OCH_2O \rightarrow CF_3C(O)O + HCHO$$

The $CF_3C(O)O$ radicals formed in this reaction would be expected to decompose to form CO_2 and CF_3 radicals. Further oxidation of the CF_3 radicals in the system would be expected to eventually produce carbonyl fluoride (CF_2O) (*30*). However, no evidence could be found in the product spectra for the

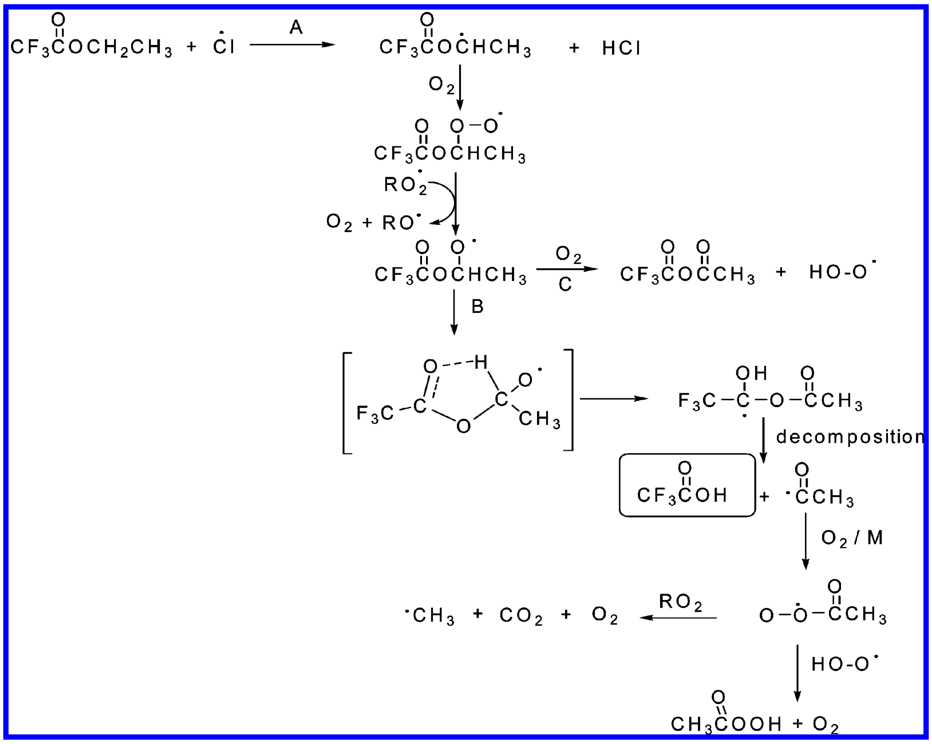

FIGURE 3. Simplified mechanism for the Cl-atom initiated oxidation of $CF_3C(O)OCH_2CH_3$ in NO_x-free air.

formation of CF_2O suggesting that this channel is negligible. Christensen et al. (*31*) have shown that the analogous channel in the Cl-atom initiated oxidation of $CH_3C(O)OCH_3$ is also negligible.

The mechanism predicts the formation of $CF_3C(O)OH$ and CO via the α-ester rearrangement. Formation of $CF_3C(O)OH$ and CO in equal yield have been observed experimentally, which is in agreement with the mechanism and supports that this channel constitutes around 20% of the overall mechanism. This is comparable to the acetic acid yield of ~30% obtained by Christensen et al. (*31*) in their study of Cl with methyl acetate under similar conditions. The other products that can be formed are $CF_3C(O)OC(O)H$, $CF_3C(O)OCH_2OH$ and $CF_3C(O)OCH_2OOH$, whereby it is expected that formation of $CF_3C(O)OC(O)H$ will dominate. The lack of OH absorptions in the 3500 cm^{-1} apart from that assigned to TFA suggests that formation of both $CF_3C(O)OCH_2OH$ and $CF_3C(O)OCH_2OOH$ is negligible.

Unfortunately, $CF_3C(O)OC(O)H$ (formic trifluoroacetic anhydride) is not commercially available for comparative purposes in order to verify its formation. However, linear anhydrides are known to give rise to two carbonyl bands, a symmetrical and antisymmetrical stretching vibration (*32*). For example, in the gas phase the following anhydrides show carbonyl bands centered at the indicated wavenumbers (cm^{-1}): formic anhydride ($HC(O)OC(O)H$) 1822 (sym) and 1769 (antisym); formic acetic anhydride ($CH_3C(O)OC(O)H$) 1808 (sym) and 1792 (antisym); acetic anhydride ($CH_3C(O)OC(O)CH_3$) 1837 (sym) and 1778 (antisym); trifluoroacetic anhydride ($CF_3C(O)OC(O)CF_3$) 1881 (sym) and 1817 (antisym). Interesting is the small split ($\Delta = 16$ cm^{-1}) between the carbonyl absorptions in formic acetic anhydride and the much larger split of 55 cm^{-1} or more for the other anhydrides. Based on a combination of ab initio calculations and gas phase electron diffraction and infrared spectroscopy studies of formic acetic anhydride, Wu et al. (*33*) have concluded that similar small splittings should occur in anhydrides of structure RCOOCHO (R = alkyl).

The carbonyl absorption region in the residual product spectrum (Figure S2, panel E) shows strong carbonyl absorption centered at 1808 cm^{-1} with a weak shoulder absorption. A calculated IR spectrum of $CF_3C(O)OC(O)H$ using Gaussian 03 predicts a strong asymmetric CO vibration and a much weaker symmetrical CO vibration the symmetric vibration being at the higher wavenumber.

Based on the calculated IR spectrum and comparisons with the IR spectra of formic anhydride and trifluoroacetic anhydride and the absorptions at 1246 and 1197 cm^{-1} appear to conform with vibrations of the CF_3-group and those at 1119 and 980 cm^{-1} with vibrations of the $CF_3C(O)-O$ and $HC(O)-O$ groups, respectively. Consequently, based on the proposed mechanism and the IR evidence we assign the residual spectrum in SI Figure S2E to the formation of $CF_3C(O)OC(O)H$ with a yield of ≤80%.

Methyl Difluoroacetate (MDFA: $CF_2HC(O)OCH_3$). For this reaction, difluoroacetic acid (DFA: $CF_2HC(O)OH$), carbonyl fluoride (CF_2O) and CO have been positively identified as products (SI Figure S6). After subtraction of identified products major unidentified bands centered at 1805, 1148, 1049, and 940 cm^{-1} remained in the residual product spectrum (Figure S6, panel F). The band at 1805 cm^{-1} has a broad shoulder on the higher wavenumber side. A plot of the concentration−time behavior of MDFA and the products is given in SI Figure S7. Plots of product formation versus loss of $CF_2HC(O)OCH_3$ are linear (SI Figure S8) and least-squares analyses of the slopes of the plots gives yields of 30 ± 5, 13 ± 2, and $40 \pm 3\%$ for $CF_2HC(O)OH$, CF_2O and CO, respectively (Table 1).

A simplified reaction mechanism for the reaction of Cl with MDFA is shown in Figure 4. DFA will be formed via H-atom abstraction from the ester CH_3 group (Figure 4A), followed by addition of O_2 and further reaction to form an alkoxy radical which undergoes an α-ester rearrangement to give the acid and HCO radicals (Figure 4B). The further reaction of HCO with O_2 will give CO in equal yield. The yield of DFA obtained is similar but a little higher than the yield of TFA from the reaction of Cl with methyl trifluoroacetate.

Since CF_2O formation was not observed in the reactions of Cl with methyl and ethyl trifluoroacetate, in order to explain its formation in the reaction of Cl with methyl difluoroacetate, abstraction of the H-atom in the CF_2H-group is suggested

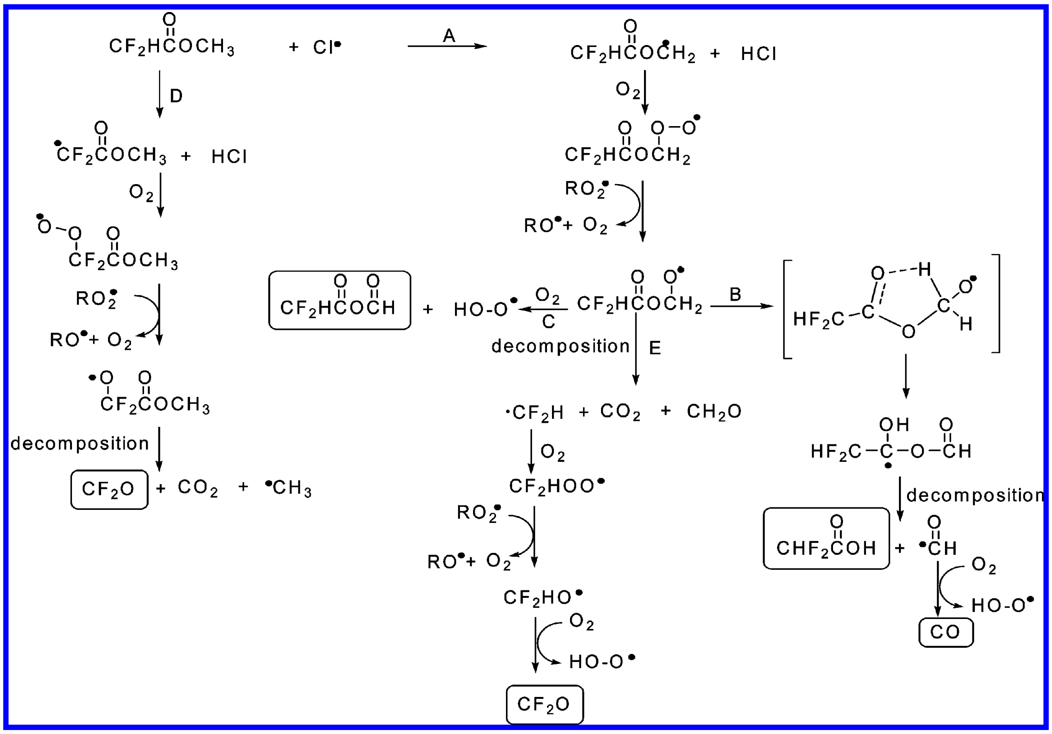

FIGURE 4. Simplified mechanism for the Cl-atom initiated oxidation of $CF_2HC(O)OCH_3$ in NO_x-free air.

followed by a series of reactions which release CF_2O and CH_3 radicals (Figure 4, channel D). The CH_3 radicals will form HCHO which will quickly oxidize to give CO. The measured total yield of CO (40%) is equal of the yield of DFA (30%) plus the yield of CF_2O (13%), which is in line with the mechanism, however, decomposition of the $CF_2HC(O)OCH_2O$ radical, formed from the H-atom abstraction at the CH_3 group, to give $CF_2HC(O)O$ and HCHO would probably also eventually give the same result (Figure 4, channel E). Therefore, it is not possible to say with certainty by which route CF_2O is being formed.

The only other primary product that can be formed in the system is formic difluoroacetic anhydride ($CF_2HC(O)OC(O)H$) (Figure 4, channel C), therefore, the remaining absorption bands are assigned to this compound. Unfortunately, this anhydride is not available commercially for identification purposes, however, its fully hydrogenated analogue, $CH_3C(O)OC(O)H$, has been detected previously in the reaction of Cl with $CH_3C(O)OCH_3$ (*31*). Based on the measured yields of DFA and CF_2O we assign an upper limit to the yield of the anhydride $CF_2HC(O)OC(O)H$ of ≤55%.

α-Ester Rearrangement vs O_2 Reaction. The observed product distributions for the reactions of Cl atoms with the different fluoroacetates can be rationalized on the basis of the relative importance of the α-ester rearrangement channel (*27*) over the other fates of the fluoroalkoxy radicals formed, that is, reaction with O_2 and decomposition. If the five-membered ring of the transition state decreases the activation barrier for the H-atom rearrangement to form the acid then this reaction pathway will be favored over the O_2 reaction and higher acid yields will be obtained. For the fluoroacetates investigated here $CF_3C(O)OCH_3$, $CF_2HC(O)OCH_3$, and $CF_3C(O)OCH_2CH_3$ the acid yields from the α-ester rearrangement are of 23, 30, and 78%, respectively. The acid yield trend is

$$CF_3C(O)OCH_3 \approx CF_2HC(O)OCH_3 < CF_3C(O)OCH_2CH_3$$

This trend can be explained by the identity of the different substituents connected to the carbon containing the hydrogen atom involved in the rearrangement. Substituents that donate electron density, by a positive inductive effect, to the carbon such as $-CH_3$ will produce a weaker C−H bond and thus facilitate the rearrangement. On the contrary, substituents that withdraw electron density such as $-CF_3$ will strengthen the C−H bond which will increase the activation energy for the rearrangement and result in a lower yield of acid. These effects are clearly evident in the measured acid yields for the fluoroesters. The acid yields for the esters $CF_3C(O)OCH_3$ and $CF_2HC(O)OCH_3$ are similar and much lower than that from $CF_3C(O)OCH_2CH_3$ since electron donation to the C−H bond involved in the rearrangement is much weaker. The 18% yield of TFA reported by Stein et al. (*20*) for the reaction of Cl with $CF_3C(O)OCH_2CF_3$ in 760 Torr air is also in line with this reasoning. The results also show that the nature of the group on the acyl side of the ester has apparently very little influence on the fraction of the reaction proceeding via α-ester rearrangement since the yields of acid obtained for $CF_3C(O)OCH_3$ and $CF_2HC(O)OCH_3$ in this study are very similar to the yield of 30% reported by Christensen et al. (*31*) for the Cl + $CH_3C(O)OCH_3$ reaction.

Atmospheric Implications. As pointed out previously (*15*) the atmospheric lifetime of the fluoroacetates studied here is determined by OH-radical initiated oxidation, although in the early morning hours in marine environments Cl-atom initiated reactions could compete with the OH reaction. The fluoroacetates survive long enough to become well dispersed from the source origin with regional scale transport being likely; urban emissions of these compounds are, therefore, unlikely to contribute to local ozone formation. Product studies on esters and fluorinated esters have shown that the oxidation of FESs leads mainly to the formation of fluorinated acetic acid and the corresponding anhydrides as well as CF_2O and its hydrolysis products, CO_2 and HF, which will be removed mainly by heterogeneous processes. In particular, acids and anhydrides, with lower molecular weight, are highly soluble compounds and may be rapidly incorporated into cloud droplets, contributing to the acidity of precipitation.

Further experiments, to study the product distribution of the fluoroacetates reactions over the range of temperatures, NO_x and pressures of oxygen typically prevailing in the troposphere would be desirable to obtain a better picture of the atmospheric implications associated with the widespread use of fluoroethers on air quality and their contribution to trifluoroacetic acid formation and acid precipitation in general. Such data would allow a more realistic representation of the tropospheric chemistry of fluorinated esters in the various types of CT-models which are used for designing environmental abatement strategies and making atmospheric policy decisions.

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Supporting Information Available

Concentration−time profile for the reaction of Cl atoms with ETFA (Figure S1), product identification plots, concentration−time profiles, yield plots and mechanism proposed for the reactions of Cl atoms with MTFA (Figures S2−S5, respectively); products identification plots, concentration−time profiles and yield plots for the reactions of Cl atoms with MDFA (Figures S6− S8, respectively) and concentration calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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