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PAPER

Atmospheric chemistry of t-$CF_3CH{=}CHCl$: products and mechanisms of the gas-phase reactions with chlorine atoms and hydroxyl radicals

M. P. Sulbaek Andersen,[*a] **O. J. Nielsen,**[b] **M. D. Hurley**[c] **and T. J. Wallington**[c]

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FTIR-smog chamber techniques were used to study the products and mechanisms of the Cl atom and OH radical initiated oxidation of *trans*-3,3,3-trifluoro-1-chloro-propene, t-$CF_3CH{=}CHCl$, in 700 Torr of air or N_2/O_2 diluent at 296 ± 2 K. The reactions of Cl atoms and OH radicals with t-$CF_3CH{=}CHCl$ occur *via* addition to the $>C{=}C<$ double bond; chlorine atoms add 15 ± 5% at the terminal carbon and 85 ± 5% at the central carbon, OH radicals add approximately 40% at the terminal carbon and 60% at the central carbon. The major products in the Cl atom initiated oxidation of t-$CF_3CH{=}CHCl$ were $CF_3CHClCHO$ and $CF_3C(O)CHCl_2$, minor products were CF_3CHO, HCOCl and CF_3COCl. The yields of $CF_3C(O)CHCl_2$, $CF_3CHClCOCl$ and CF_3COCl increased at the expense of CF_3CHO, HCOCl and $CF_3CHClCHO$ as the O_2 partial pressure was increased over the range 10–700 Torr. Chemical activation plays a significant role in the fate of $CF_3CH(O)CHCl_2$ and $CF_3CClHCHClO$ radicals. In addition to reaction with O_2 to yield CF_3COCl and HO_2 the major competing fate of CF_3CHClO is Cl elimination to give CF_3CHO (not C–C bond scission as previously thought). As part of this study $k(Cl + CF_3C(O)CHCl_2) = (2.3 \pm 0.3) \times 10^{-14}$ and $k(Cl + CF_3CHClCHO) = (7.5 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} were determined using relative rate techniques. Reaction with OH radicals is the major atmospheric sink for t-$CF_3CH{=}CHCl$. Chlorine atom elimination giving the enol $CF_3CH{=}CHOH$ appears to be the sole atmospheric fate of the $CF_3CHCHClOH$ radicals. The yield of CF_3COOH in the atmospheric oxidation of t-$CF_3CH{=}CHCl$ will be negligible (<2%). The results are discussed with respect to the atmospheric chemistry and environmental impact of t-$CF_3CH{=}CHCl$.

1. Introduction

Recognition of the adverse environmental consequences of the release of chlorofluorocarbons (CFCs) and Halon into the atmosphere[1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. While safeguarding the ozone layer has been at the center of these efforts, concerns related to global climate change are becoming an increasingly important consideration in the choice of alternative compounds.

Saturated hydrofluorocarbons (HFCs), such as CH_2FCF_3 (HFC-134a), have become widely used CFC replacements. HFCs do not contain chlorine and therefore do not contribute to chlorine based catalytic destruction of stratospheric ozone.[3]

trans-3,3,3-Trifluoro-1-chloro-propene, t-$CF_3CH{=}CHCl$ (HCFO-1233zd), is an unsaturated hydrochlorofluorocarbon (HCFC) which has been developed as a potential replacement for blowing agents CFCs and saturated HFCs in the manufacture of thermosetting foams. t-$CF_3CH{=}CHCl$ reacts rapidly with OH radicals, has a short atmospheric lifetime (26 days),[4] and a small global warming potential (7 for a 100 year time horizon):[4]

$$t\text{-}CF_3CH{=}CHCl + OH \rightarrow \text{products} \qquad (1)$$

Prior to any large-scale use, an assessment of the oxidation mechanism and environmental impact of t-$CF_3CH{=}CHCl$ is needed. In the present work smog chamber/FTIR techniques were used to determine the products of the Cl atom and OH radical initiated oxidation of t-$CF_3CH{=}CHCl$.

2. Experimental

The product studies and relative rate measurements were performed in a 140 litre Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[5] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to

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[a] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Mail stop 183-901, Pasadena, CA 91109, USA. E-mail: mpsa@jpl.nasa.gov; Fax: +1 818 393-5019; Tel: +1 818 393-3279*
[b] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark*
[c] *System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, MI 48121-2053, USA*

photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

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

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (3)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \qquad (4)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. O_3 was produced from O_2 *via* silent electrical discharge using a commercial O_3 ozonizer. Samples of *t*-$CF_3CH{=}CHCl$ were supplied by Honeywell International Inc. Anhydrous 3,3-dichloro-1,1,1-trifluoroacetone, $CF_3C(O)CHCl_2$, was obtained from SynQuest Laboratories with a stated purity of $>97\%$. All other reagents were obtained from commercial sources at purities $>99\%$. Experiments were conducted in 700 Torr total pressure of air or N_2/O_2, diluent at 296 ± 2 K. Concentrations of reactants and products were monitored by FTIR spectroscopy using an analytical path length of 27.1 m and a spectral resolution of 0.25 cm^{-1}. A liquid nitrogen cooled midband MCT detector was used in this study. Infrared spectra were derived from 32 coadded interferograms.

In smog chamber experiments it is important to check for unwanted loss of reactants and products *via* photolysis, dark chemistry and heterogeneous reactions. Control experiments were performed in which mixtures of reactants (except Cl_2 or CH_3ONO) in air were subjected to UV irradiation for 5 minutes and reactant/product mixtures obtained after the UV irradiation were allowed to stand in the dark in the chamber for 30–120 minutes. There was no observable loss of reactants or products suggesting that photolysis, dark chemistry and heterogeneous reactions are not a significant complication in the present work.

The relative rate method is a well established and widely used procedure for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[6] Kinetic data are derived by monitoring the loss of a reactant compound relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression:

$$\mathrm{Ln}\left(\frac{[\mathrm{Reactant}]_{t_o}}{[\mathrm{Reactant}]_t}\right) = \frac{k_{\mathrm{Reactant}}}{k_{\mathrm{Reference}}}\mathrm{Ln}\left(\frac{[\mathrm{Reference}]_{t_o}}{[\mathrm{Reference}]_t}\right) \qquad (\mathrm{I})$$

where $[\mathrm{Reactant}]_{t_o}$, $[\mathrm{Reactant}]_t$, $[\mathrm{Reference}]_{t_o}$, $[\mathrm{Reference}]_t$, are the concentrations of reactant and reference at times "t_o" and "t", and k_{Reactant} and $k_{\mathrm{Reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the reactant and reference. Unless stated otherwise, quoted uncertainties are 2 standard deviations from least squares regressions.

3. Results and discussion

3.1 Cl atom initiated oxidation of *t*-$CF_3CH{=}CHCl$ in the absence of NO_x

To investigate the products of the Cl atom initiated oxidation of *t*-$CF_3CH{=}CHCl$ in the absence of NO_x, mixtures consisting of 5.40–6.46 mTorr *t*-$CF_3CH{=}CHCl$, 82.3–150 mTorr Cl_2, and 10–700 Torr of O_2 in 700 Torr total pressure of N_2/air diluent were introduced into the reaction chamber and subjected to UV irradiation.

$$t\text{-}CF_3CH{=}CHCl + Cl \rightarrow \text{products} \qquad (6)$$

Fig. 1 shows typical IR spectra obtained before (A) and after (B) a 17 s irradiation of a mixture containing 6.32 mTorr *t*-$CF_3CH{=}CHCl$ and 101 mTorr Cl_2 in 700 Torr total pressure of air diluent. The consumption of *t*-$CF_3CH{=}CHCl$ was 49%. Comparison of panel B with the reference spectra for CF_3CHO, CF_3COCl and HCOCl shown in panels C, D and E show the formation of these species. Subtraction of IR features attributed to *t*-$CF_3CH{=}CHCl$, CF_3CHO, CF_3COCl, and HCOCl from panel B gives the residual spectrum in panel F. As seen from panel F, several residual IR bands are visible in the carbonyl stretching band region (1700–1850 cm^{-1}).

Fig. 2 shows the carbonyl region of residual product spectra obtained for experiments conducted with 10 (panel A), 140 (panel B), 700 (panel C) and 140 Torr (+ NO_x, panel D) O_2 partial pressure. Approximately 3 mTorr (2.5–3.1 mTorr) of *t*-$CF_3CH{=}CHCl$ were consumed in each of the experiments shown in panels A through D. The residual spectra were obtained after subtraction of the IR features attributable to *t*-$CF_3CH{=}CHCl$, CF_3CHO, CF_3COCl and HCOCl.

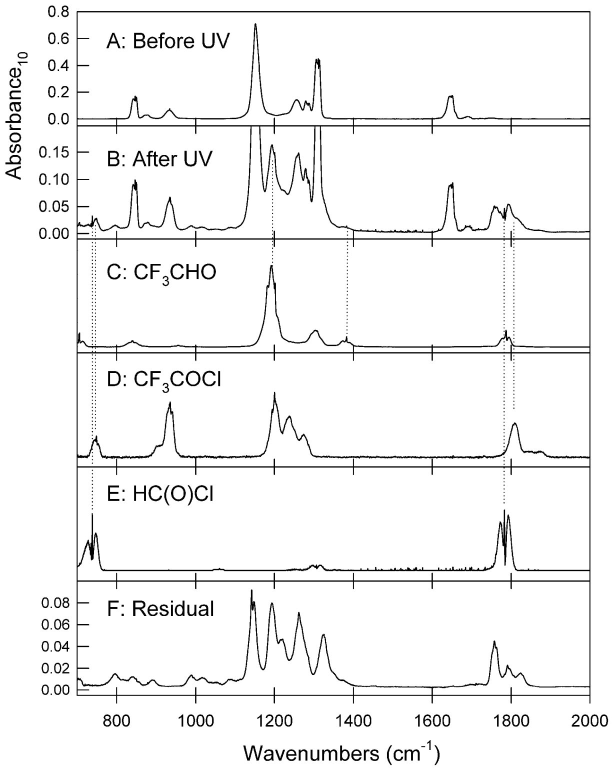

Fig. 1 IR spectra obtained (A) before and (B) after a 17 s UV irradiation of a mixture containing 6.32 mTorr *t*-$CF_3CH{=}CHCl$ and 101 mTorr Cl in 700 Torr of air diluent at 295 K. Panels C, and D and E show reference spectra of CF_3CHO, CF_3COCl and HCOCl. Subtraction of features attributable to *t*-$CF_3CH{=}CHCl$, CF_3CHO, CF_3COCl and HCOCl from panel B gives the residual IR spectrum shown in panel F.

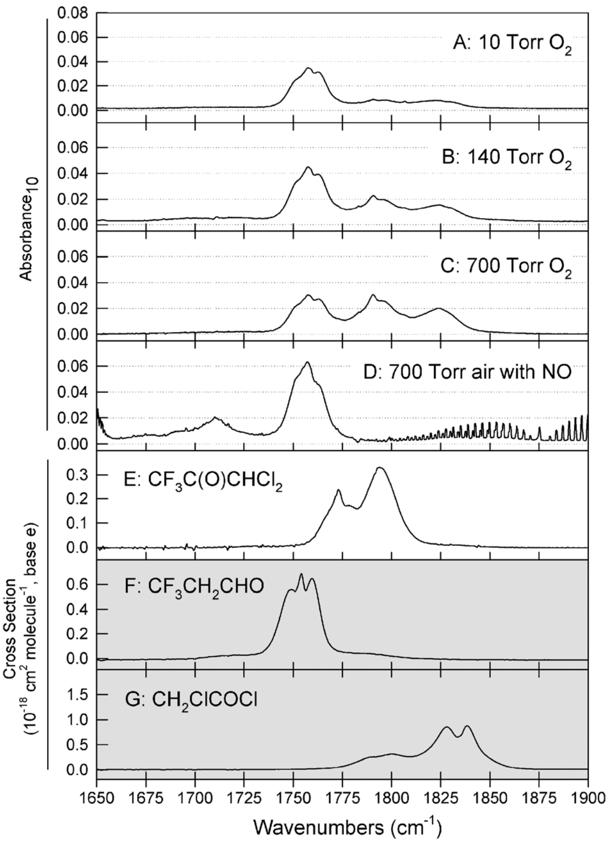

Fig. 2 Residual IR spectra obtained in the presence of 10 (panel A), 140 (panel B) and 700 (panel C) Torr of O_2 in 700 Torr of N_2. Panel D shows the residual spectrum obtained in the presence of NO_x in 700 Torr of air diluent. All spectra were obtained after subtraction of the IR features attributable to *t*-$CF_3CH{=}CHCl$, CF_3CHO, CF_3COCl and HCOCl only (as well as NOCl in experiment shown in panel D). Panels E, F and G show calibrated reference spectra for $CF_3C(O)CHCl_2$, and CF_3CH_2CHO, and $CH_2ClCOCl$ (the latter two are not predicted to be formed in the present experiment, but they have absorption bands with positions and band strengths similar to the products shown in panels A through D).

Careful comparison of the residual spectra, Panels A though C, with the reference spectrum of $CF_3C(O)CHCl_2$, panel E, reveals the formation of this compound. However, in the presence of NO_x (panel D), there is no observable formation of $CF_3C(O)CHCl_2$. At least three other carbonyl absorption features are present in panels A through D: a broad feature at 1757 cm^{-1} and two additional bands at 1790 and 1825 cm^{-1}. The broad IR feature at 1757 cm^{-1}, present under all experimental conditions, is consistent with a carbonyl containing compound (C=O stretching band) and scaled linearly with the loss of the parent compound for low (<60%) consumptions of *t*-$CF_3CH{=}CHCl$. This carbonyl feature is similar in shape to, but slightly blue shifted from, the reference spectrum for CF_3CH_2CHO, shown in panel F. An indistinguishable carbonyl absorption feature at 1757 cm^{-1} was observed by Nakayama *et al.*[7] in the Cl atom oxidation of $CF_3CH{=}CH_2$ and assigned to $CF_3CHClCHO$. Based on the similarity with the reference spectrum for CF_3CH_2CHO shown in panel F and the work by Nakayama *et al.*,[7] we attribute the IR feature at 1757 cm^{-1} to $CF_3CHClCHO$.

The last two bands at 1790 and 1825 cm^{-1} are likely due to one or more unknown products containing a carbonyl functional group. Panel G in Fig. 2 shows the reference spectrum for $CH_2ClC(O)Cl$. Comparison of panels A–C with panel G in Fig. 2, reveals that the IR features located at 1790 and 1830 cm^{-1} occur at frequencies consistent with those expected for an acid chloride. A possible product of the Cl initiated oxidation of *t*-$CF_3CH{=}CHCl$ is the acid chloride, $CF_3CHClCOCl$. The greatly reduced absorption strength of both 1790 and 1825 cm^{-1} relative to the 1757 cm^{-1} IR band, in the experiments conducted at low partial oxygen pressure (panel A) *versus* experiments conducted at high O_2 partial pressure, is indeed consistent with the mechanism outlined in the following. Based on these considerations, we attribute the IR absorption bands at 1790 and 1825 cm^{-1} to the formation of $CF_3CHClCOCl$.

Fig. 3 shows the formation of CF_3CHO, CF_3COCl, $CF_3CHClCHO$, and HCOCl *versus* the loss of *t*-$CF_3CH{=}CHCl$ observed following UV radiation of gas mixtures containing *t*-$CF_3CH{=}CHCl$ and Cl_2 in 700 Torr of air diluent. Product formation and loss of *t*-$CF_3CH{=}CHCl$ have been normalized to the initial *t*-$CF_3CH{=}CHCl$ concentration. In addition to the products mentioned above, small amounts of COF_2, CF_3OH, and $COCl_2$ were observed as secondary or tertiary products ($\Delta[t\text{-}CF_3CH{=}CHCl]/[t\text{-}CF_3CH{=}CHCl]_o > 0.9$). CF_3CHO and HCOCl react with Cl atoms and small corrections (<13%) for loss of *via* reaction with Cl atoms have been

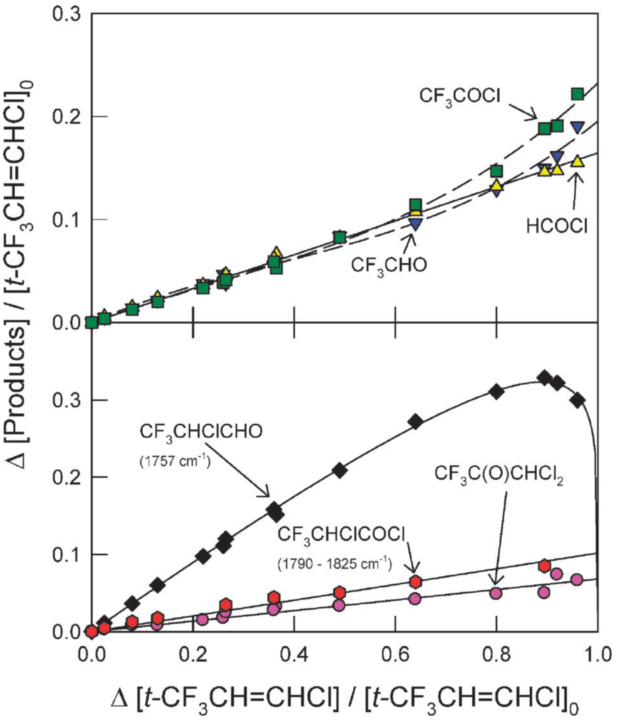

Fig. 3 Yields of CF_3CHO (downward triangles); CF_3COCl (squares); HCOCl (upward triangles); unknown at 1757 cm^{-1}, which we attribute to $CF_3CHClCHO$ (diamonds); $CF_3C(O)CHCl_2$ (circles); and unknown at 1790–1825 cm^{-1}, which we attribute to $CF_3CHClCOCl$ (hexagons), *versus* loss of *t*-$CF_3CH{=}CHCl$, normalised to the initial *t*-$CF_3CH{=}CHCl$ concentration, following the Cl initiated oxidation of *t*-$CF_3CH{=}CHCl$ in 700 Torr of air diluent. The curve fit to $CF_3CHClCHO$ follows expression (V) while the other lines are linear least squares regressions or second order polynomial fits to aid visual inspection of the data trends.

applied to the CF_3CHO and HCOCl data obtained in the experiments shown in Fig. 3 and 4. Corrections were computed using $k(\mathrm{Cl} + \mathrm{product})/k_2(\mathrm{Cl} + t\text{-}CF_3CH{=}CHCl) = 2.1 \times 10^{-12}$[8]$/5.22 \times 10^{-11}$[4] $= 0.040$ and 7.8×10^{-13}[9]$/5.22 \times 10^{-11}$[4] $= 0.015$ for CF_3CHO and HCOCl, respectively, and expression (II):

$$\text{Correction factor} = \left(\frac{x}{\left(\frac{1}{1-\frac{k_{\text{Product}}}{k_6}}\right)(1-x)\left[(1-x)^{\left(\frac{k_{\text{Product}}}{k_6}-1\right)}-1\right]} \right) \quad \text{(II)}$$

where x is the fractional consumption of t-$CF_3CH{=}CHCl$, and k_6 and k_{Product} are the bimolecular rate constants for the reactions of Cl atoms with t-$CF_3CH{=}CHCl$ and the product.

We do not have calibrated reference spectra for $CF_3CHClCHO$ and $CF_3CHClCOCl$. The concentrations for these compounds in the chamber were estimated assuming that the integrated absorption cross section of carbonyl stretching band is the same as that in CF_3CH_2CHO (1.8×10^{-17} cm molecule^{-1}, unpublished value for spectrum shown in Hurley *et al.*,[10] Fig. 2 panel F) and in $CH_2ClCOCl$ (3.6×10^{-17} cm molecule^{-1}, Fig. 2 panel G), respectively. While the yield of $CF_3CHClCOCl$ was linear, the yield of $CF_3CHClCHO$ was only initially linear with evidence for loss *via* secondary reactions at high (>60%) consumptions of t-$CF_3CH{=}CHCl$. Substantial positive curvature in the yields of CF_3CHO and CF_3COCl was observed for high consumptions of t-$CF_3CH{=}CHCl$ suggesting secondary sources of these compounds. Linear least-squares fits to the data for HCOCl, $CF_3C(O)CH_2Cl$ and $CF_3CHClCOCl$ gives molar yields of 17 ± 2, 8 ± 2, and 13 ± 4%. Initial molar yields of 15 ± 2% CF_3CHO and 15 ± 2% CF_3COCl were obtained from the data in Fig. 3 using least-squares fits for t-$CF_3CH{=}CHCl$ consumptions less than 40%. As discussed in Section 3.5, the yield of $CF_3CHClCHO$ in Fig. 3 was determined as 46 ± 10% using a non-linear regression.

Experiments were performed in which the oxygen partial pressure was varied over the range 10–700 Torr, and the yields of the products identified above are plotted in Fig. 4A as a function of oxygen partial pressure. In all experiments, the yields of CF_3CHO and CF_3COCl showed significant contributions from secondary sources at high consumptions of t-$CF_3CH{=}CHCl$. In contrast, the yield of $CF_3C(O)CHCl_2$, $CF_3CHClCOCl$, and HCOCl remained linear, throughout each experiment. As seen from Fig. 4A, there was a significant effect of $[O_2]$ on the initial product yields (for t-$CF_3CH{=}CHCl$ consumptions less than 40%). The yield of $CF_3CHClCHO$, CF_3CHO and HCOCl were inversely dependent on O_2 partial pressure, while the yield of $CF_3C(O)CHCl_2$, $CF_3CHClCOCl$ and CF_3COCl showed a positive correlation with oxygen partial pressure (see Table 1). Fig. 5 shows a proposed mechanism which can explain our experimental observations. The reaction is initiated by electrophilic addition of Cl to the double bond. As both resulting radical species are secondary

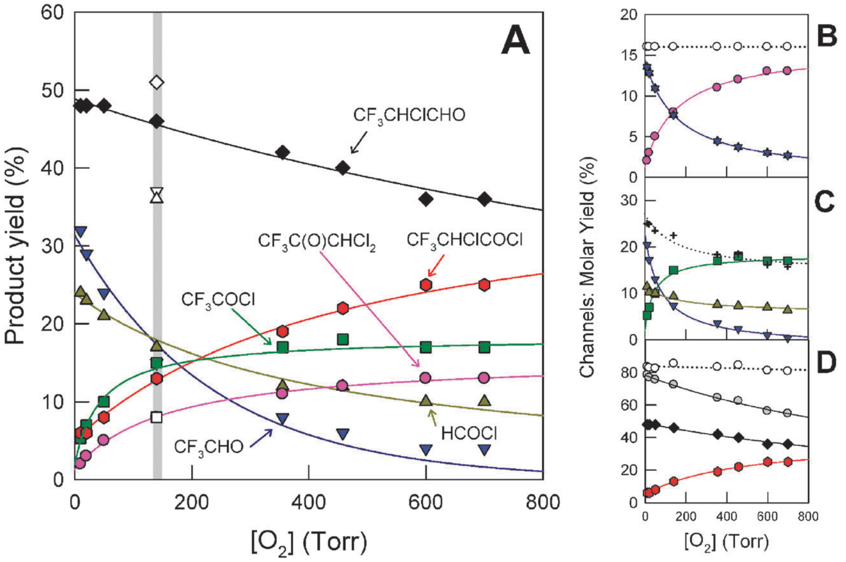

Fig. 4 Panel A: observed molar yields of $CF_3C(O)CHCl_2$ (circles), CF_3CHO (downward triangles), CF_3COCl (squares), HCOCl (upward triangles), $CF_3CHClCHO$ (diamonds), and $CF_3CHClCOCl$ (hexagons) *versus* the O_2 partial pressure following UV radiation of t-$CF_3CH{=}CHCl/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure, in the absence (solid symbols) and presence (open symbol) of NO_x. The gray bar serves to highlight the product yield differences obtained in one atmosphere of air (140 Torr O_2 partial pressure) and in the presence (open symbols)/absence (solid symbols) of NO_x. The curves through the CF_3CHO, HCOCl, and $CF_3CHClCHO$ data are polynomial fits to aid visual inspection of the data trends. The line through the $CF_3C(O)CHCl_2$ and CF_3COCl data are fits using the expressions described in the text. Panels B–D correspond to the groupings of reaction pathways indicated in Fig. 5. Panel B: yield of $CF_3C(O)CHCl_2$ and the corresponding yields of CF_3CHO and HCOCl as a function of $[O_2]$ (see text for details). The sum of yields is shown as open circles. Panel C: yields of CF_3COCl together with the residual amount of CF_3CHO and HCOCl, and calculated yield of CF_3CHClO radicals (crosshairs) as a function of $[O_2]$ (see text for details). Panel D: yields of $CF_3CHClCOCl$, $CF_3CHClCHO$, the sum of the decomposition channels (gray circles) and the sum of decomposition channels + $CF_3CHClCOCl$ (open circles) as a function of $[O_2]$ (see text for details).

Table 1 Product data for the Cl atom initiated oxidation of t-$CF_3CH{=}CHCl$ in 700 Torr of N_2/O_2/air diluent at 295 ± 2 K

	Molar yields (%) in the absence of NO_x								Molar yields (%) in the presence of NO_x
Product	$[O_2]$ = 10 Torr	$[O_2]$ = 20 Torr	$[O_2]$ = 50 Torr	$[O_2]$ = 140 Torr	$[O_2]$ = 355 Torr	$[O_2]$ = 458 Torr	$[O_2]$ = 600 Torr	$[O_2]$ = 700 Torr	$[O_2]$ = 140 Torr
CF_3CHO[a]	34 ± 2%	30 ± 2%	24 ± 2%	15 ± 2%	8 ± 2%	6 ± 2%	4 ± 1%	3 ± 1%	37 ± 3%
$HCOCl$[a]	25 ± 2%	23 ± 2%	21 ± 2%	17 ± 2%	12 ± 2%	11 ± 2%	10 ± 2%	9 ± 1%	36 ± 2%
CF_3COCl[a]	6 ± 2%	7 ± 2%	10 ± 2%	15 ± 2%	17 ± 2%	18 ± 2%	17 ± 2%	17 ± 2%	8 ± 1%
$CF_3CHClCHO$	48 ± 10%	48 ± 10%	48 ± 10%	46 ± 10%	42 ± 9%	40 ± 9%	36 ± 8%	35 ± 8%	51 ± 11%
$CF_3C(O)CHCl_2$	2 ± 1%	3 ± 1%	5 ± 1%	8 ± 2%	11 ± 2%	12 ± 2%	13 ± 2%	13 ± 2%	<3%
$CF_3CHClCOCl$	5 ± 2%	6 ± 2%	7 ± 5%	13 ± 4%	19 ± 5%	22 ± 5%	25 ± 6%	26 ± 6%	<3%
Total Carbon Balance[a]	90 ± 16%	89 ± 16%	90 ± 19%	93 ± 19%	93 ± 19%	94 ± 19%	91 ± 19%	90 ± 18%	99 ± 14%
Estimated CF_3CHClO yield[b]	27%	25%	24%	23%	18%	19%	16%	16%	12%
k_{34}/k_6[c]	0.169 ± 0.019	0.160 ± 0.015	0.149 ± 0.015	0.157 ± 0.019	0.140 ± 0.020	0.125 ± 0.019	0.125 ± 0.019	0.145 ± 0.018	0.152 ± 0.20

[a] Initial yields ($\Delta[t\text{-}CF_3CH{=}CHCl/[t\text{-}CF_3CH{=}CHCl]_0 < 40\%$). [b] Using $k_{18}/k_{19} = 2.1 \times 10^{-19}$ cm^3 molecule^{-1}.[15] [c] Based on fits to the data as shown in Fig. 6.

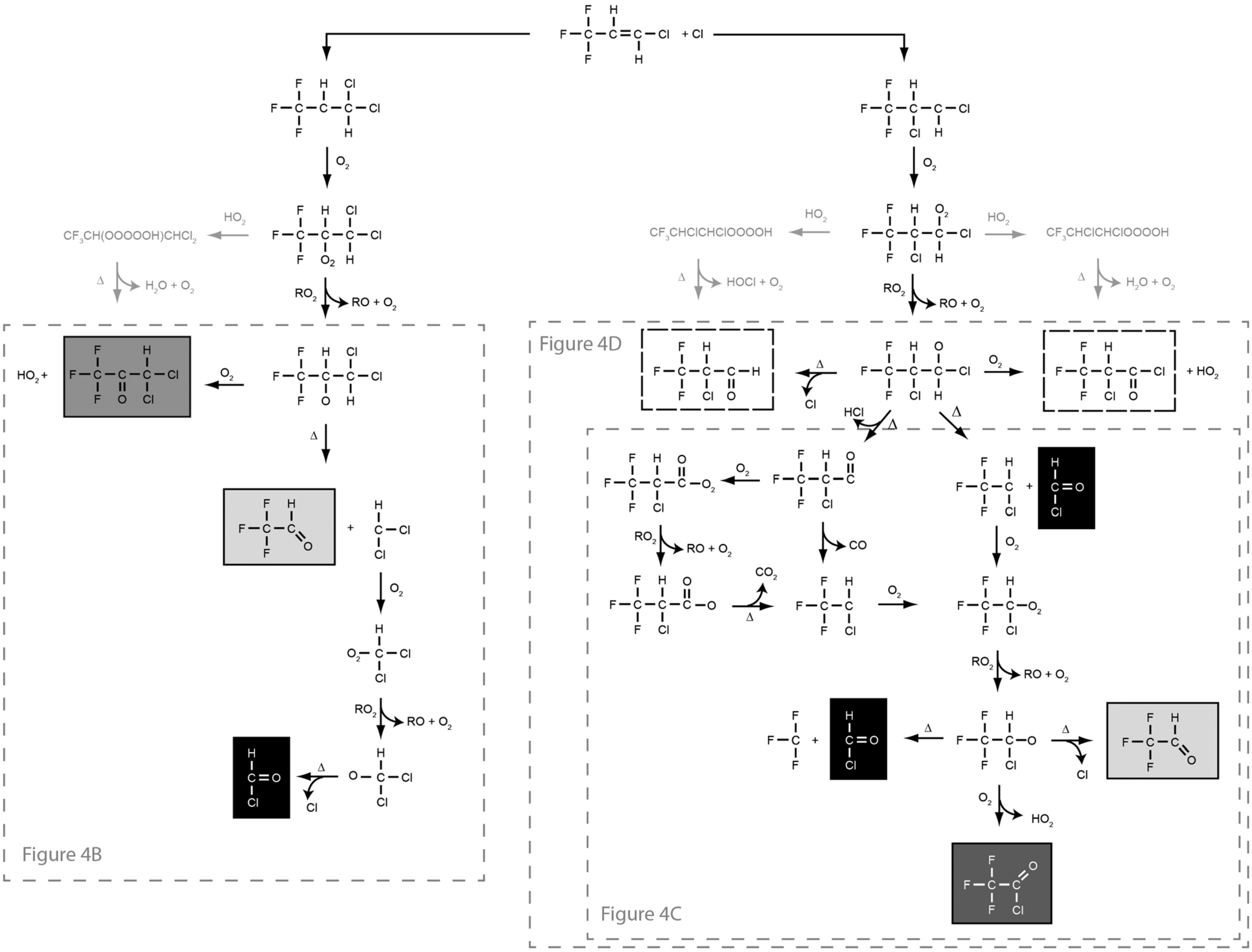

Fig. 5 Proposed mechanism of the Cl atom initiated oxidation of t-$CF_3CH{=}CHCl$. Solid boxes indicate the experimentally observed products. Dashed gray boxes include reactions for which oxygen dependencies are illustrated in Fig. 4B through D.

radicals, one might expect that Cl addition will occur at the terminal and the central carbon with equal importance (in the equations below M represents a third body); however, as we shall see the electron withdrawing effect of the CF_3 substituent has a profound effect on the stability of the resulting radicals.

$$t\text{-}CF_3CH{=}CHCl + Cl + M \rightarrow CF_3CHCHCl_2 + M \tag{7a}$$

$$t\text{-}CF_3CH{=}CHCl + Cl + M \rightarrow CF_3CHClCHCl + M \tag{7b}$$

The radicals produced in reaction (7) will add O_2 to give peroxy radicals, which will undergo self- and cross-reactions to give the corresponding alkoxy radicals:

$$CF_3CHCHCl_2 + O_2 + M \rightarrow CF_3CH(OO)CHCl_2 + M \tag{8a}$$

$$CF_3CHClCHCl + O_2 + M \rightarrow CF_3CHClCHCl(OO) + M \tag{8b}$$

$$CF_3CH(OO)CHCl_2 + RO_2 \rightarrow CF_3CH(O)CHCl_2 + RO + O_2 \tag{9a}$$

$$CF_3CHClCHCl(OO) + RO_2 \rightarrow CF_3CHClCHClO + RO + O_2 \tag{9b}$$

While reaction (9) is expected to be the dominant fate of the peroxy radicals, self-reaction and reaction with any α-H containing peroxy radicals could also lead to the formation of small amounts of carbonyl containing compounds, *e.g.*:

$$2\ CF_3CH(OO)CHCl_2 \rightarrow CF_3C(O)CHCl_2 + CF_3CH(OH)CHCl_2 + O_2 \tag{10a}$$

$$2\ CF_3CHClCHCl(OO) \rightarrow CF_3CHClCOCl + CF_3CHClCHClOH + O_2 \tag{10b}$$

As seen from Fig. 4, the yields of both $CF_3CHClCOCl$ and $CF_3C(O)CHCl_2$ have small but discernable non-zero *y* axis intercepts, which probably reflects contributions by reactions (10a) and (10b).

3.2 Fate of the $CF_3CH(O)CHCl_2$ radical

The $CF_3CH(O)CHCl_2$ radicals, generated in reaction (9a) can undergo reaction with O_2 and decomposition *via* C–C bond scission:

$$CF_3CH(O)CHCl_2 + O_2 \rightarrow CF_3C(O)CHCl_2 + HO_2 \tag{11}$$

$$CF_3CH(O)CHCl_2 + M \rightarrow CF_3 + CHCl_2CHO + M \tag{12a}$$

$$CF_3CH(O)CHCl_2 + M \rightarrow CF_3CHO + CHCl_2 + M \tag{12b}$$

The formation of $CF_3C(O)CHCl_2$ *via* reaction (11) was evident in the product spectra by comparison with the reference spectra for $CF_3C(O)CHCl_2$ (see Fig. 2). Evidence for the formation of $CHCl_2CHO$ were sought in the product spectra, using the characteristic carbonyl stretch absorption feature at 1759 cm^{-1}, but not found. The absence of any discernable $CHCl_2CHO$ in our product spectra suggests that the decomposition pathway (12a) is of negligible importance. It should be mentioned though, that $CHCl_2CHO$ may be rather reactive towards Cl atoms, which could render any small yield of $CHCl_2CHO$ difficult to detect in the present experiments. Still, the CF_3 radicals co-generated in reaction (12a) will react with oxygen, followed by reactions with RO_2 to give CF_3O radicals, for which the dominant fate in the chamber is abstraction of a H-atom from a hydrogen containing molecule:

$$CF_3O + RH \rightarrow CF_3OH + R \tag{13}$$

An upper limit of <1% initial molar yield of CF_3OH was established in all experiments, also suggesting that the decomposition pathway (12a) is indeed of minor importance.

The yield of $CF_3C(O)CHCl_2$ can be described by the expression

$$Y_{CF_3C(O)CHCl_2} = Y_{CF_3CH(O)CHCl_2} \times (k_{11}[O_2]/(k_{11}[O_2] + k_{12b})) + C, \tag{III}$$

where $Y_{CF_3CH(O)CHCl_2}$ is the yield of $CF_3CH(O)CHCl_2$ radicals in the system, k_{11} and k_{12b} are the rate constants for reaction (11) and decomposition channel (12b), and *C* is the $[O_2]$ independent yield of $CF_3C(O)CHCl_2$ due to reaction (10a). The curve through the $CF_3C(O)CHCl_2$ data in Fig. 4A is a fit of expression (III) to the data which gives $k_{11}/k_{12b} = (1.9 \pm 0.4) \times 10^{-19}$ cm^3 $molecule^{-1}$, $Y_{CF_3CH(O)CHCl_2} = 0.14 \pm 0.01$ and $C = 0.01 \pm 0.01$. The rate constant ratio k_{11}/k_{12b} is similar to the analogous rate constant ratio $k_{O_2}/k_{diss} = (3.8 \pm 1.8) \times 10^{-18}$ cm^3 $molecule^{-1}$ measured for $CF_3CH(O)CH_2Cl$ radicals.[11]

Carbon–carbon bond scission through reaction (12b) leads to the formation of CF_3CHO and $CHCl_2$ radicals. The $CHCl_2$ radicals will add O_2 and then undergo self- and cross-reactions with other peroxy radicals to generate $CHCl_2O$ radicals, which will decompose *via* Cl atom elimination to give HCOCl:[12]

$$CHCl_2 + O_2 \rightarrow CHCl_2O_2 \tag{14}$$

$$CHCl_2O_2 + RO_2 \rightarrow CHCl_2O + RO + O_2 \tag{15}$$

$$CHCl_2O + M \rightarrow HCOCl + Cl + M \tag{16}$$

It is possible that small amounts of $COCl_2$ can be formed in the chamber *via* reaction of $CHCl_2O_2$ with HO_2:[13]

$$CHCl_2O_2 + HO_2 \rightarrow COCl_2 + H_2O + O_2 \tag{17a}$$

$$CHCl_2O_2 + HO_2 \rightarrow HCOCl + HOCl + O_2 \tag{17b}$$

An upper limit of <0.5% initial molar yield of $COCl_2$ was established for all experiments, suggesting that reaction (17a) is not significant.

At low O_2 partial pressures both CF_3CHO and HCOCl were observed in significant yields, which declined with increasing O_2 concentrations, consistent with a competition between reactions (11) and (12b). However, the yields of both compounds exceed that expected from reactions (12b) and (14) through (16), based on $Y_{CF_3CH(O)CHCl_2} = 14\%$. As seen from Fig. 5, and further discussed below, there are multiple sources of CF_3CHO and HCOCl in the system. For the purpose of carbon balance accounting and assistance in the further analysis of the oxidation mechanism, we assume that through reactions (12b) and (14)–(16), CF_3CHO and HCOCl are formed in a ratio of 1 : 1 and in yields of $Y = Y_{CF_3CH(O)CHCl_2} \times 1/(k_{11}/k_{12} \times [O_2] + 1) = 0.14 \times 1/(1.9 \times 10^{-19} \times [O_2] + 1)$ as shown in Fig. 4B. The combined total of the $CF_3C(O)CHCl_2$ yield and the yield of CF_3CHO due to reaction (12a) (or yield of HCOCl due to reaction (14)–(16)) is shown as open circles in Fig. 4B.

3.3 Fate of the $CF_3CHClCHClO$ radical

Addition of the Cl atom to the central carbon atom in *t*-$CF_3CH{=}CHCl$ can lead to several oxygen dependent reaction pathways. The $CF_3CHClCHClO$ radicals generated in reaction (9b) can undergo reaction with O_2, decomposition *via* C–C bond scission or elimination of HCl or Cl:

$$CF_3CHClCHClO + O_2 \rightarrow CF_3CHClCOCl + HO_2 \quad (18)$$

$$CF_3CHClCHClO + M \rightarrow CF_3CHCl + HCOCl + M \quad (19a)$$

$$CF_3CHClCHClO + M \rightarrow CF_3CHClC(O) + HCl + M \quad (19b)$$

$$CF_3CHClCHClO + M \rightarrow CF_3CHClCHO + M + Cl \quad (19c)$$

The yield of $CF_3CHClCOCl$ formed in reaction (18) can be described by an expression analogous to expression (III), yielding $k_{18}/k_{19} = (5.8 \pm 1.8) \times 10^{-20}$ cm^3 molecule^{-1}, $Y_{CF_3CHClCOCl} = 0.38 \pm 0.06$ and $C = 0.05 \pm 0.02$. The significant non-zero y axis intercept can be explained by the formation of $CF_3CHClCOCl$ *via* reaction of $CF_3CHClCHCl(OO)$ radicals with other peroxy radicals (reaction (10b)).

Decomposition of $CF_3CHClCHClO$ *via* C–C bond scission leads to one molecule of HCOCl and a CF_3CHCl radical. The $CF_3CHClC(O)$ radicals formed in reaction (19b) can also be converted into CF_3CHCl radicals *via*

$$CF_3CHClC(O) + M \rightarrow CF_3CHCl + CO + M \quad (20)$$

$$CF_3CHClC(O) + O_2 + M \rightarrow CF_3CHClC(O)O_2 + M \quad (21)$$

$$CF_3CHClC(O)O_2 + RO_2 \rightarrow CF_3CHClC(O)O + RO + O_2 \quad (22)$$

$$CF_3CHClC(O)O + M \rightarrow CF_3CHCl + CO_2 + M \quad (23)$$

The formation of both CO and CO_2 was observed in all experiments and suggests, but does not prove, that reaction (19b) is an important loss fate of $CF_3CHClCHClO$; intramolecular elimination of HCl has also been proposed as a fate for the analogous $CH_2ClCHClCHClO$ radicals.[14] Interestingly, CO was observed as a primary product, and in significant amounts at low [O_2], while largely absent at high [O_2], consistent with a competition between reaction (20) and (21). The relative importance of reactions (19a) *versus* (19b) is discussed further below.

The CF_3CHCl radicals formed in reactions (19a), (20) and/or (23) will add O_2, and undergo peroxy radical self- and cross-reactions to give the corresponding alkoxy radical, CF_3CHClO:

$$CF_3CHCl + O_2 + M \rightarrow CF_3CHClO_2 + M \quad (24)$$

$$CF_3CHClO_2 + RO_2 \rightarrow CF_3CHClO + O_2 \quad (25)$$

Loss processes for CF_3CHClO radicals are reaction with O_2 to give $CF_3COCl + HO_2$ and decomposition *via* intramolecular elimination of HCl or Cl and C–C scission:[15]

$$CF_3CHClO + O_2 \rightarrow CF_3COCl + HO_2 \quad (26)$$

$$CF_3CHClO + M \rightarrow CF_3CO + HCl + M \quad (27a)$$

$$\rightarrow CF_3CHO + Cl + M \quad (27b)$$

$$\rightarrow CF_3 + HCOCl + M \quad (27c)$$

Inspection of Fig. 4A shows a non-zero intercept for CF_3COCl which provides a measure of the importance of the molecular channel:

$$CF_3CHClO_2 + CF_3CHClO_2 \rightarrow CF_3COCl + CF_3ClHOH + OH \quad (28)$$

A rate constant ratio $k_{26}/k_{27} = (2.1 \pm 0.4) \times 10^{-19}$ cm^3 molecule^{-1} has been determined by Møgelberg *et al.*[15] in the photolysis of $CF_3CH_2Cl/O_2/Cl_2/N_2$ and $CF_3CH_2Cl/O_2/F_2/N_2$ mixtures; hence, reactions (26) and (27) are expected to be of comparable importance in one atmosphere of air. The yield of CF_3COCl, Y_{CF_3COCl}, can be described by an equation, analogous to expression (III):

$$Y_{CF_3COCl} = Y_{CF_3CHClO} \times (k_{26}[O_2]/(k_{26}[O_2] + k_{27})) + C \quad (IV)$$

where Y_{CF_3CHClO} is the yield of CF_3CHClO radicals in the system, and C is the [O_2] independent yield of CF_3COCl. The curve through the CF_3COCl data in Fig. 4A is a fit to the expression (IV) yielding $k_{26}/k_{27} = (5.5 \pm 2.6) \times 10^{-19}$ cm^3 molecule^{-1} and $C = 4 \pm 2\%$. This value of k_{26}/k_{27} is significantly higher than the previous determination by Møgelberg *et al.*[15] This is due to the fact that in the present system CF_3CHClO is formed *via* competing and oxygen dependent reactions. As shown in Fig. 5 decomposition and reaction with O_2 are competing fates of $CF_3CHClCHClO$ radicals. As more $CF_3CHClCHClO$ radicals are lost *via* reaction with O_2 with increasing O_2 partial pressure, a decreasing yield of CF_3CHClO radicals will in turn emerge. The net effect is an effective yield of CF_3COCl that is plateauing early and producing an overestimation of k_{26}/k_{27} as evidenced by the data in Fig. 4A.

Using the observed yields of CF_3COCl at each [O_2], C and the rate constant ratio k_{26}/k_{27} established by Møgelberg *et al.* we can infer the net yield of CF_3CHClO radicals in the system at each oxygen partial pressure (see Table 1). It follows that CF_3CHClO radicals are formed in a yield ranging from approximately 16% (700 Torr O_2) to 27% (10 Torr O_2). The sum of this value and C gives an estimation of the importance of the decomposition channels (19a) and (19b) (sum), as a function of O_2 partial pressure (20 to 31%).

Let us now consider the reactions competing with reaction (26). Any CF_3CO radicals formed in reaction (27a) will add O_2 to form $CF_3C(O)O_2$,[16,17] which in turn will react with other peroxy radicals to give $CF_3C(O)O$. The fate of $CF_3C(O)O$ is decomposition *via* elimination of CO_2 to give CF_3 radicals. As discussed above, CF_3 will react with oxygen, followed by reactions with RO_2 to give CF_3O radicals, for which the dominant fate in the chamber is abstraction of a H-atom from a hydrogen containing molecule to give CF_3OH. As all experiments showed $<1\%$ initial molar yield of CF_3OH we conclude that decomposition pathway (27a) is of minor importance.

CF_3CHO and HCOCl are the products of reactions (27b) and (27c), respectively. There are several possible pathways leading to HCOCl and CF_3CHO in the system which complicate the product assignments. Møgelberg *et al.*[15] studied the atmospheric fate of CF_3CHClO radicals generated in the reaction of CF_3CH_2Cl with Cl atoms in 700 Torr total pressure of O_2/N_2 diluent. CF_3CHO and HCOCl are much (approximately 300 and 1000 times, respectively) more reactive than CF_3CH_2Cl towards chlorine atoms and hence Møgelberg *et al.* were not able to detect any formation of HCOCl or CF_3CHO in their experiments. However, CF_3COCl, which is unreactive towards Cl atoms, was easily detected and used to establish the O_2 dependency of reaction (26) *vs.* reaction (27). They proposed that C–C bond scission (reaction (27c)), is the sole competing decomposition pathway for CF_3CHClO, based on the similarity between the O_2 dependency of the CF_3COCl yield in the CF_3CHClO system, and that found for CF_3COF in the analogous CF_3CHFO system. The CF_3CHFO system has been extensively studied and found to have only one major decomposition route giving CF_3 and HCOF.[18–20] Although the results of Møgelberg *et al.* showed similar O_2 dependence for the products of both the CF_3CHClO and CF_3CHFO systems, it is worth mentioning that decomposition of CF_3CHFO to give CF_3CHO and F would be very unlikely in any case, due to the strong C–F bond. Interestingly, the present experiments suggest that C–C bond scission may in fact be of lesser importance than Cl elimination in the CF_3CHClO system. After allocation of CF_3CHO to account for reaction (12b) (3–14%), a significant amount of CF_3CHO remains to be allocated. As seen from Fig. 5, in addition to reaction (12), the only possible source of CF_3CHO in the system is reaction (27b). Furthermore, the absence of any significant amount of CF_3OH formed in the system points to reaction (27c) not being of substantial importance. In Fig. 4C, the remaining proportion of the CF_3CHO yield, *i.e.*, after allocation of CF_3CHO to account for reaction (12b), has been plotted together with the yield of CF_3COCl as a function of $[O_2]$. This shows CF_3CHO as the dominant, and possibly sole, decomposition product of reaction (27). In fact, the sum of CF_3CHO and CF_3COCl, adjusted for $RO_2 + RO_2$ reactions leading to CF_3COCl, is in very good agreement with our calculated yield of CF_3CHClO radicals, also shown in Fig. 4C. The remaining HCOCl yield, after allocation of HCOCl to account for reactions (14)–(16), is also plotted in Fig. 4C. This shows an oxygen dependence that closely mimics that of the calculated yield of CF_3CHClO radicals, and with a molar yield approximately one-half that of CF_3CHClO, *i.e.*, $k_{19a}/(k_{19a} + k_{19b}) \approx 0.5$.

Finally, let us turn our attention to $CF_3CHClCHO$ formed in reaction (19c). $CF_3CHClCHO$ was the major product identified at all oxygen partial pressures (see Table 1). The lower 3 traces in Fig. 4D shows the yields of $CF_3CHClCOCl$, $CF_3CHClCHO$ alone, and the sum of the decomposition channel products (reactions (19a) through (c)). The combined total of the yields of $CF_3CHClCOCl$ and decomposition channels are shown as open circles.

3.4 Reaction site selectivity for Cl + *t*-$CF_3CH{=}CHCl$

It is clear that the chemistry occurring in the Cl atom initiated oxidation of *t*-$CF_3CH{=}CHF$ in the chamber is complex. From the total yields in Fig. 4B and D we conclude that the addition of Cl atoms to *t*-$CF_3CH{=}CHCl$ proceeds 85 ± 5% at the central carbon and 15 ± 5% at the terminal carbon, *i.e.*, $k_{7a}/(k_{7a} + k_{7b}) = 0.15 \pm 0.05$. Table 1 lists carbon balances based on the identified and quantified products for each set of experiments at different oxygen partial pressures, ranging from 89 to 94%. These values do not include missing carbon from the formation of hydroxy compounds in the $RO_2 + RO_2$ cross reactions, nor do they account for CO/CO_2 eliminated in reactions (20) or (23). Accounting for those reactions would add an estimated 9–13% to the total carbon balance bringing it very close to unity. This result is gratifying, but from Fig. 4D it can also be observed that the oxygen dependence of $CF_3CHClC(O)Cl$ and that of the total of the decomposition reactions (19a)–(c) do not completely agree. The fit to the data points for $CF_3CHClCOCl$ suggested a yield of $CF_3CHClCHClO$ radicals of approximately 39%, while that of the sum of the decomposition channels (reaction (19a)–(c)), clearly suggests a value much higher (~85%). It appears that either the $CF_3CHClCHO$ yield is too high while at the same time the yield of $CF_3CHClC(O)Cl$ is too low, or *vice versa*.

It is difficult to imagine any additional source of $CF_3CHClCHO$ in the O_2/RO_2 reaction system. It is not inconceivable that the reaction of $CF_3CHClCHCl$ with O_2 could result in excited peroxyradicals, $[CF_3CHCl(COO)HCl]^*$, which could have two possible fates; elimination of HOCl to give the corresponding aldehyde, $CF_3CHClCHO$, or collisional relaxation to give the thermalized peroxy radical.There is, however, no precedence for this pathway in similar reaction systems. It is probably more likely that as $[O_2]$ is increased, the yield of HO_2 radicals is also increased, and so the probability for the reaction of $CF_3CHClCHClO_2$ with HO_2:

$$CF_3CHClCHClO_2 + HO_2$$

$$\rightarrow CF_3CHClCHO + HOCl + O_2 \qquad (29a)$$

$$\rightarrow CF_3CHClCOCl + H_2O + O_2 \qquad (29b)$$

$$\rightarrow CF_3CHClCHClOOH + O_2 \qquad (29c)$$

$$\rightarrow CF_3CHClCHO + Cl + OH + O_2 \qquad (29d)$$

The rate constants for the reactions of chlorinated C1 and C2 peroxy radicals with HO_2 are on the order of 5×10^{-12} cm^3 molecule^{-1} s^{-1}. Larger peroxy radicals react faster with HO_2 ($k > 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}),[21] but the electron withdrawing effect of fluorine substituents is likely to lower the rate constants substantially. It is reasonable to assume that the rate constant for the reaction of HO_2 with $CF_3CHClCHClO_2$ (and $CF_3C(OO)HCHCl_2$) is similar to that for the reaction of RO_2 with $CF_3CHClCHClO_2$. Catoire *et al.*[13] showed that the product distribution for the $HO_2 + RO_2$ reaction is strongly determined by the substituent makeup of the peroxy radical. Depending on the relative importance in our system of reactions (29a), (29b) and (29d), a larger fraction of $CF_3CHClCHClO_2$ radicals may be converted to $CF_3CHClCHO$, due to the reaction with HO_2, than can be explained from reactions with RO_2/O_2 alone. This would become increasingly important as the yields of HO_2 as a co-product of reactions (11), (18) and (26) become more important with increasing $[O_2]$.

Reaction of HO_2 with the peroxy radical generated after Cl addition to the terminal carbon, $CF_3C(OO)HCHCl_2$, could also lead to additional formation of carbonyl compounds:

$$CF_3CH(OO)CHCl_2 + HO_2 \rightarrow CF_3C(O)CHCl_2 + H_2O + O_2 \quad (30a)$$

$$CF_3CH(OO)CHCl_2 + HO_2 \rightarrow CF_3CHO + CHCl_2OH + O_2 \quad (30b)$$

$$CF_3CH(OO)CHCl_2 + HO_2 \rightarrow CF_3CH(OOH)CHCl_2 + O_2 \quad (30c)$$

Thus, reaction of HO_2 with $CF_3CH(OO)CHCl_2$ could be an additional source of CF_3CHO in the system. But this source would be more important at higher, rather than at lower, O_2 partial pressures. We observed a strong trend of decreasing CF_3CHO yield with higher O_2, and thus conclude that reaction (30b) probably is not of major importance in the system, and that the observed yield of CF_3CHO, is exclusively due to reactions (12b) and (27b).

3.5 The reactivity of Cl atoms towards the carbonyl products $CF_3C(O)CHCl_2$, $CF_3CHClCHO$ and $CF_3CHClCOCl$

Secondary reactions of Cl atoms with $CF_3C(O)CHCl_2$ is expected to proceed slowly (*e.g.*, $k(Cl + CF_3C(O)CH_2Cl) = 5.63 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}).[7] Indeed, the yield of $CF_3C(O)CHCl_2$ in the experiments discussed in the previous section did not show any sign of decreasing, even at high consumptions of t-$CF_3CH{=}CHF$, suggesting a reactivity towards Cl atoms that is significantly slower than k_6. To confirm this, a relative rate study was performed to measure $k(Cl + CF_3C(O)CHCl_2)$. Experiments were performed in 700 Torr of N_2 diluent using mixtures of 15 mTorr $CF_3C(O)CHCl_2$, 7–16 mTorr of either CH_2F_2 or CH_4 and 180 mTorr of Cl_2.

$$CF_3C(O)CHCl_2 + Cl \rightarrow \text{products} \quad (31)$$

$$CH_2F_2 + Cl \rightarrow \text{products} \quad (32)$$

$$CH_4 + Cl \rightarrow \text{products} \quad (33)$$

Rate constant ratios of $k_{31}/k_{32} = 0.74 \pm 0.05$ and $k_{31}/k_{33} = 0.22 \pm 0.02$ were derived. Using $k_{32} = 3.3 \times 10^{-14}$[9] and $k_{33} = 1.0 \times 10^{-13}$[9] gives $k_{31} = (2.4 \pm 0.2) \times 10^{-14}$ and $(2.2 \pm 0.2) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We choose to cite a final value which is the average of the two determinations with uncertainties which span the extremes of the determinations, hence $k_{31} = (2.3 \pm 0.3) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction of $CF_3C(O)CHCl_2$ with Cl atoms is three orders of magnitude slower than that of t-$CF_3CH{=}CHF$.[4] This is consistent with the absence of any curvature in the $CF_3C(O)CHCl_2$ product data.

We do not have a sample of the major product, $CF_3CHClCHO$. As discussed in Section 3.1, the yield of $CF_3CHClCHO$ in the Cl initiated oxidation of t-$CF_3CH{=}CHCl$ showed evidence for significant loss *via* secondary reactions at high (>60%) consumptions of t-$CF_3CH{=}CHCl$:

$$CF_3CHClCHO + Cl \rightarrow CF_3CHClC(O) + HCl \quad (34)$$

The concentration profile of the reactive primary product, $CF_3CHClCHO$, can be described[22] by the expression

$$\frac{[CF_3CHClCHO]_t}{[t\text{-}CF_3CH{=}CHCl]_o} = \frac{\alpha(1-x)\left\{(1-x)^{\left(\frac{k_{34}}{k_6}-1\right)}\right\}}{1-(k_{34}/k_6)} \quad (V)$$

where $x = 1 - ([t\text{-}CF_3CH{=}CHCl]_t/[t\text{-}CF_3CH{=}CHCl]_o)$ is the fractional consumption of t-$CF_3CH{=}CHCl$, and α is the yield of $CF_3CHClCHO$ from reaction of Cl atoms with t-$CF_3CH{=}CHCl$. The nonlinear fit to the $CF_3CHClCHO$ data shown in Fig. 3 (140 Torr air), is a fit to expression (V) yielding $\alpha = 46 \pm 3\%$, and $k_{34}/k_6 = (0.157 \pm 0.014)$. The stated uncertainty in the yield includes two standard deviations to the fit and an estimated 5% uncertainty in the calibration of our $CF_3CHClCHO$ reference spectrum.

Fig. 6 shows a plot of $[CF_3CHClCHO]_t/[t\text{-}CF_3CH{=}CHCl]_o$ *versus* $\Delta[t\text{-}CF_3CH{=}CHCl]/[t\text{-}CF_3CH{=}CHCl]_o$ for the nine experiments in which the oxygen concentration was varied from 10 Torr to 700 Torr, including one experiment in the presence of NO_x in air. Results of the nonlinear fit of expression (V) to the data in Fig. 6 are given in Table 1. The yield (α) of $CF_3CHClCHO$ varied between 35 and 48% as a function of O_2 partial pressure. The rate constant ratios k_{34}/k_6 should be the same for all $[O_2]$. Inspection of the results in Table 1 reveals that k_{34}/k_6 is indistinguishable within the uncertainties throughout the different O_2 partial pressures employed in this work. Taking the average of the nine determinations with error limits that encompass the extremes of the individual determinations gives $k_{34}/k_6 = 0.144 \pm 0.038$. Using $k_6 = 5.22 \times 10^{-11}$

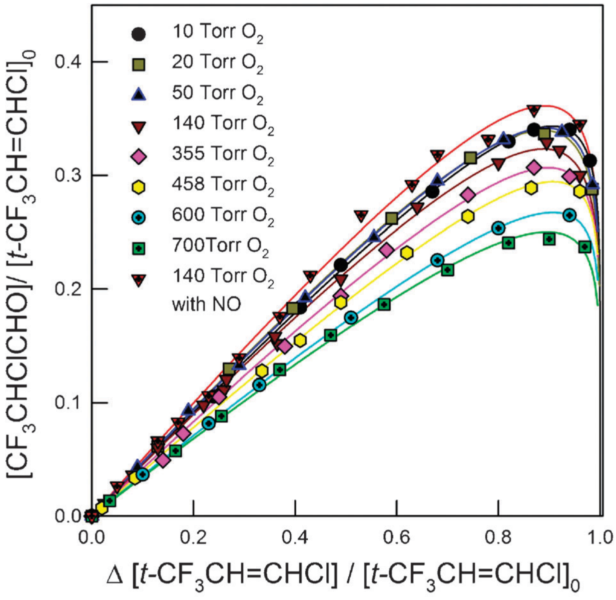

Fig. 6 Yield of $CF_3CHClCHO$ following the Cl initiated oxidation of t-$CF_3CH{=}CHCl$ in 700 Torr total pressure of N_2/O_2 diluent at 296 K with $[O_2]$ = 10 Torr (circles), 20 Torr (squares), 50 Torr (upward triangles), 140 Torr (downward triangles), 355 Torr (diamonds), 458 Torr (hexagons), 600 Torr (x-haired circles), 700 Torr (x-haired squares) and 140 Torr with NO added (x-haired triangles). The lines through the data are fits of expression (V) to the data.

to put k_{34} on an absolute scale gives $k_{34} = (7.5 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The value for k_{34} determined in this work appears in good agreement with expectations based on the rate constant for the reaction of Cl atoms with similar compounds, *e.g.*, $k(\text{Cl} + \text{CHClFCHO}) = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported by Scollard *et al.*[23] Although aldehydes are moderately reactive species, $CF_3CHClCHO$ is a factor of 7 less reactive towards Cl atoms than *t*-$CF_3CH{=}CHCl$.

We also do not have a sample of $CF_3CHClCOCl$. The yield of $CF_3CHClCOCl$ in the experiments discussed in Section 3.1 did not show any sign of decreasing, even at high consumptions of *t*-$CF_3CH{=}CHF$. Secondary reaction of $CF_3CHClCOCl$ could lead to the formation of CF_3COCl. In some of the experiments conducted in 700 Torr of air (140 Torr O_2), the reaction mixture was subjected to further radiation after all of the *t*-$CF_3CH{=}CHCl$ was consumed and no discernable decrease in the IR feature at 1850 cm^{-1} was observed during these extended periods of radiation. We conclude that the reactivity of Cl atoms towards $CF_3CHClCOCl$ is likely on the order of 10^{-14} cm^3 molecule^{-1} s^{-1} and any contribution of $CF_3CHClCOCl$ oxidation to the formation of CF_3COCl is expected to be negligible.

3.6 Cl atom initiated oxidation of *t*-$CF_3CH{=}CHCl$ in the presence of NO_x

Reaction of alkyl peroxy radicals with NO can produce alkoxy radicals possessing internal excitation that is comparable to, or greater than, the barrier to decomposition. A limited set of experiments were conducted to determine if chemical activation is an important factor in the fate of $CF_3CH(O)CHCl_2$ and $CF_3CHClCHClO$ radicals. Panel D in Fig. 2 shows the carbonyl region of the residual product spectra obtained for an experiment employing 6.03 mTorr *t*-$CF_3CH{=}CHCl$, 101 mTorr Cl_2 and 25.6 mTorr NO in 700 Torr of air. When compared to the spectra obtained in the absence of NO_x (Fig. 2, panels A though C), clear differences emerge in the relative distribution of the carbonyl containing products. Instead of three broad C=O stretch bands in the region 1725–1850 cm^{-1}, only one major carbonyl IR absorption feature at 1757 cm^{-1}. This feature resembles closely the absorption band which we earlier attributed to $CF_3CHClCHO$. Close inspection of the residual spectrum in panel D also reveals smaller IR features at 1710 and 1754 cm^{-1}, the latter slightly overlapping with the band at 1757 cm^{-1}. These minor bands are presumably due to the formation of alkyl, and possibly acylperoxy nitrates formed in the chamber in the presence of high concentrations of NO_x.

A total carbon balance of 99 ± 14% was obtained in the experiment conducted in the presence of NO_x, with $CF_3CHClCHO$ being the major product (51 ± 11%). In addition to major differences in product yields for $CF_3CHClCHO$, CF_3CHO and CF_3COCl, relative to the experiments conducted in the absence of NO_x (see Fig. 4), the yields remained linear even at high (>60%) fractional consumptions of *t*-$CF_3CH{=}CHCl$. This is in stark contrast to the observed behavior in the absence of NO_x (see Fig. 3).

The alkyl radicals produced in reaction (7) will react with O_2 to give peroxy radicals, $CF_3CHClCHClO_2$ and $CF_3CH(O_2)CHCl_2$, which are then converted into alkoxy radicals, either *via* self- and cross-reactions or, when NO is present, *via* reaction with NO:

$$CF_3CHClCHClO_2 + NO \rightarrow CF_3CHClCHClO + NO_2 \tag{35a}$$

$$CF_3CH(OO)CHCl_2 + NO \rightarrow CF_3CH(O)CHCl_2 + NO_2 \tag{35b}$$

The alkoxy radicals formed in reactions (35a) and (35b) may possess significant internal excitation. Let us first consider the fate of the alkoxy radical formed following addition of Cl atoms to the central carbon atom in *t*-$CF_3CH{=}CHCl$. Chemical excitation of $CF_3CHClCHClO$ radicals produced in reaction (35a) could result in a greater fraction of these radicals undergoing prompt decomposition. In this case, one would expect increased yields of both $CF_3CHClCHO$ *via* reaction (19c), and HCOCl and CF_3CHO *via* reaction (19a), (19b) and subsequent reactions. As seen from Table 1, the molar yields of CF_3CHO (37 ± 3%) and HCOCl (36 ± 2%) are approximately double those observed in the absence of NO_x in 700 Torr of air. A similar comparison for the yield of CF_3COCl (8 ± 1%) in the presence of NO_x to that in the absence of NO_x reveals a decrease by a factor of two. The sharply decreased yield of CF_3COCl in the experiment conducted in the presence of NO_x suggests that CF_3CHClO can potentially be formed with excess excitation in the reaction between NO and CF_3CHClO_2 radicals:

$$CF_3CHClO_2 + NO \rightarrow CF_3CHClO + NO_2 \tag{36}$$

If formed with excess excitation, a greater fraction of the resulting CF_3CHClO radicals may potentially undergo decomposition *via* C–C bond scission or elimination of a Cl atom to yield CF_3CHO. As neither CF_3CHO nor HCOCl are unique products of the decomposition of CF_3CHClO in the present system, it is difficult to assess the importance of chemical excitation in reaction (36).

Let us now consider the fate of the alkoxy radical formed following addition of Cl atoms to the terminal carbon atom in *t*-$CF_3CH{=}CHCl$. The $CF_3CH(O)CHCl_2$ radicals can either react with O_2 (reaction (11)), or decompose *via* C–C bond scission (reactions (12a) and/or (12b)). Chemically excited $CF_3CH(O)CHCl_2$ radicals produced in reaction (35b) could result in a greater fraction of the $CF_3CH(O)CHCl_2$ radicals undergoing decomposition *via* reactions (12a) and/or (12b). Increased decomposition of $CF_3CH(O)CHCl_2$ will result in enhanced yields of CF_3CHO and HCOCl. As discussed above, increased yields of CF_3CHO and HCOCl were observed in the presence of NO_x. Furthermore, the absence of C=O stretching bands at 1790 and 1825 cm^{-1}, indicates a much diminished importance of the formation of carbonyl containing compounds such as $CF_3C(O)CHCl_2$ and $CF_3CHClCOCl$ *via* reaction (11) and (18), respectively. As in the experiments conducted in the absence of NO_x, no product IR features attributable to $CHCl_2CHO$ were observed. With these differences in the product yields, it is clear that chemical activation plays a significant role in the fate of the alkoxy radicals, $CF_3CHClCHClO$, $CF_3CH(O)CHCl_2$ and possibly CF_3CHClO.

3.7 Products of the OH radical initiated oxidation of *t*-$CF_3CH{=}CHCl$

To investigate the products and mechanism of the reaction of OH radicals with *t*-$CF_3CH{=}CHCl$, reaction mixtures consisting of 30.7–98.5 mTorr *t*-$CF_3CH{=}CHCl$, 98.5–303 mTorr CH_3ONO and 10–700 Torr O_2 were introduced into the reaction chamber in a total pressure of 700–710 Torr N_2 and subjected to UV irradiation. Fig. 7 shows typical spectra acquired before (A) and after (B) a 27 minute irradiation of a mixture containing 30.9 mTorr *t*-$CF_3CH{=}CHCl$ and 301 mTorr CH_3ONO in 700 Torr of air. The consumption of *t*-$CF_3CH{=}CHCl$ was 26%. Comparison with reference spectra of CF_3CHO, HCOCl and HCl in panels C, D and E shows the formation of these species.

CF_3CHO and HCOCl were the only carbon containing products identified. Fig. 8 shows a plot of the formation of CF_3CHO, HCOCl and HCl (normalized to the initial concentration of *t*-$CF_3CH{=}CHCl$) *versus* the fractional loss of *t*-$CF_3CH{=}CHCl$. As seen from Fig. 8, there was no discernable effect of $[O_2]$ on the product distribution. Corrections ($<$22%) for loss of CF_3CHO and HCOCl *via* reaction with OH radicals have been applied to the data in Fig. 8. These corrections were computed using expression (II) (substituting k_1 for k_6) and $k_{\text{Product}}/k_1 = 6.5 \times 10^{-13}/4.4 \times 10^{-13}$ for CF_3CHO and $k_{\text{Product}}/k_1 = 3.2 \times 10^{-13}/4.4 \times 10^{-13}$ for HCOCl.[4,8,24] Corrections ($<$4%) have also been applied to the data obtained for HCl, to offset HCl produced by the secondary reaction of HCOCl with OH:

$$\text{HCOCl} + \text{OH} \rightarrow \text{ClCO} + \text{H}_2\text{O} \qquad (37)$$

$$\text{ClCO} + \text{M} \rightarrow \text{Cl} + \text{CO} + \text{M} \qquad (38)$$

$$\text{Cl} + \text{R}_{x\text{H}} \rightarrow \text{HCl} + \text{R}_{x\text{H}-1} \qquad (39)$$

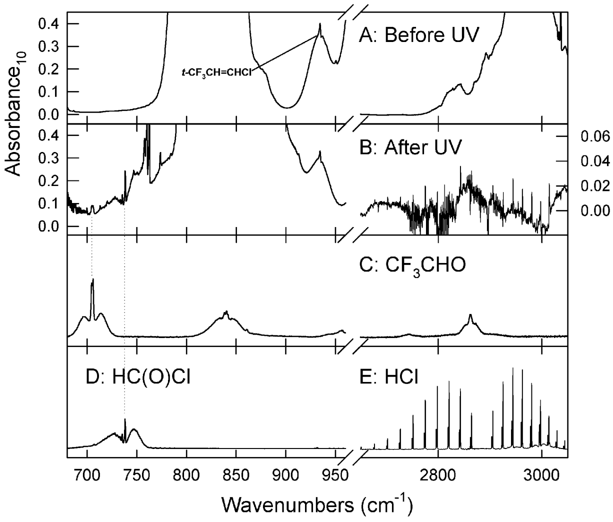

Fig. 7 The wave number ranges 680–960 and 2500–3200 cm^{-1} from IR spectra obtained (A) before and (B) after a 27 min UV irradiation of a mixture containing 30.9 mTorr *t*-$CF_3CH{=}CHC$ and 301 mTorr CH_3ONO in 700 Torr of air at 295 K. For the ease of spectral identification, IR features due to CH_3ONO_2 and HCHO have been subtracted from the right segment of panel B. Panels C, D and E show reference spectra of CF_3CHO, HCOCl and HCl.

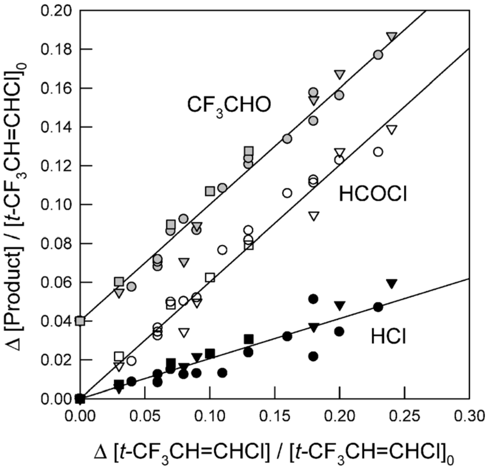

Fig. 8 Yields of CF_3CHO, HCOCl and HCl following the OH initiated oxidation of *t*-$CF_3CH{=}CHCl$ in the presence of NO in 700 Torr of air/O_2/N_2 diluent: squares, $[O_2]$ = 10 Torr; circles, $[O_2]$ = 140 Torr; triangles, $[O_2]$ = 700. For clarity, the CF_3CHO data have been vertically displaced by 0.04 units.

The lines through the data in Fig. 8 are least-squares regressions which give yields of 60 ± 5%, 60 ± 5% and 21 ± 6% for CF_3CHO, HCOCl and HCl, respectively.

By analogy to the well established oxidation mechanism of propene, the reaction of OH radicals with *t*-$CF_3CH{=}CHCl$ is expected to proceed *via* addition to the $>C{=}C<$ double bond. The simplest mechanism that explains the observed product formation is illustrated in Fig. 9.

Irrespectively of whether the OH radical adds to the terminal or central carbon atom, the subsequent reactions have the possibility of leading to one molecule of both HCOCl and CF_3CHO. Javadi *et al.*[11] studied the products of the OH radical initiated oxidation of the analogous fluorine-only substituted compound, *t*-$CF_3CH{=}CHF$, and found that CF_3CHO and HCOF were formed in yields of essentially 100%. The less than unity yield of CF_3CHO and HCOCl and the observation of HCl as a major product in OH initiated oxidation of *t*-$CF_3CH{=}CHCl$ is surprising. The formation of HCl as a primary product suggests a significant chlorine-elimination reaction pathway:

$$\text{CF}_3\text{CHCH(OH)Cl} + \text{M} \rightarrow \text{Cl} + \text{CF}_3\text{CH}{=}\text{CH(OH)} + \text{M} \qquad (40)$$

In the present system, free chlorine atoms will abstract hydrogen rapidly from available hydrocarbons to give HCl and alkyl radicals. Addition of OH to *t*-$CF_3CH{=}CHCl$ followed by elimination of the chlorine substituent will yield a polyfluorinated prop-1-en-1-ol, $CF_3CH{=}CHOH$. IR features belonging to $CF_3CH{=}CHOH$ were sought in the product spectra in the characteristic OH stretch region (3300–3700 cm^{-1}), but no distinctive bands were observed. While we have no reference spectrum for $CF_3CH{=}CHOH$ with which to compare, the detection of HCl is achieved using the characteristic IR features in the wave number range 2600–3100 cm^{-1} (see Fig. 7). Still, the total molar product yield observed is less than unity (81 ± 16%). This may reflect that, in addition to hydrogen abstraction, Cl atoms will also undergo addition to carbon–carbon

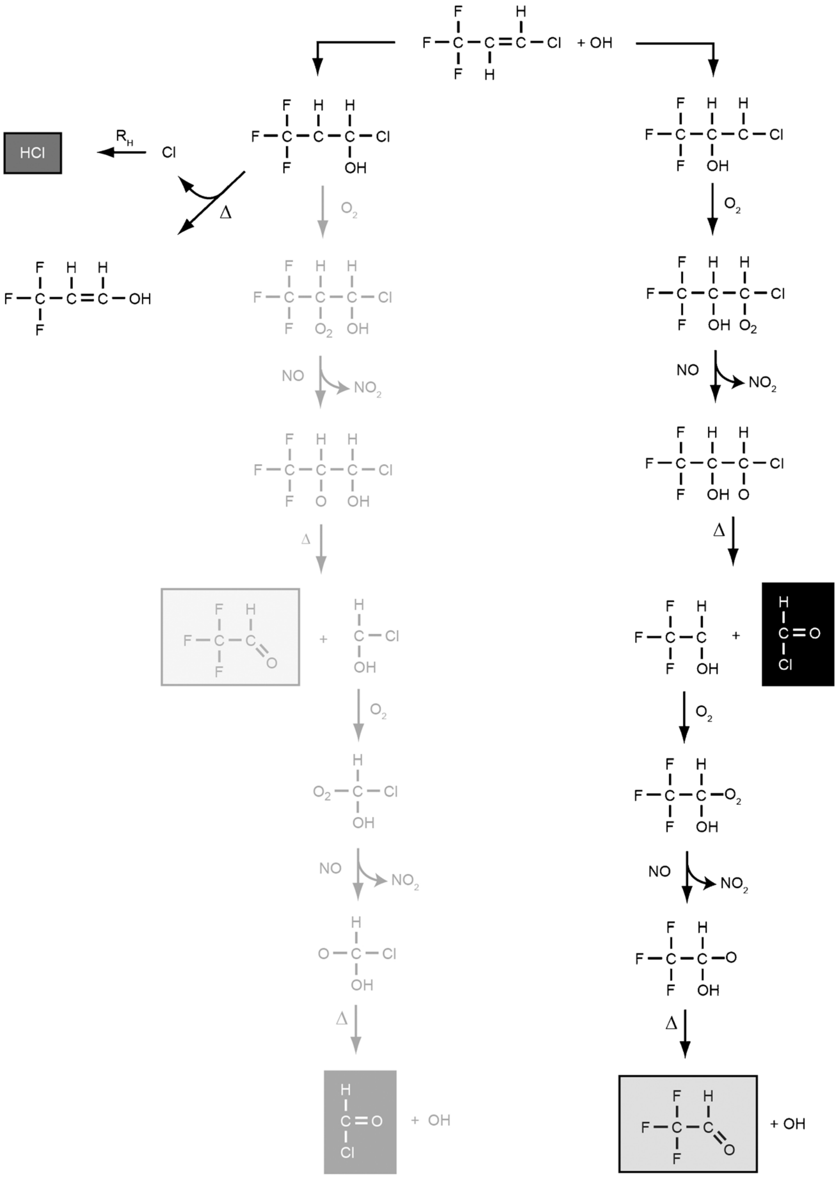

Fig. 9 Mechanism of the OH radical initiated oxidation of *t*-$CF_3CH{=}CHCl$ in the presence of NO_x. Rectangular boxes indicate the experimentally observed products.

double bonds, affecting the apparent consumption of *t*-$CF_3CH{=}CHCl$ and leading to products different from those resulting from the OH initiated oxidation. Thus, the observed yield of HCl (after correction for secondary chemistry of HCOCl) is a lower limit for the yield of Cl atoms in the enol-forming reaction pathway.

By analogy to the similar reactions in the oxidation of $CH_3CH{=}CH_2$,[25] it is expected that small amounts of the alkyl nitrates, $CF_3CH(OH)CHClONO_2$ and $CF_3CH(ONO_2)$-CHClOH will be formed in the reaction of the peroxy radicals with NO. Unfortunately, our experimental method is not sufficiently sensitive to detect these species. As shown in Fig. 9, the observed products, CF_3CHO and HCOCl, cannot be unambiguously assigned to a single reaction pathway on the basis of this study. A different line of argument has to be evoked to access the relative importance of OH addition at the terminal and central carbon atom, respectively. As seen from Fig. 8, the yields of CF_3CHO, HCOCl and HCl appear to be independent of O_2 partial pressure. The absence of a $[O_2]$ dependency on the yield of HCl suggests that the $CF_3CHCHCl(OH)$ radicals undergo decomposition on a timescale too short for the bimolecular reaction (41) to compete:

$$CF_3CHCH(OH)Cl + O_2 \rightarrow CF_3C(OO)HCH(OH)Cl \quad (41)$$

On the basis of this evidence, we propose that decomposition *via* chlorine elimination is likely the sole fate of $CF_3CHCH(OH)Cl$, and that CF_3CHO and HCOCl atoms are predominantly, if not exclusively, formed through the reaction channel initiated by addition of OH to the central carbon. Hence, the addition of OH radicals to the terminal and central carbon atom would account for approximately 40% and 60% of reaction (1), respectively.

This is the first study of the OH radical initiated oxidation mechanism for *t*-$CF_3CH{=}CHCl$. Perry *et al.*[26] investigated the reaction of OH radicals with vinyl halides and found the halogen elimination channel thermochemically favorable for vinyl halides containing Cl or Br, but not F. This may serve to explain the marked difference in observed reaction pathways for *t*-$CF_3CH{=}CHCl$, when compared to *t*-$CF_3CH{=}CHF$.[11] Based on heat of formation, prop-1-en-1-ol has been calculated to be less stable than its corresponding oxo form, propanal, and will exist only in negligible amounts in a keto–enol mixture, but the keto–enol tautomerization has a significant energy barrier in the uncatalysed gas-phase.[27] It is thus unclear if our enol tautomer, $CF_3CH{=}CHOH$, which may also be stabilized through fluorine mediated hydrogen bonding, would tautomerize to the aldehyde configuration. IR features belonging to CF_3CH_2CHO were sought in the product spectra but were not observed. However, reaction of OH radicals with CF_3CH_2CHO proceeds quickly $k(OH + CF_3CH_2CHO)/k_1 \approx 6$,[4,10] and would render the detection of CF_3CH_2CHO in the present system difficult. If $CF_3CH{=}CHOH$ is stable in the chamber, reaction of OH radicals with $CF_3CH{=}CHOH$ is expected to proceed rapidly through addition of OH radicals to the carbon–carbon double bond, followed by reaction with O_2 and/or decomposition to yield, CF_3CHO, HCHO and HCOOH. Unfortunately, HCHO and HCOOH are also byproducts of the photolysis of CH_3ONO, rendering these species of no value as further evidence for the formation of $CF_3CH{=}CHOH$.

4. Atmospheric implications

We present the results of the first study of the atmospheric oxidation mechanism of *t*-$CF_3CH{=}CHCl$. The major products in the Cl atom initiated oxidation of *t*-$CF_3CH{=}CHCl$ were $CF_3CHClCHO$ and $CF_3C(O)CHCl_2$, minor products were CF_3CHO, HCOCl and CF_3COCl. Chemical activation plays a significant role in the fate of $CF_3CHClCHClO$, $CF_3CH(O)CHCl_2$, and possibly CF_3CHClO, radicals in the system. The dominant atmospheric fate of *t*-$CF_3CH{=}CHCl$ is addition of OH radicals to the $>C{=}C<$ double bond. The OH radical initiated oxidation of *t*-$CF_3CH{=}CHCl$ in one atmosphere of air gives CF_3CHO and HCOCl in molar yields of approximately 60%. Chamber experiments indicate a significant decomposition channel involving chlorine elimination with formation of the fluorinated enol $CF_3CH{=}CHOH$, although the latter product was not observed directly in the residual spectra. There are competing fates for Cl atoms and the observed yield of HCl (approximately 20%) gives only a lower limit for the importance of a chlorine elimination channel. The observed products of the OH initiated oxidation of *t*-$CF_3CH{=}CHCl$ accounts for 81 ± 16% of the total carbon balance. It is possible that the enol forming pathway also accounts for the remaining unidentified products, but in the absence of a genuine reference spectrum for $CF_3CH{=}CHOH$, this is difficult to confirm. Computational studies would be helpful in this regard, but beyond the scope of this work.

The atmospheric fate of the oxidation product HCOCl is expected to be incorporation into rain, cloud and fog water followed by hydrolysis and removal by wet deposition, within probably 5–15 days.[28] Hydrolysis of HCOCl gives formic acid which is a ubiquitous component of the environment and is of no concern. The dominant fate of CF_3CHO is photolysis resulting in an estimated atmospheric lifetime of ≤ 2 days.[29] Photolysis of CF_3CHO gives CF_3 and HCO radicals while reaction with OH, which is of lesser importance, but also represents a sink for CF_3CHO, gives CF_3CO radicals.[30] Atmospheric degradation routes by which CF_3CO radicals can be transformed into CF_3COOH (TFA) as a minor (<10%) product have been documented.[31] TFA is a natural trace component of the oceanic environment[32] and any additional burden from *t*-$CF_3CH{=}CHCl$ oxidation will be negligible. The remaining oxidation fragments will be converted into CO_2 and HF through oxidation and hydrolysis.[33] No long-lived chlorine containing oxidation products were identified in the OH radical initiated oxidation of *t*-$CF_3CH{=}CHCl$. The atmospheric fate of the hypothesized oxidation product, $CF_3CH{=}CHOH$, is likely reaction with OH (directly, or indirectly *via* reaction with the tautomer CF_3CH_2CHO) to yield CF_3CHO, HCHO and HCOOH. With an estimated atmospheric lifetime of 26 days[4] for *t*-$CF_3CH{=}CHCl$, any contribution from *t*-$CF_3CH{=}CHCl$ oxidation to the stratospheric Cl atom loading will be insignificant (the Ozone Depletion Potential (ODP) has recently been estimated at 0.00034[34]). At the anticipated levels in the environment, the atmospheric oxidation products of *t*-$CF_3CH{=}CHCl$ are not of concern.

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