2. Chlorofluorocarbon (CFC) Substitutes and Their Potential Impact on Climate Change

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Abstract:

Hydrofluoroethers (HFEs) are promising next-generation climate-friendly compounds that can substitute ozone-depleting substances like ((chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs)) and other potent greenhouse gases ((Hydrofluorocarbon (HFC)) compounds. These alternative compounds, used in various industrial applications (e.g. detergents, propellants, solvents, lubricants, etc.) have shorter atmospheric lifetime due to bond activation by the presence of ether oxygen. However, these compounds have -CF_3- *and* -CF_2- *groups, making it a very active fluorinated greenhouse gas (GHG) in the atmosphere. In this chapter, we present kinetic data for few selected hydrofluoroethers* ($CF_3CF_2OCH_3$, $CHF_2CF_2OCHF_2$, $CF_3CF_2CF_2OCH_3$, $CF_3CF_2CF_2CF_2OCH_3$, $CF_3CH_2OCH_2CF_3$, *and* $CHF_2CF_2OCH_2CF_3$) *calculated using computational quantum chemistry and transition state theory. Our study discusses factors affecting climate change, include atmospheric lifetime, radiative efficiency, and global warming potential of these compounds. Therefore, the information presented here will expand the database for future applications and assess the suitability of HFE as a CFC replacement.*

Keywords:

Chlorofluorocarbon; Greenhouse Gases; Hydrofluoroether; Global warming Potential.

2.1 Introduction:

Global warming is not a myth but a well-accepted environmental problem caused by the cumulative accumulation of greenhouse gases observed in the stratosphere over the past four decades. Back in the 1970s, M. J. Molina and F. S. Roland discovered the loss of stratospheric ozone and recognized that man-made gases, fully halogenated chlorofluorocarbons (CFCs), posed a serious threat to the ozone layer.[1] They postulated a theory that unusually stable chlorofluorocarbons may migrate up the atmosphere over time and be destroyed by intense radiation, releasing chlorine atoms that catalyze ozone depletion and cause the Antarctic "ozone hole", as shown in Figure 2.1.

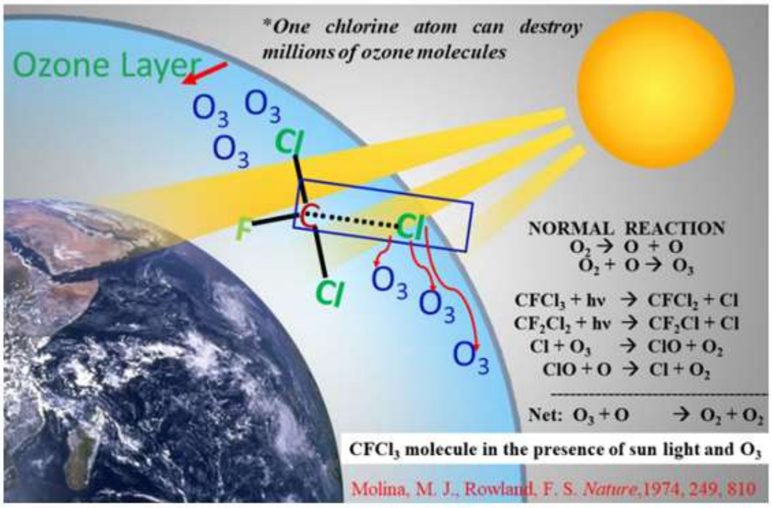

Figure 2.1: Stratospheric photodissociation of CFCl3 and Cl atom-catalyzed ozone destruction process

This breakthrough insight brought global attention to the scientific community, led to widespread awareness of the need to limit CFC production, and inspired a collective determination to find better alternative compounds for industrial and commercial appliances, such as refrigerants, detergents, propellants, solvents, lubricants, etc.

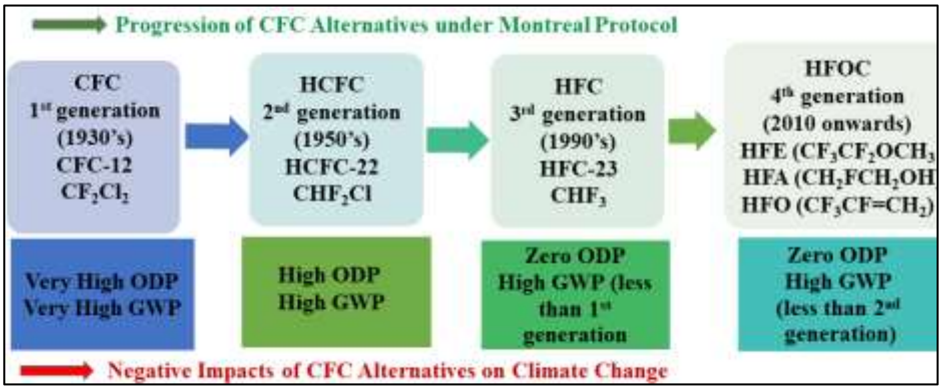

Figure 2.2: Progress of CFC alternatives and their negative effects and one of their representative compounds GWP and ODP indicate global warming potential and ozone depletion potential

In 1987, the Montreal Protocol, an international treaty designed to protect ozone layer, which stipulated the phasing out CFCs, HCFCs and other ozone-depleting substances (ODS) globally, while replacing them by hydrofluorocarbons (HCFCs) which have zero ozone-depleting potential (ODP) due to the absence of chlorine atoms.[2] However, due to the early focus on protecting the ozone layer, the scientific community and policy makers have paid little attention to the enormous global warming potential (GWP) of HFCs.[3] Recent disclosures of this potential climate impact have have sparked debate over the Montreal Protocol.

This led to further amendment of Montreal Protocol[4,5] and various other amendments such as the Kyoto protocol,[6] the 2016 Kigali Amendment,[7] the Paris agreement[8] etc. The further revised critique calls for developed countries and the rest of the world to phase out 85% of high-GWP HFCs by 2036.[9,10] In addition, there has been an unexpected and sustained increase in global emissions of the ozone-depleting substance CFC-11 recently showing: Unreported new production is on the rise.[11,12] This is inconsistent with the Montreal Protocol's agreement to phase out global CFC production by 2010, causing delays in the recovery of the ozone hole.[13,14] To this end, the global scientific community has made every effort to replace these compounds with low-GWP candidates.

In recent years, oxygenated hydrofluorocarbons (HFOCs) such as hydrofluoroethers (HFE), hydrofluoroalcohols (HFA), and hydrofluoroolefins (HFO) have emerged as a promising next-generation CFC replacement for various applications.[15-36] These compounds do not contain chlorine, therefore not harmful to the ozone layer, and ODP.

In this regard, the relative applicability of HFOCs to CFCs will be determined primarily by measuring their GWP indices.[37,38] However, these compounds have $-CF_3-$ and $-CF_2-$ groups, and the presence of C-F bonds in these compounds can effectively absorb the infrared radiation emitted by the earth, enhancing their role as effective greenhouse gases (GHG). These gases contribute to the GWP. Therefore, before large-scale commercialization and industrialization, it is necessary to understand their lifetime in the atmosphere to assess their impact on the environment, especially their GWP, which needs to be thoroughly evaluated to determine their suitability as a CFCs substitute.

In general, tropospheric oxidation of volatile organic compounds (VOCs) is initiated by short-lived radicals such as OH, HO_2•, and RO_2• (peroxy) radicals, mainly OH radicals via hydrogen abstraction reactions. Although the reaction with OH radicals is the main removal pathway for HFOCs in the troposphere, the reaction with Cl atoms may also make an important contribution to the removal process in coastal or oceanic boundary layers or in polluted urban area. The computational research focus of tropospheric chemistry has grown rapidly in recent years, allowing advanced quantum chemical theory to be applied to solutions with near-experimental precision.[27-36,39]

In this chapter, we have chosen to discuss the kinetic data and climatic implications of the reactions of some selected hydrofluoroethers (HFEs)[15-36] such as non-segregated HFEs (CF_3OCH_3, $CF_3CF_2OCH_3$, $CHF_2CF_2OCHF_2$, $CF_3CF_2CF_2OCH_3$ and n-$CF_3CF_2CF_2CF_2OCH_3$) and segregated HFEs ($CF_3CH_2OCH_2CF_3$ and $CHF_2CF_2OCH_2CF_3$) with OH radicals and Cl atoms using computational quantum chemistry.

2.2 Computational Methods:

Electronic structure calculations on the gas-phase reaction of HFE with OH radicals and Cl atoms were carried out employing the Gaussian 09 program suite.[40] All the stationary points on the potential energy surface (PES) i.e. the reactants, products, transition states and reaction complexes were optimized using the DFT-based M06-2X[41,42] and MPWB1K[43] methods and *ab initio* MP2 method,[44] which has been shown to produce reliable results for kinetic studies of atmospheric molecular-radical reactions. Rate coefficient have calculated using BIRATE, GAUSSRATE,[45] and POLYRATE[46] was employed to carry out the kinetic calculations for the HFEs gas-phase reaction with OH radicals and Cl atoms using conventional transition state TST with Eckarts[47] tunneling and canonical variational transition state theory (CVT) with small curvature tunneling (SCT) corrections.[48]

2.3 Results and Discussions:

Table 2.1: Experimental and theoretical rate coefficients (cm^{3}molecule^{-1}s^{-1}) at 298 K of hydrofluoroethers and theoretical methods.

Compound	Calculated	Experimental	Method
CF_3OCH_3	$k_{OH}=6.9\times10^{-14}$ Ponnusamy et al.[27]	$(1.28\pm0.19)\times10^{-14}$ Østerstrøm et al.[15]	CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(d,p)
		$(1.4\pm0.2)\times10^{-13}$ Christensen et al.[16]	
$CF_3CF_2OCH_3$	$k_{OH}=1.09\times10^{-14}$ Lily et al.[28]	$(1.28\pm0.19)\times10^{-14}$ Østerstrøm et al.[15]	M06-2X/6-31+G(d,p)
		$(1.09\pm0.16)\times10^{-13}$ Østerstrøm et al.[16]	
$CHF_2CF_2OCHF_2$	$k_{OH}=1.01\times10^{-15}$ Lily et al.[29]	2.36×10^{-15} Chen et al.[17]	G2(MP2)// MPWB1K
	$k_{Cl}=4.55\times10^{-16}$ Baidya et al.[30]	5.5×10^{-16} Andersen et al.[18,19]	M06-2X/ 6-311++G(d,p)
$CF_3CF_2CF_2OCH_3$	$k_{OH}=0.77\times10^{-14}$ Mishra et al.[31]	$(1.18\pm0.05)\times10^{-14}$ Tokuhashi et al.[20]	M06-2X/ 6-31+G(d,p)
	$k_{Cl}=4.6\times10^{-14}$ Mishra et al.[31]	$(9.1\pm1.3)\times10^{-13}$ Bravo et al.[21]	M06-2X/ 6-31+G(d,p)
n-$CF_3CF_2CF_2CF_2OCH_3$	$k_{OH}=1.11\times10^{-14}$ Mishra et al.[32]	$(1.49\pm0.13)\times10^{-14}$ Bravo et al.[21]	M06-2X/ 6-31+G(d,p)
	$k_{Cl}=0.17\times10^{-13}$ Mishra et al.[32]	$(0.97\pm1.4)\times10^{-13}$ Wallington et al.[22]	M06-2X/ 6-31+G(d,p)
$CF_3CH_2OCH_2CF_3$	$k_{OH}=1.32\times10^{-13}$ Lily et al.[33]	1.30×10^{-13} Wilson et al.[23]	M06-2X/ 6-31+G(d,p)

Compound	**Calculated**	**Experimental**	**Method**
	$k_{Cl}=1.95\times10^{-13}$ Lily et al.[34]	$(7.1\pm0.9)\times10^{-13}$ Wallington et al.[24]	CCSD(T)//BHandHLY/6-311++G(d,p)
$CHF_2CF_2OCH_2CF_3$	$k_{OH}=1.01\times10^{-14}$ Lily et al.[35]	9.08×10^{-15} Tokuhashi et al.[25]	G2(MP2)//M06-2X /6-31+G(d,p)
	$k_{Cl}=1.21\times10^{-14}$ Lily et al.[36]	$(8.63\pm6.66)\times10^{-15}$ Papadimitriou et al.[26]	M06-2X/ 6-311++G(d,p)

Rate coefficient values k_{OH} and k_{Cl} calculated are listed in Table 1 along with the experimental values at 298K. The calculated k_{OH} values of $\sim10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} for non-segregated HFE (CF_3OCH_3, $CF_3CF_2OCH_3$, $CF_3CF_2CF_2OCH_3$, and n-$CF_3CF_2CF_2CF_2OCH_3$) with OH radicals at the M06-2X barrier height, which agreed well with the experimental values.

The calculated rate coefficients of $CF_3CF_2CF_2OCH_3$+Cl and $CF_3CF_2CF_2CF_2OCH_3$+Cl reactions are about 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, which are also in reasonable agreement with the experimental results. For the reaction of $CHF_2CF_2OCHF_2$ with OH radicals and Cl atoms, using G2(MP2)//MPWB1K method, the rate coefficient of the reaction with OH radicals is reduced by an order of magnitude to $\sim10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and by two orders of magnitude for reactions with Cl atoms by $\sim10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. This suggests that the substitution of hydrogen atoms for fluorine atoms reduces the reaction rate.

For the segregated HFE reaction with OH radicals, according to M06-2X/6-31+G(d,p) barrier height of $CF_3CH_2OCH_2CF_3$ + OH reaction and CCSD(T)//BHandHLY/6-311++G(d, p) method for the $CF_3CH_2OCH_2CF_3$ + Cl reaction is close to the experimental results, however, our calculated k_{Cl} is slightly higher than the experimental results by 3.64 times. For the $CF_3CH_2OCH_2CF_3$ + OH reaction, our calculated G2(MP2)//M06-2X/6-31+G(d,p) rate coefficient values are in good agreement, and recent experimental results are available, allowing us to confirm our kinetic model quality using the G2(MP2)//M06-2X/6-31+G(d,p) method. In fact, the G2(MP2)//M06-2X/6-31+G(d,p) method combined with DFT-level geometry optimization produces reliable kinetic results. CHF_2- sites ($k_1=0.566\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}) had slightly higher H-abstraction than $-CH_2$- sites ($k_2=0.450\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}). Our analysis suggests that this is mainly due to the presence of a large Arrhenius pre-exponential factor at the CHF_2-. For example, the Arrhenius pre-exponential factor of k_1 is 4.2×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K, and the Arrhenius pre-exponential factors of k_{2a} and k_{2b} are 2.5×10^{-13} and 2.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. To estimate the accuracy of the rate coefficient, we assume that there is an error of ±4 $kJmol^{-1}$ in the barrier heights calculated from the G2(MP2) results. Based on this estimate, k_{OH} at 298 K should be in the range of 1.9×10^{-15}–5.5×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. For the $CF_3CH_2OCH_2CF_3$+Cl reaction, our calculated M06-2X/6-311++G(d,p) rate coefficient values are in good agreement with the existing experimental results. From the obtained rate coefficient values, it can be seen that the segregated HFE reacts slightly faster with Cl atoms than with OH radicals. The lifetime of VOCs is an important parameter that is used to predict their future abundances which will directly contribute towards GWPs. The obtained rate coefficients will be used to estimate radiative efficiency (RE) and GWP.

2.4 Atmospheric Implications:

To determine the effectiveness of greenhouse gas of a compound over its atmospheric lifetime, RE one needs to calculate the GWP. The RE and GWP are useful metrics for assessing the relative impact of long-lived greenhouse gases, such as fluorinated ethers, on climate. These highly fluorinated compounds have vibrational stretching transitions associated with C-F bonds occurring in the atmospheric window 700-1250 cm^{-1}.[49,50] These compounds are absorbed by the atmospheric window, hindering the escape of terrestrial radiation and warming the Earth's surface.

A. Atmospheric Lifetime: The tropospheric lifetime (τ_{eff}) of HFEs is calculated assuming that their removal from the atmosphere is decided by the reaction with OH radicals and Cl atoms alone.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} \qquad (1)$$

B. Global Warming Potential (GWP: Global-warming potential is a relative measure of how much heat greenhouse gas traps in the atmosphere. The GWP is generally predicted based on the time-integrated radiative efficiency from the instantaneous emission of 1 kg of a compound relative to that of 1 kg of a reference gas (CO_2). It can be expressed as an absolute GWP for a gas i($AGWP_i$) by the AGWP of a reference gas (CO_2). Here, GWPs for HFEs are estimated (relative to CO_2) using the expression given by Hodnebrog et al.[42]

$$GWP_i(H) = \frac{\int_0^H RF_i(t)dt}{\int_0^H RF_{CO_2}(t)dt} = \frac{AGWP_i(H)}{AGWP_{CO_2}(H)} \qquad (2)$$

The radiative efficiency of HFE molecules was calculated using the relationship RE

$$RE = \sum_k A_v \, F(\bar{v}_k) \qquad (3)$$

where $A_k$is the absorption cross-section in cm^2 $molecule^{-1}$averaged over a 10 cm^{-1} interval around the wave number$(\vartheta_k)$and $F(\vartheta_k)$ is the instantaneous, cloudy sky, radiative forcing per unitcross section per wave number (($W\ m^{-2}\ cm\ (cm^2\ molecule^{-1})^{-1}$) evaluated at the band scaled center wave number (ϑ_k). The instantaneous RE is derived from a line-by-line model simulation in Oslo, and the adjusted Pinnock curve model is within 10% of the model-derived value.[54]

To understand the suitability of proposed HFEs replacements for ODS (CFCs and HCFCs) and high-GWP substances (HFCs), it is crucial to recognize the potential impact of this species on climate. When HFEs are released into the atmosphere from commercial and industrial sources, their primary fate is to react with OH radicals on a global scale and Cl atoms in the ocean boundary layer. HFE is estimated to have a significantly shorter atmospheric lifetime than CFCs and HFCs, resulting in less accumulation levels in the atmosphere. Although HFEs possess zero ODP when compared to CFCs and HCFCs, they still exhibit a considerable GWP and therefore can be classified as an active fluorinated gas.

Table 2.2: Atmospheric lifetime, radiative efficiency, and GWP-100-year time horizon (calculated values are given in brackets) for HFE and CFC-11, HCFC-21, and HFC-23 values obtained from WMO (2022).[43]

Reaction	**Lifetime (Years)**	**Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)**	**GWP- 100-year time horizon**
CF_3OCH_3	4.5 (4.82)[27]	0.189	660 (607)[27]
$CF_3CF_2OCH_3$	3.9 (4.99)[28]	0.296 (0.34)[28]	497 (754)[28]
$CHF_2CF_2OCHF_2$	35 (18.9)[30]	0.32 (0.638)[30]	4131 (4750)[30]
$CF_3CF_2CF_2OCH_3$	4.4 (5.1)[31]	0.343	579
n-$CF_3CF_2CF_2CF_2OCH_3$	1.2 (5.05)[32]	0.3	132 (59)[32]
$CF_3CH_2OCH_2CF_3$	79-270 days (87 days)[34]	0.19	21 (24)[34]
$CHF_2CF_2OCH_2CF_3$	3.14 (6.1)[36]	0.483	601 (964)[36]
CFC-11 (CCl_3F)	1770	0.299	5910
HCFC-21 ($CHCl_2F$)	1.82	0.145	161
HFC-23 (CHF_3)	243	0.192	14,700

2.5 Conclusion:

A new generation of CFC, HFC and HCFC substitutes has been commercialized in the market for various industrial applications with serious environmental concerns. To assess the environmental impact of new CFC, HFC and HCFC alternatives, it is important to study the greenhouse gas effects of the compounds in terms of atmospheric lifetime, radiative efficiency and GWP. To achieve scientific goals, the kinetic data and climatic influence factors of non-segregated HFE (CF_3OCH_3, $CF_3CF_2OCH_3$, $CF_3CF_2CF_2OCH_3$ and $CF_3CF_2CF_2CF_2OCH_3$) and segregated HFE ($CF_3CH_2OCH_2CF_3$ and $CHF_2CF_2OCH_2CF_3$) with OH radicals and Cl atoms were investigated using computational quantum chemistry, as they are considered as a potential replacement for CFC, HFC, HCFC in various industrial applications. In the evaluation of the kinetic data, we observed that the DFT theory at the M06-2X level is one of the best tools for developing the atmospheric H-abstraction reaction potential energy profile, which leads to accurate kinetic parameters when compared with existing experiments and reliable result values. The same basis sets were then used for single-point CCSD(T) and G2(MP2) calculations on the M06-2X and MPW1K optimized structures to improve the accuracy of the results. Rate coefficients for simple bimolecular reactions of atmospheric importance are estimated by using conventional transition state theory (TST). However, significant variation effects were observed in many H-abstraction reactions. Such reactions were treated using variational transition state theory (VTST).
From these observations, we have reported that theoretical calculations, especially kinetics, may be as good as laboratory studies when experimental data for a specific reaction are not available. Therefore, this knowledge should be useful in understanding future laboratory and field studies and in developing atmospheric modelling studies and climate impacts of HFEs. Therefore, this knowledge should be useful in understanding future laboratory and field studies and in developing atmospheric modelling studies. It is believed that this comprehensive report has answered some existing questions about the climate impact of

HFEs, thereby making an important contribution to policy formulation and economic development of green alternatives to CFCs, HCFCs and HFCs.

2.6 References:

1. M. J., Molina, F. S., Rowland, Nature, 1974, 249, 810–812.
2. G. J. M. Velders, D. W. Fahey, J. S. Daniel, S. O. Andersen, M. McFarland, Atmos. Environ., 2015, 123, 200–209.
3. X. Fang, A. R. Ravishankara, G. J. M. Velders, M. J. Molina, S. Su, J. Zhang, J. Hu, R. G. Prinn, Environ. Sci. Tech. 2018,52, 11359-11366.
4. G. J. M. Velders, A. R. Ravishankara, M. K. Miller, M. J. Molina, J. Alcamo, J. S. Daniel, D.W. Fahey, S.A. Montzka, S.Reimann, Science 2012, 335, 922–923.
5. P. J. Young, A. B. Harper, C. Huntingford, N. D. Paul, O. Morgenstern, P. A. Newman, L.D. Oman, S. Madronich, R. R. Garcia, Nature, 2021, 596, 384–388.
6. UNFCCC. Report of the Subsidiary Body for Scientific and Technological Advice on its twenty-eighth session, held in Bonn from 4 to 13 June 2008. Calculation of accounting quantities for activities under Article 3, paragraphs 3 and 4, of the Kyoto Protocol. (FCCC/SBSTA/2008/6, annex IV). Available at: http://unfccc.int/resource/docs/2008/sbsta/eng/06.pdf.
7. EIA: Kigali amendment to the Montreal Protocol–A Crucial Step in the Fight Against Catastrophic Climate Change, Environmental Investigation Agency (EIA) briefing to the 22nd Conference of the Parties (COP22) to the United Nations Framework Convention on Climate Change (UNFCCC), Marrakech, Morocco, 7–18 November, 2016.
8. X. Fang, A. R. Ravishankara, G. J. M. Velders, M. J. Molina, S. Su, J. Zhang, J. Hu, R. G Prinn, Environ. Sci. Technol., 2018, 52, 11359–11366.
9. J. Rogelj, M. den Elzen, N. Höhne, T. Fransen, H. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi, M. Meinshausen, Nature, 2016, 534, 631–639.
10. P. Purohit, L. Höglund-Isaksson, J. Dulac, N.Shah, M. Wei, P. Rafaj, W.Schöpp, Atmos. Chem. Phys. 2020, 20, 11305-11327.
11. X.Fang, G. J. M. Velders, A. R. Ravishankara, M. J. Molina, J. Hu, R. G. Prinn, Environ. Sci. Technol. 2016, 50, 2027–2034.
12. E. L. Fleming, P. A. Newman, Q. Liang, J. S. Daniel, J. Geophy. Res.: Atmos., 2020, 125, e2019JD031849.
13. M. Lickley, S.Solomon, S. Fletcher, G.J.M. Velders, J. Daniel, M. Rigby, S.A. Montzka, L. J. M. Kuijpers, K. Stone, Nat. Commun. 2020,11, 4, 1380.
14. S.S.Dhomse, W.Feng, S.A. Montzka, R. Hossaini, J. Keeble, J.A. Pyle, J.S. Daniel, M.P. Chipperfield, Nat. Commun. 2019, 10, 5781.
15. R. R. Cordero, S. Feron, A. Damiani, A. Redondas, J. Carrasco, E. Sepúlveda1, J. Jorquera, F. Fernandoy, P. Llanillo, P.M. Rowe, G. Seckmeyer, Sci. Rep. 2022, 12, 1266.
16. F.F. Østerstrøm, O.J. Nielsen, T.J. Wallington, Chem. Phys. Lett.2016, 653,149–154.
17. L.K. Christensen, T.J. Wallington, A. Guschin, M.D Hurley, J. Phys. Chem. A, 103, 4202–4208
18. M. P. S. Andersen, O. J. Nielsen, T. J. Wallington, M. D. Hurley and W. B. DeMore, J. Phys. Chem. A, 2005, 109, 3926–3934.
19. M. P. S. Andersen, M. D. Hurley, V. F. Andersen, O. J. Nielsen and T. J. Wallington, J. Phys. Chem. A, 2010, 114, 4963–4967.

20. K. Tokuhashi, A. Takahashi, M. Kaise, S. Kondo, A. Sekiya, S. Yamashita, H. Ito, Int. J. Chem. Kinet. 1999, 31, 846–853.
21. I. Bravo, Y. Diaz-de-Mera, A. Aranda, K. Smith, K.P. Shine, G. Marston, Phys. Chem. Chem. Phys. 2010, 12, 5115–5125.
22. L. Chen, T. Uchimaru, S. Kutsuna, K. Tokuhashi, A. Sekiya, Chem. Phys. Lett., 2011, 514, 207
23. 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, 8264–8274.
24. W. E. Wilson Jr., A.W. Hamilton, R.H. Mount, J.Phys.Chem. A 2007,111,1610–1617.
25. T. J. Wallington, A. Guschin, T. N. N. Stein, J. Platz, J. Sehested, L.K. Christensen, O. J. Nielsen, J. Phys. Chem. A 1998,102,1152–1161.
26. K. Tokuhashi, A. Takahashi, M. Kaise, S. Kondo, A. Sekiya, S. Yamashita, H. Ito, J. Phys. Chem. A 2000, 104, 1165−1170.
27. V. C. Papadimitriou, K. G. Kambanis, Y. G. Lazarou, P. Papagiannakopoulos, J. Phys. Chem. A 2004,108, 2666–2674.
28. S. Ponnusamy, L. Sandhiya, K. Senthilkumar, J. Phys. Chem. A, 2018, 122, 4972- 4982.
29. M. Lily, B. Baidya, A. K. Chandra, Chem. Phys. Lett. 2017, 669, 211–217
30. M. Lily, D. Sutradhar, A. K. Chandra, Comput. Theor. Chem., 2013, 1022, 50–58.
31. B. Baidya, M. Lily, D. Patgiri, S. Hynniewta, A. K. Chandra, New J. Chem. 2020, 44, 4276–4284.
32. B. K. Mishra, M. Lily, A.K. Chandra, R.C.Deka, J.Phy.Org.Chem.2014,87, 811-817.
33. B. K. Mishra, M. Lily, R. Deka, A. K. Chandra, New J. Chem.2016, 40, 6148-6155.
34. M. Lily, B. K. Mishra, A. K. Chandra. J. Fluorine Chem. 2014, 161, 51–59
35. M. Lily, B. Baidya, A. K. Chandra. Chem. Phys. Lett. 2019, 721, 141–148
36. M. Lily, A. K. Chandra, Mol. Phys. 2015, 113 508–520.
37. M, Lily, B, Baidya, W. Wang, F. Liu, A. K. Chandra, Amos. Environ. 2020, 242, 117805.
38. Ø. Hodnebrog, B. Aamaas, J. S. Fuglestvedt, G. Marston, G., Myhre, C. J. M. Nielsen, M. Sandstad, K. P. Shine, T. J. Wallington Rev. Geophys., 2020, 58, e2019RG000691.
39. World Meteorological Organization (WMO). Scientific Assessment of Ozone Depletion: 2022, GAW Report No. 278, 509 pp.; WMO: Geneva, 2022.
40. L. Vereecken, D. R. Glowacki, M. J. Pilling, Chem. Rev. 2015, 115, 4063–4114.
41. M. J. Frisch, et al. Gaussian 09, Revision C.01. Gaussian Inc, Wallingford, CT,2010.
42. Y. Zhao, D. G. Truhlar, Theor. Chem. Acc., 2007, 120, 215–241.
43. Y. Zhao, D. G. Truhlar, Acc. Chem. Res., 2008, 41, 157–167.
44. Y. Zhao, D.G. Truhlar, J. Phys. Chem. A 2004, 108, 6908–6918.
45. M. J. Frisch, M. Head-Gordon, J. A. Pople, Chem. Phys. Lett. 1990, 166, 281-298.
46. J. Zheng et al. Gaussrate 17, University of Minnesota, Minneapolis, MN, 2017
47. J. Zheng et al. Polyrate 17-C, University of Minnesota, Minneapolis, 2018.
48. K. J. Laidler, Chemical Kinetics, third ed., Pearson Education, Delhi, 2004.
49. A. Fernandez-Ramos, B. A. Ellingson, B. C. Garrett, D. G. Truhlar, "Variational Transition State Theory with Multidimensional Tunnelling," in Reviews in Computational Chemistry, Vol. 23, edited by K. B. Lipkowitz and T. R. Cundari (Wiley-VCH, Hoboken, NJ, 2007), pp. 125-232.
50. K. P. Shine, G. J. Myhre, Adv. Model. Earth Syst. 2020, 12, e2019MS001951
51. C. J. Young, M. D. Hurley, T. J.; Wallington, S. A. Mabury. J. Geophys. Res., 2008, 113(D24), D24301.