Research Article

Journal of Physical Organic Chemistry

Received: 31 December 2009, Revised: 12 March 2010, Accepted: 22 April 2010,

(wileyonlinelibrary.com) DOI 10.1002/poc.1741

Product distribution in the Cl-initiated photooxidation of $CF_3C(O)OCH_2CF_3$[†]

M. B. Blanco[a], I. Barnes[b] and Mariano A. Teruel[a]*

The product distribution and the mechanism of the reaction of Cl atoms with 2,2,2-trifluoroethyl 2,2,2-trifluoroacetate (TFETFA; $CF_3C(O)OCH_2CF_3$) were investigated using a 1080 L environmental chamber with *in situ* Fourier transform infrared (FTIR) spectroscopy detection. The experiments were performed at (296 ± 2) K and atmospheric pressure (760 ± 10) Torr of synthetic air free of NO_x. A yield of (45 ± 3)% was obtained for the $CF_3C(O)OC(O)CF_3$ formation. CF_2O and CO were produced with estimated yields of 35 and 28%, respectively. No trifluoroacetic acid (TFA; $CF_3C(O)OH$) was observed. The yields determined are rationalized in terms of the competitive reaction channels for the fluoroalcoxy radicals formed in the H-abstraction process: (a) reaction with O_2, (b) C—C, C—O, C—H decomposition, and (c) a possible α-ester rearrangement pathway. The negligible importance of the α-ester channel, to produce TFA, was explained by the reduction of the stability of the five-membered transition state of the α-ester rearrangement. Atmospheric implications, particularly regarding the fluorocarboxylic acid formation, are discussed. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper

Keywords: chlorine atoms; fluoroacetate; gas-phase mechanisms; trifluoroacetic acid; trifluoroacetic anhydride

INTRODUCTION

Since the large amount of oxygenated hydrocarbons, especially haloethers, released to the atmosphere have increased in the last few years, it is necessary to perform kinetic and product studies of these compounds and their oxidation products in the troposphere in order to assess the impact of the degradation processes on the air quality, global warming, and the stratospheric ozone layer. Hydrofluoroethers (HFEs) have been developed as new alternatives to replace chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) in applications such as refrigerants, blowing and cleaning agents, and they are also used as fuels additives, solvents, and medical products.[1] HFEs replace CFCs, HCFCs, and HFCs due to the similarity in their physical and chemical properties, relatively low warming potentials, and zero ozone depletion potentials in the Earth's stratosphere. The main sink of HFEs in the atmosphere is the reaction with OH radicals and possibly with Cl atoms in marine environments and also heavily industrialized urban areas with high levels of chloride-containing aerosol. In both cases, the reactions proceed by H-atom abstraction followed by the addition of O_2 to form a peroxy radical which reacts further to eventually give the corresponding hydrofluorinated esters (FESs).[2–11] Consequently, knowledge of the rate coefficients for the reactions with tropospheric oxidants like OH radicals and Cl atoms and the degradation pathways is required to estimate the persistence, fate, and harmful effects of fluoroesters in the atmosphere.

FESs are removed from the troposphere mainly by reaction with OH radicals[12,13] or chlorine atoms in the early morning of the marine troposphere,[14,15] also with possible contributions from wet and dry depositions. The degradation of FES may contribute to the environmental burden of trifluoroacetic acid, HF, and CO_2. Trifluoroacetic acid (TFA: $CF_3C(O)OH$) has been detected in surface waters (oceans, rivers, and lakes) and in the 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 TFA 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, kinetic and product data for the reactions of FESs with tropospheric oxidants, as well as the associated degradation pathways, 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 virtually no information available on the degradation mechanisms of fluorinated esters in the atmosphere and the resulting products.[11,20]

Kinetic and product information of these atmospheric relevant reactions is necessary to be obtained at different temperatures and NO_x concentrations to model polluted (high NO_x levels) as well as remote and non-polluted areas (free of NO_x).

---

* *Correspondence to: M. A. Teruel, Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba 5000, Argentina.*
E-mail: mteruel@fcq.unc.edu.ar

[a] *M. B. Blanco, M. A. Teruel*
Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba 5000, Argentina

[b] *I. Barnes*
Physikalische Chemie/FBC, Bergische Universitaet Wuppertal, Gauss Strasse 20, Wuppertal 42119, Germany

[†] *This article is published in Journal of Physical Organic Chemistry as a special issue on Tenth Latin American Conference on Physical Organic Chemistry, edited by Faruk Nome, Dept de Quimica, Universidade Federal de Santa Catarina, Campus Universitario – Trindade 88040-900, Florianopolis-SC, Brazil.*

In this work, we report on the product distributions observed from the Cl-atom initiated oxidation of **2**,**2**,**2**-trifluoroethyl **2**,**2**,**2**-trifluoroacetate ($CF_3C(O)OCH_2CF_3$, TFETFA) performed at room temperature and atmospheric pressure in NO_x-free air:

$$\mathrm{Cl} + \mathrm{CF_3C(O)OCH_2CF_3} \rightarrow \text{Products} \qquad (1)$$

The only previous product study of the title reaction was carried out by Stein *et al.*[20] by using the Fourier transform infrared (FTIR) technique. They reported the formation of TFA and perfluoroacetic anhydride as major products.

The aim of the present work is to determine the fate of the fluoroalkoxy radical formed in the Cl-initiated photodegradation of the fluoroacetate studied, and appraise its possible contribution to the accumulation in the environment of fluorinated compounds such as TFA. The study forms part of ongoing work in our laboratories on haloesters; it provides insights into the determination of the environmental suitability of such oxygenated volatile organic compounds (VOCs) as acceptable candidates to replace the harmful CFCs and their derivatives in industrial uses.

EXPERIMENTAL

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. A detailed description of the reactor can be found elsewhere;[21] 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 a homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40 W: 320–480 nm, $\lambda_{max} = 360$ nm), spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation in the light intensity, and also in 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 of 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 FTIR spectrometer, equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector.

Chlorine atoms were generated by the 360 nm photolysis of Cl_2 with the fluorescent lamps:

$$\mathrm{Cl_2} + h\nu \rightarrow 2\mathrm{Cl} \qquad (2)$$

The quantification of reactants and products was performed by comparison with calibrated reference spectra stored in the IR spectral database of the laboratories in Wuppertal, Germany and Córdoba, Argentina.

The initial concentrations used in the experiments for the fluoroacetates and Cl_2 in ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) were 0.34–0.78 for TFETFA and around 4.6 ppm for Cl_2. The reactants and products were quantified at the following infrared absorption frequencies (in cm^{-1}): TFETFA at 1426 and 739; carbonyl fluoride at 774.3; carbon monoxide at 2169; and trifluoroacetic anhydride at 1054.

MATERIALS

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%), TFETFA (Aldrich, 99%), and Cl_2 (Messer Griesheim, ≥99.8%).

RESULTS AND DISCUSSION

To investigate the mechanism of the Cl-atom initiated oxidation of $CF_3C(O)OCH_2CF_3$, mixtures of Cl_2/TFETFA/air were photolyzed with the fluorescent lamps. The reactant and products were analyzed by *in situ* FTIR spectroscopy whereby typically 64 interferograms were co-added per spectrum and 15 such spectra were collected over 1 min.

Figure 1, panel (A), shows a spectrum of TFETFA prior to irradiation and panel (B) shows the spectrum obtained after 1827 s of irradiation and subtraction of the spectral features due to $CF_3C(O)OCH_2CF_3$. The consumption of $CF_3C(O)OCH_2CF_3$ in the experiments was typically around 5%. Panels (C), (D), and (E) in Fig. 1 show reference spectra of $CF_3C(O)OC(O)CF_3$, CF_2O, and CO, respectively. These products were positively identified as reaction products and were only observed upon the irradiation of the reaction mixture; there was no evidence for their formation in the dark due to wall reactions of TFETFA. No evidence could be found for the formation of TFA. Moreover, in the absence of Cl_2, photolysis of the TFETFA in air did not show any decrease in the reactant concentrations over the time span of the experiments.

Yield of (45 ± 3)% has been obtained for the formation of $CF_3C(O)OC(O)CF_3$. The corresponding yields for CF_2O and CO were estimated to 35 and 28%, respectively; the products are thought to be primary, however, because of the low and slow conversion of TFETFA it is difficult to be absolutely certain. The error quoted is a combination of the 2σ statistical errors from the regression analysis together with the errors from the spectral subtraction procedure.

The results can be compared with the Cl + TFETFA reported by Stein *et al.*[20] in which they studied the UV irradiation of TFETFA/

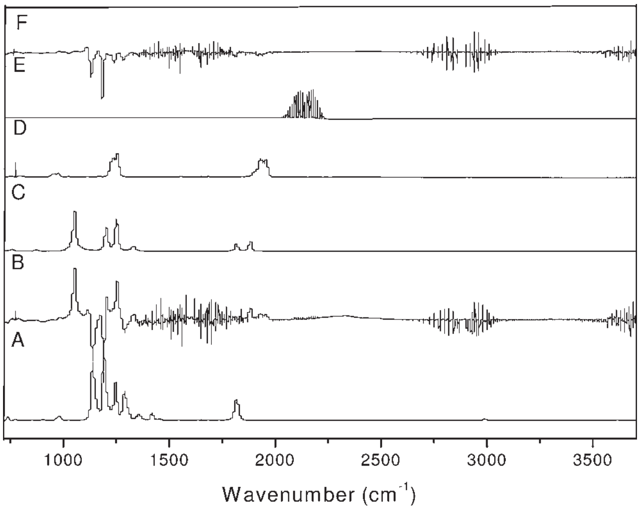


Figure 1. IR spectra before (A) and after (B) 1827 s of irradiation of a mixture of $CF_3C(O)OCH_2CF_3$, Cl_2, and air. The consumption of $CF_3C(O)OCH_2CF_3$ was 5%. Panels C, D, and E show the reference spectra of $CF_3C(O)OC(O)CF_3$, CF_2O, and CO, respectively. Panel F shows the residual spectrum after subtraction of features belonging to $CF_3C(O)OC(O)CF_3$, CF_2O, and CO from the spectrum in panel B

Table 1. Oxidation products and yields from the Cl atom oxidation of the fluoroacetate studied in this work and comparison with reported data from Ref. [20]

Fluoroacetate	Products	Yields (%)[a]	Yields (%)[b]
$CF_3C(O)OCH_2CF_3$	CO	28	—
	CF_2O	35	—
	$CF_3C(O)OH$	Not observed	18
	$CF_3C(O)OC(O)CF_3$	45 ± 3	65
	Unidentified products	—	17

[a] This work.
[b] From ref. [20].

$Cl_2/O_2/N_2$ mixtures in a 140 L Pyrex reactor using FTIR for the product analysis. For atmospheric conditions, they found the formation of $CF_3C(O)OH$ and $CF_3C(O)OC(O)CF_3$ from reactions of the $CF_3C(O)OCH(O\cdot)CF_3$ radical with yields of 18 and 65%, respectively. Table 1 shows, for comparative purposes, the product yields obtained in this work and those previously reported by Stein *et al.*[20] They observe residual spectral features attributable to CF_2O, CF_3OH, $CF_3O_2CF_3$, and CO_2; however, the products are not quantified and no mention is made of the observation of formation of CO. The yield of 45% obtained for the anhydride in this work is lower than that reported by Stein *et al.*[20] However, considering the low reactant conversions of TFETFA, the agreement is reasonable. Yet, even with the low reactant conversion of the present study, evidence for the formation of TFA should have been found in the residual spectrum with a TFA reaction yield of 18%. We have presently no explanation for the absence of TFA formation. The main difference between the study of Stein *et al.*[20] and that reported here is the high concentration of molecular Cl_2 used in their experiments 0.1–2 Torr. The high Cl_2 concentrations may be possibly influencing the intermediate RO_2 and RO chemistry in the system and thus the product yields obtained.

A simplified reaction mechanism for the reaction of Cl with TFETFA is shown in Fig. 2. Attack of Cl at the —CH_2— group will produce the alkoxy radical $CF_3C(O)OCH(O\cdot)CF_3$. Positive identification of trifluoroacetic anhydride shows that reaction with molecular oxygen is a major reaction pathway. In contrast to the reactions of Cl with other acetates[22] under the conditions of the present study, the α-ester rearrangement pathway[23] does not appear to be important in the reaction of Cl with TFETFA.

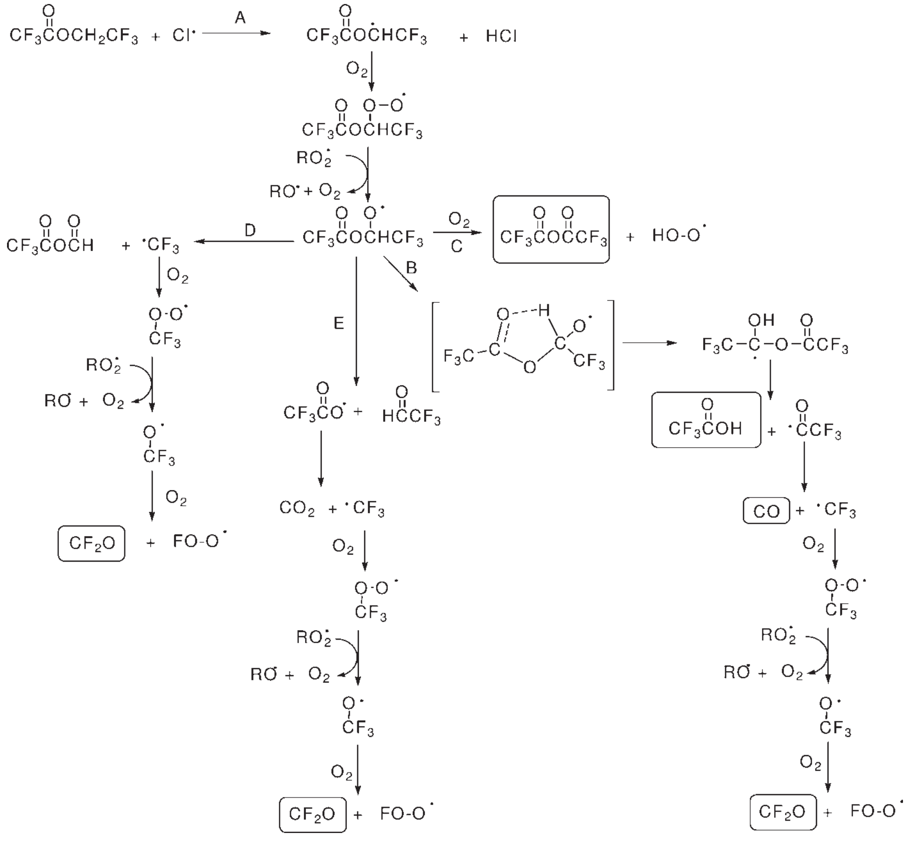


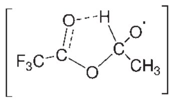
Figure 2. Simplified mechanism for the Cl-atom initiated oxidation of $CF_3C(O)OCH_2CF_3$ in NO_x-free air

The other reaction option for the $CF_3C(O)OCH(O\cdot)CF_3$ radical is decomposition via C—C or C—O bond cleavage to form (i) the formyl trifluoromethyl anhydride ($CF_3C(O)OCH(O)$) and CF_3 radicals and/or (ii) trifluoroacetaldehyde ($CF_3CH(O)$) and CF_3 and CO_2, whereby cleavage of the weaker C—C bond is more favored. It is not possible to confirm whether $CF_3C(O)OCH(O)$ and/or $CF_3CH(O)$ are being formed in the system since, in case they were formed, their absorption bands will be overlapped by those of $CF_3C(O)OC(O)CF_3$. Further reactions of CF_3 with O_2 will result in the formation of CF_2O observed. Subsequent reaction of either $CF_3C(O)OCH(O)$ and/or $CF_3CH(O)$ with Cl could lead to the CO formation identified. Formation of high yields of CO has been found in the Cl-atom initiated oxidation of fluorinated aldehydes by Solignac *et al.*[24] They suggest that the CO is formed via the decomposition channel of the perfluoroacyl radicals ($C_nF_{2n+1}CO$) which competes with the combination channel with molecular oxygen. Such a decomposition is possible in the reactions of Cl with both $CF_3C(O)OCH(O)$ and $CF_3CH(O)$. The further reactions of CF_3 with O_2, which can be formed in both possible $CF_3C(O)O$-$CH(O\cdot)CF_3$ decomposition channels described, will result in the formation of CF_2O observed.

The relative importance of the different channels for the reactions of a series of fluoroacetates, in agreement with the product yields obtained, can be correlated with the structure of the molecule regarding the nature and position of the group substituents (e.g., H atoms by CH_3, CF_3, or F groups). The importance of the α-ester channel to produce $CF_3C(O)OH$ can be explained by the identity of the different substituents connected to the carbon containing the hydrogen atom involved in the rearrangement. Figure 3 shows the α-ester rearrangement and the experimentally trifluoro acetic acid yields obtained for the reactions of Cl with $CF_3C(O)OCH_2CF_3$ and for $CF_3C(O)OCH_3$ and $CF_3C(O)OCH_2CH_3$ for comparative purposes. The measured acid yields for the reactions of Cl with $CF_3C(O)OCH_2CF_3$, $CF_3C(O)CH_3$ and $CF_3C(O)OCH_2CH_3$ are 0, 23 and 78 %, respectively.

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. By contrast, 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 fluoroacetates. The electron-withdrawing effect of the —CF_3 group on the alkoxy side of the ester in $CF_3C(O)OCH_2CF_3$ considerably reduces the α-ester rearrangement compared to the high yield from $CF_3C(O)OCH_2CH_3$ which contains an electron donating CH_3 group.

0 % of trifluoroacetic acid 23 % of trifluoroacetic acid



78 % of trifluoroacetic acid

Figure 3. α-ester rearrangements and the corresponding trifluoroacetic acid yields obtained for the reactions of Cl with $CF_3C(O)OCH_2CF_3$ from this work and for $CF_3C(O)OCH_3$ and $CF_3C(O)OCH_2CH_3$ from Ref. [22] for comparative purposes

The atmospheric lifetime of $CF_3C(O)OCH_2CF_3$, around 4 months,[13] is determined mainly by the reaction with OH radicals, even though in the early morning hours in marine environments, Cl-atom initiated reactions could compete with the OH reaction. The $CF_3C(O)OCH_2CF_3$ survive long enough to become well dispersed from the source origin, with regional scale transport being likely; the urban emission of this compound is, therefore, unlikely to contribute to local ozone formation. Product studies on esters and fluorinated esters have shown that the oxidation of fluoroacetates 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 mostly by heterogeneous processes. In particular, 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 carried out to study the product distribution of the fluoroacetate reactions over the range of temperatures, NO_x, and pressures of oxygen typically prevailing in the troposphere would be desirable to obtain a comprehensive description of the atmospheric implications associated with the widespread use of fluoroethers on air quality and their contribution to TFA formation and acid precipitation in general. Such data would allow a more accurate representation of the tropospheric chemistry of fluorinated esters in the various types of CT models used for designing environmental abatement strategies and making atmospheric policy decisions.

Acknowledgements

We acknowledge DAAD-PROALAR (Germany), the Deutsche Forschungsgemeinschaft (DFG), the EU project EUROCHAMP, SECYT (Argentina), CONICET (Argentina), ANPCyT (FONCYT, Argentina), SECyT-UNC (Córdoba, Argentina), Fundación Antorchas (Argentina), TWAS (Italy), and RSC (UK) for financial support of this research. We also thank J. Orlando and G. Tyndall for a copy of their manuscript prior to publication.

REFERENCES

[1] J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics*, J Wiley, NY, **1998**.

[2] T. J. Wallington, W. F. Schneider, J. Sehested, M. Bilde, J. Platz, O. J. Nielsen, L. K. Christensen, M. J. Molina, L. T. Molina, P. W. Wooldridge, *J. Phys. Chem. A* **1997**, *101*(44), 8264.

[3] L. K. Christensen, J. Sehested, O. J. Nielsen, M. Bilde, T. J. Wallington, A. Guschin, L. T. Molina, M. J. Molina, *J. Phys. Chem. A* **1998**, *102*, 4839.

[4] L. K. Christensen, T. J. Wallington, A. Guschin, M. D. Hurley, *J. Phys. Chem. A* **1999**, *103*(21), 4202.

[5] Y. Ninomiya, M. Kawasaki, A. Guschin, L. T. Molina, M. J. Molina, T. J. Wallington, *Environ. Sci. Technol.* **2000**, *34*(14), 2973.

[6] L. Chen, S. Kutsuna, K. Nohara, K. Takeuchi, T. Ibusuki, *J. Phys. Chem. A* **2001**, *105*, 10854.

[7] K. Nohara, M. Toma, S. Kutsuna, K. Takeuchi, T. Ibusuki, *Environ. Sci. Technol.* **2001**, *35*(1), 114.

[8] N. Oyaro, S. R. Sellevag, C. J. Nielsen, *Environ. Sci. Technol.* **2004**, *38*, 5567.

[9] M. P. Sulbaek Andersen, O. J. Nielsen, T. J. Wallington, M. D. Hurley, G. W. DeMoore, *J. Phys. Chem. A* **2005**, *109*(17), 3926.

[10] L. Chen, K. Kutsuna, K. Tokuhashi, A. Sekiya, R. Tamai, Y. Hibino, *J. Phys. Chem. A* **2005**, *109*, 4766.

[11] L. Chen, K. Kutsuna, K. Tokuhashi, A. Sekiya, *J. Phys. Chem. A* **2006**, *110*, 12845.
[12] M. B. Blanco, M. A. Teruel, *Atmos. Environ.* **2007**, *41*(34), 7330.
[13] M. B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M. A. Teruel, *Chem. Phys. Lett.* **2008**, *453*, 18.
[14] C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastidge, J. M. Hubbe, J. D. Fast, C. M. Berkowitz, *Nature* **1998**, *394*, 353.
[15] M. J. Ezell, W. Wang, A. A. Ezell, G. Soskin, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5813.
[16] D. Zehavi, J. N. Seiber, *Anal. Chem.* **1996**, *68*(19), 3450.
[17] H. Frank, A. Klein, D. Renschen, *Nature* **1996**, *382*, 34.
[18] A. Jordan, H. Frank, *Environ. Sci. Technol.* **1999**, *33*, 522.
[19] C. E. Wujcik, D. Zehavi, J. N. Seiber, *Chemosphere* **1998**, *36*, 1233.
[20] T. N. N. Stein, L. K. Christensen, J. Platz, J. Sehested, O. J. Nielsen, T. J. 'Wallington, *J. Phys. Chem. A* **1999**, *103*, 5705.
[21] I. Barnes, K. H. Becker, *J. Atmos. Chem.* **1994**, *18*, 267.
[22] M. B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M. A. Teruel, *Environ. Sci. Technol.* **2010**, *44*(7), 2354.
[23] E. C. Tuazón, S. M. Aschmann, R. Atkinson, W. P. L. Carter, *J. Phys. Chem. A* **1998**, *108*, 2316.
[24] G. Solignac, A. Mellouki, G. Le Bras, I. Barnes, T. Benter, *J. Phys. Chem. A* **2006**, *110*, 4450.