Low-temperature oxidation pathways are critical to thermal incineration of PFAS-laden materials

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ABSTRACT

With growing desire to destroy per- and poly-fluoroalkyl substances (PFAS) now known to be detrimental to human health, a sound understanding of fluorocarbon combustion chemistry is important to efficient thermal destruction within incinerators. While most fluorocarbon combustion models and the sets of reactions contained within them were originally developed for the high temperatures encountered in flame suppression applications, they have often been used to assess PFAS destruction in incinerators, which emphasize a lower range of temperatures. We present results that demonstrate that low-temperature fluorocarbon oxidation pathways—not yet known to play a role in fluorocarbon combustion—impact key incinerator performance metrics, including: PFAS surrogate mole fractions, products of incomplete destruction, and waste destruction efficiencies. The results further point to the utility of NO as a potential additive. The present results show the influence of these pathways for CF_3O_2, for which some data are available, but analogous pathways would also occur for other fluoroalkylperoxy radicals, for which little is known. The results demonstrate the need for future work to identify and characterize low-temperature pathways more generally, consider such pathways in kinetic model development, and experimentally probe intermediate temperature conditions to better understand, design, and control thermal destruction technologies for improved PFAS management.

1. Introduction

Throughout the world, per- and poly-fluoroalkyl substances (PFAS) have seen widespread use across an astonishing range of applications that include firefighting foams, energetic materials and munition components, heat transfer fluids for semiconductor manufacturing, stain- and water-resistant coatings for active wear, and non-stick cookware and food packaging, among countless others (Shojaei et al., 2022; Dewapriya et al., 2023; Wallace et al., 2023). Due to their widespread use and long-lasting nature, PFAS – aptly coined "forever chemicals" – have been detected at significant concentrations in water, air, soil, food, animals, and humans that continue to increase at an alarming rate (Borthakur et al., 2021; Zhang et al., 2021; Lasee et al., 2022). It is now widely believed that PFAS exposure at elevated concentrations can lead to serious health complications in humans (e.g., reduced infant birth weights) – prompting efforts to both phase out their future use and safely dispose of PFAS-laden materials from prior uses.

A common approach to destroying PFAS (like many other hazardous wastes) is thermal destruction within incinerators (Altarawneh et al., 2022; Winchell et al., 2021), where the elevated temperatures and radicals produced during their co-combustion with hydrocarbon fuels and/or other wastes lead to the conversion of PFAS to HF and other compounds. In this regard, knowledge of the key reaction pathways – and associated predictive models – are of paramount importance in ensuring their efficient destruction with minimal formation of undesirable compounds (e.g. species that are highly toxic or have high global warming potential) over wide ranges of incinerator conditions (including variations in temperature and waste composition).

Essentially all combustion kinetic mechanisms for fluorocarbons to date find their basis in those developed for the evaluation of

fluorocarbons as flame suppressants. Consequently, fluorocarbon combustion models have primarily been validated against experimental data from shock tubes (Takahashi et al., 1998; Yamamori et al., 1999; Yamamoto et al., 2005; Mathieu et al., 2023) and flames (Saso et al., 1998; Takahashi et al., 2019, 2020). Likewise, these models are primarily composed of high-temperature, flame-relevant kinetic pathways for fluorocarbon combustion, i.e. unimolecular decomposition reactions and abstraction reactions by radicals. Due to the burgeoning interest in PFAS destruction, there has been considerable recent literature focused on improving such mechanisms and, more specifically, the rate constants for the known reactions within them (Sharma et al., 2023; Burgess and Manion, 2021; Burgess et al., 2022a,b; Babushok et al., 2021a,b; Linteris and Babushok, 2020).

While these kinetic models were originally developed for high temperature flame suppression applications, they have often been used to assess PFAS destruction in incinerators (Tsang et al., 1998; Altarawneh et al., 2022; Narimani et al., 2022), which emphasize a lower range of temperatures (~ 700–1400 K). At such temperatures, hydrocarbons are well known to engage in a very different set of low-temperature chemical pathways (Zádor et al., 2011; DeSain et al., 2003; Taatjes, 2006) involving oxygen addition to alkyl radicals (R)

$$R + O_2 \leftrightarrow RO_2 \tag{RI}$$

to form alkylperoxy radicals (RO_2), which can lead to an internal H abstraction (whose fluorocarbon counterpart would be energetically unfavorable – at least for internal F abstraction, owing to the very strong C-F bond), self-reaction, and/or cross-reaction with other RO_2, e.g.

$$RO_2 + RO_2 \leftrightarrow RO + RO + O_2 \tag{RII}$$

Interestingly, while low-temperature fluorocarbon oxidation pathways are known to be important to atmospheric chemistry (Burkholder et al., 2020; Atkinson et al., 1989, 2007), they are not included within present fluorocarbon combustion models, even though they are likely important to the intermediate temperature ranges encountered in incinerators based on analogous low-temperature hydrocarbon oxidation pathways known to be critical to combustion behavior.

Furthermore, within the context of hydrocarbon combustion, the mediating radicals in this low-temperature sequence are known Dagaut and Nicolle (2005) to provide a means of coupling with NO_x kinetics via the (typically barrierless) radical-radical reactions

$$RO_2 + NO \leftrightarrow RO + NO_2 \tag{RIII}$$

$$R + NO_2 \leftrightarrow RO + NO \tag{RIV}$$

which effectively catalyze the conversion of R to RO. This sequence, and coupling with NO_x kinetics in general, could be important to PFAS evolution in incinerators given that NO_x can be formed during combustion of any fuel in air and could reach high fractions when nitrogen is a co-occurring element in the waste stream or plasma is used to enhance the destruction process. For context, nitrogen-containing PFAS have been found near AFFF testing sites Barzen-Hanson et al. (2017) and PFAS-laden materials may comprise nitrogen compounds in the form of fertilizers on agricultural lands, unexploded ordinance on military sites, or synthetic fabrics in clothing and protective equipment. Likewise, based on our results shown below, this catalytic NO_x sequence points to the potential value of NO_x as a promising waste stream additive. While such reactions are known to be important in atmospheric chemistry and electronics fabrication, interactions of fluorinated compounds with NO_x have apparently not been considered previously within the context of PFAS incineration.

Therefore, the objective of the present work is to provide a first study on the role of these low-temperature fluorocarbon oxidation pathways in PFAS incineration and the role of their mediating RO_2 radicals in coupling with NO_x. In particular, this study focuses on the role of pathways mediated by CF_3O_2 as a case study, for which limited kinetic

data are available (despite its exclusion from fluorocarbon combustion mechanisms).

2. Simulation methods

Simulations Goodwin et al. (2022) were conducted for models without ('nominal') and with ('modified') the CF_3O_2 reaction set presented in Table 1. Both models were assembled by combining the CFHO model of Babushok et al. (2021b) and Burgess et al. (2022b) with the CHNO model of Glarborg et al. (2018). The influence of CF_3O_2 kinetics and NO_x addition was explored using plug flow reactor simulations representative of incinerators (similar to prior work on incinerator kinetics (Tsang et al., 1998; Babushok et al., 1995)). Analogous perfectly stirred reactor simulations were also performed, but those results are not shown here as they exhibited similar trends. For simplicity and clarity, equivalence ratios were calculated assuming the fuel was 100% C_2H_6 – 10% of each resulting fuel mole fraction was then replaced with an equivalent number of CHF_3 moles.

3. Results and discussion

Results are shown in Figs. 1–3 for a waste stream consisting of a representative fluorocarbon (CHF_3, whose primary abstraction product is CF_3), auxiliary fuel (C_2H_6), and air with and without NO addition.

As shown in Fig. 1, inclusion of CF_3O_2 kinetics yields a 5-fold peak reduction in and a much stronger equivalence ratio dependence for predictions of CF_3-CF_3, an important species often used as a PFAS destruction surrogate and known for its extraordinarily high global warming potential. Likewise, Fig. 2 reveals that inclusion of CF_3O_2 kinetics for simulations with NO addition yields a 3-fold peak increase in and stronger equivalence ratio dependence for predictions of CF_2O (an exceedingly toxic and corrosive PIC). Finally, Fig. 3 shows that NO addition and CF_3O_2 kinetics also influence overall destruction efficiencies – 1000 ppm NO addition yields a ~ 50 K reduction in the predicted onset temperature for CHF_3 destruction that increases to a ~ 75 K reduction when CF_3O_2 kinetics are added to the nominal model.

4. Conclusions and future work

Altogether, the results demonstrate that low-temperature

Table 1
The selected CF_3O_2 reaction set.

R#	Reaction	A	n	E_a	Ref.
1	$CF_3 + O_2 (+M) \leftrightarrow CF_3O_2 (+M)$				Burkholder et al. (2020)
	Low pressure limit	8.87×10^{28}	-4.00	0.00	
	High pressure limit	5.38×10^{14}	-1.00	0.00	
2	$CF_3O_2 + CF_3O_2 \leftrightarrow CF_3O + CF_3O + O_2$	1.02×10^{12}	0.00	0.00	Atkinson et al. (2001)
3	$CF_3O_2 + HO_2 \leftrightarrow CF_3OOH + O_2$	7.83×10^{10}	0.00	-1569.80	Hayman et al. (1994)
4	$CF_3O_2 + CO \leftrightarrow CF_3O + CO_2$	3.01×10^{08}	0.00	0.00	Burkholder et al. (2020)
5	$CF_3O_2 + NO \leftrightarrow CF_3O + NO_2$	3.25×10^{12}	0.00	−635.90	Burkholder et al. (2020)
6	$CF_3O_2 + OH \leftrightarrow CF_3O + HO_2$	2.41×10^{13}	0.00	0.00	Biggs et al. (1997)
7	$CF_3O_2 + H \leftrightarrow CF_3O + OH$	6.62×10^{13}	0.00	0.00	Biggs et al. (1997)
8	$CF_3O_2 + O \leftrightarrow CF_3O + O_2$	3.61×10^{13}	0.00	0.00	Ravishankara et al. (1994)

units: length = cm, time = s, quantity = mole, activation energy = cal/mol, temperature = K modified Arrhenius expression coefficients: $k = AT^n e^{-E_a/RT}$
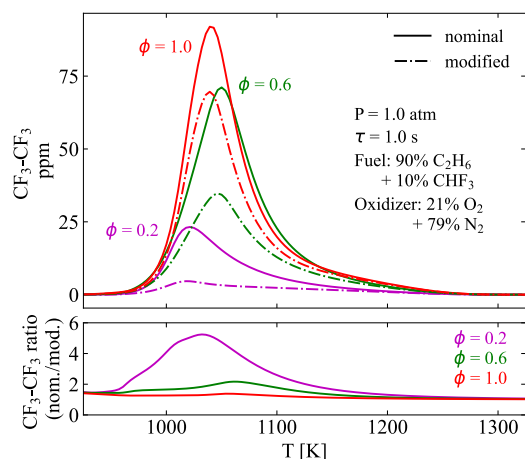
Fig. 1. Predicted CF_3-CF_3 mole fractions from isothermal plug flow reactor simulations for models with and without CF_3O_2 kinetics (top) and their ratio (bottom) for the conditions indicated.
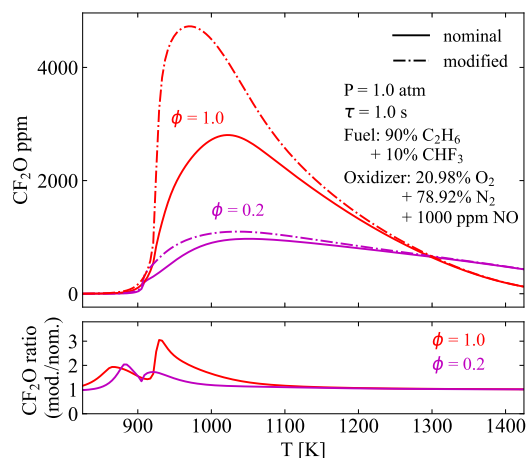

Fig. 2. Predicted CF_2O mole fractions from isothermal plug flow reactor simulations for models with and without CF_3O_2 kinetics (top) and their ratio (bottom) for the conditions indicated.
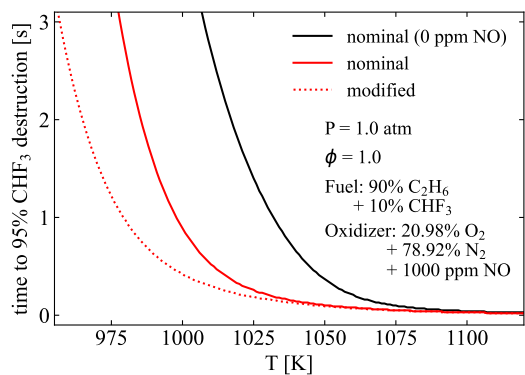

Fig. 3. Predicted times to 95% CHF_3 destruction in isothermal plug flow reactor simulations for the model without CF_3O_2 kinetics without NO addition and for models with and without CF_3O_2 kinetics with 1000 ppm NO addition.

fluorocarbon oxidation pathways play a critical role in the evolution of multiple key species during PFAS incineration and point to the utility of NO as a potential additive. While these pathways are first explored here for one fluorocarbon-derived RO_2 for which limited kinetic data are available, analogous pathways are likely to occur for other

fluorocarbon-derived RO_2, whose characterization would be a worthwhile topic for future study and future inclusion in fluorocarbon incineration models. In fact, even more significant impacts might be expected for larger fluorine-containing RO_2 that also contain H—such that internal abstraction to yield carbon-centered QOOH radicals (Zádor et al., 2011; Hansen et al., 2021) responsible for radical chain branching may be energetically favorable. Furthermore, given that the rate constants in Table 1 are based on limited studies near atmospheric temperature (where the only kinetic data are available) and would correspondingly have high uncertainties at higher temperatures, the results highlight the need for rate constant studies at higher temperatures and a broader set of kinetic pathways even for CF_3O_2. Likewise, the present results emphasize the need for experimental combustion validation data at intermediate temperatures, which are much less studied than previous literature oriented to fluorocarbons as flame suppressants.

CRediT authorship contribution statement

Cornell Rodger E.: Data curation, Formal analysis, Investigation, Validation, Writing – original draft, Visualization. **Burke Michael P.:** Conceptualization, Investigation, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2023.100100.

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