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Comment on “Assessing the atmospheric fate of trifluoroacetaldehyde (CF_3CHO) and its potential as a new source of fluoroform (HFC-23) using the AtChem2 box model” by Pérez-Peña *et al.*, *Environ. Sci.: Atmos.*, 2023, 3, 1767–1777, DOI: 10.1039/D3EA00120B

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Recently Pérez-Peña *et al.* published a paper in this journal on the potential atmospheric fate of trifluoroacetaldehyde (CF_3CHO) as a source of CF_3H (HFC-23). In their work they utilized both a box model and a global chemistry and transport model to evaluate the production of CF_3H from the photolysis of CF_3CHO, the latter generated from photochemical oxidation of HFO-1234ze ($CF_3CH{=}CHF$). Certain chemical assumptions and simplifications were made. We believe the assumptions utilized by Pérez-Peña *et al.* misrepresent the environmental fate of CF_3CHO. In the following, we present our comments on both the photolysis and the wet and dry deposition of CF_3CHO. Furthermore, we contemplate the impact of the potential deposition of CF_3CHO on the formation of trifluoroacetic acid (CF_3COOH) during the environmental processing of CF_3CHO.

Environmental significance

The question of trifluoromethane (HFC-23) formation in the UV photolysis of trifluoroacetaldehyde has recently become a topic of heightened research interest. Trifluoromethane is a strong greenhouse gas and trifluoroacetaldehyde is a reaction intermediate formed during the degradation of several fluorinated gases, including some commercially important hydrofluoroolefins (HFOs). The atmospheric burden of trifluoromethane is increasing and it is important to know the contribution of HFO chemistry. Pérez-Peña *et al.* (2023) presented an atmospheric model of the degradation of HFO-1234ze (1,3,3,3-tetrafluoropropene), a fourth-generation refrigerant. Their study included several faulty assumptions leading to erroneous conclusions. Here we clarify what those errors are and further discuss the importance of wet and dry deposition as a possible environmental sink for trifluoroacetaldehyde.

1. Introduction

Halogenated gases are widely used in many industrial applications. There has been and continues to be a concerted effort to replace traditional CFCs (chlorofluorocarbons) and their replacements with chemicals that minimize the impact on the ozone layer, global climate, and air quality and result in benign atmospheric degradation products. Hydrofluoroolefins (HFOs) are a class of compounds developed in support of this goal. The olefinic double bond provides a site for fast reaction with OH radicals, increasing the OH radical reactivity of HFOs in comparison to those compounds that the HFOs replace. This reduces their atmospheric lifetime, which again leads to small global warming potentials (GWPs) for the HFOs. CF_3CHO is a product from the atmospheric degradation of some HFOs.[1] Atmospheric photolysis of CF_3CHO involves several channels resulting in different molecular fragments and it has been shown that photolysis of CF_3CHO can produce CF_3H under certain atmospheric conditions.[2] CF_3H is a long-lived greenhouse gas (GHG) with a 100 year global warming potential (GWP_{100}) of 14 600.[3] Recently, it has also been shown that ozonolysis of some HFOs can produce CF_3H in molar yields of up to 3%.[4] There is a need for quantification of CF_3H production from the atmospheric dissemination of HFOs and other halogenated compounds that yield CF_3CHO as a degradation intermediate. Pérez-Peña *et al.* have recently published a modelling study in this journal on the atmospheric fate of CF_3CHO as a new source of CF_3H.[5] This paper is hereinafter referred to as PP23. In that work, the authors employed the AtChem2 v1.2.1 box model with the Master Chemical Mechanism MCMv3.3.1 to model the atmospheric fate of HFO-1234ze ($CF_3CH{=}CHF$) and the GEOS-Chem chemical transport model

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to estimate deposition rates for CF_3CHO. Emissions of HFO-1234ze were assumed as 12.6 Gg y^{-1} for 2015 and projected to 2050 as 124.4 Gg y^{-1}. Two important input parameters for the model are the wavelength and pressure dependent quantum yield of CF_3H from photolysis of CF_3CHO, and the Henry's Law Coefficient (HLC) for CF_3CHO used in the calculations of the wet and dry deposition of CF_3CHO. We believe errors in the assumptions for these parameters in the model result in an overstatement of the CF_3H yield in PP23. The following sections discuss the two factors in isolation.

2. Overestimating the formation of CF_3H in CF_3CHO photolysis

It has been shown that the formation of CF_3H from CF_3CHO photolysis (reaction (2)) is only significant in the high atmosphere above 30 km:[2]

$$CF_3CHO + h\nu \rightarrow CF_3 + HCO \quad (1)$$

$$CF_3CHO + h\nu \rightarrow CF_3H + CO \quad (2)$$

The relevant quantum yield, ϕ_2, adopted in the PP23 modelling study are reportedly derived in part from a PhD thesis by Campbell.[6] Part of the thesis has been published in Campbell *et al.*,[7] but the latter publication does not include the study of the molecular channel. Sulbaek Andersen and Nielsen reported an upper limit for the molecular channel yield of 0.3% based on chamber experiments at atmospheric pressure.[8] PP23 used the *upper* limit of <0.3% reported by Sulbaek Andersen and Nielsen[8] as the *lower* limit for ϕ_2 in their study, and $\phi_2 = 0.01$ as a "realistic upper bound" (page 1769 of PP23), extrapolated from data at low-pressure in the non-peer-reviewed thesis. Using the upper limit of Sulbaek Andersen and Nielsen[8] as a lower limit, is puzzling. The 0.003 (0.3%) reported by Sulbaek Andersen and Nielsen[8] is an upper limit for the molar yield of CF_3H, not the quantum yield (ϕ_2 would be on the order of 10^{-4} based data shown in Fig. 5 of Sulbaek Andersen and Nielsen[8]). Furthermore, it is unclear how PP23 arrived at their "realistic upper bound" of $\phi_2 = 0.01$. There are internal inconsistencies in the reported works of Campbell and coworkers: the thesis states on page 151: "From the fit shown in Fig. 9.2, we extrapolate our measurements to atmospheric pressure, determining a CHF_3 quantum yield of 0.33%, with a lower limit of 0.15% from the 95% confidence bounds on the fit. This measurement is remarkably consistent with the most recent study [*i.e.* Sulbaek Andersen and Nielsen],[8] which determined an upper limit of 0.3% for the atmospheric pressure quantum yield of CHF_3 at 308 nm." It appears that PP23 may have misinterpreted the conclusions in the Campbell PhD thesis, as well as those of Sulbaek Andersen *et al.*[8] In any event, the choices of PP23 for ϕ_2 will substantially overestimate the yield of CF_3H from the atmospheric photolysis of CF_3CHO.

2.1 Erroneous Henry's law coefficient for CF_3CHO

The estimation of CF_3CHO dry and wet deposition velocities requires knowledge of the air-to-water HLC for CF_3CHO. However, as will be discussed below, this term is not simply the ratio (H) of aqueous to gas-phase concentrations of the species CF_3CHO, typically defined as the "*intrinsic*" HLC:

$$H = [CF_3CHO]_{aq}/[CF_3CHO]_g \quad (3)$$

CF_3CHO forms a stable gem-diol, *i.e.*, hydrate, in the presence of water:

$$CF_3CHO + H_2O \rightarrow CF_3CH(OH)_2 \quad (4)$$

This has been known since the 1930s at least,[9] although the hydrate formation is not discussed explicitly in PP23. The relevant parameter for dry and wet deposition modelling is the "*apparent*" or "*effective*" HLC, H^*, defined by:

$$H^* = \{[CF_3CHO]_{aq} + [CF_3CH(OH)_2]_{aq}\}/[CF_3CHO]_g \quad (5)$$

The hydration equilibrium constant is defined as:

$$K_{hyd} = [CF_3CH(OH)_2]_{aq}/[CF_3CHO]_{aq} \quad (6)$$

Combining and subsequent rearrangement of expressions (3), (5) and (6) gives the effective HLC expressed by H and K_{hyd}:

$$H^* = H(1 + K_{hyd}) \quad (7)$$

When $K_{hyd} \gg 1$, as will be shown to be the case here, then:

$$H^* \cong H \times K_{hyd} \quad (8)$$

Neither H^* nor H has been measured for CF_3CHO. The approach used in PP23 to estimate H^* for CF_3CHO is flawed for two reasons. First, it relies on "proxy" data derived for CF_3COF, which is known to hydrolyse rapidly in contact with water to form the highly soluble trifluoroacetic acid, CF_3COOH (TFA). Second, the values adopted in PP23 are not effective HLCs (H^*), but intrinsic ones (H). The values were taken from a review paper[1] that cites as its source De Bruyn *et al.*[10] but in fact also includes results from a study by George *et al.*[11] on the uptake of gaseous CF_3COF to water surfaces. In both studies, the parameter measured was $H \times k_{rxn}^{1/2}$, where k_{rxn} is the first-order rate constant for hydrolysis of CF_3COF. The deconvolution of $H \times k_{rxn}^{1/2}$ to yield separate estimates for H and k_{rxn} was subject to very large uncertainties, but the H values reported in ref. [10] and [11] for CF_3COF (namely 0.96 and 3.0 M atm^{-1}, respectively) were those adopted in PP23 for CF_3CHO, although the range was extended to 13.17 M atm^{-1} by including this value for acetaldehyde, taken to be an "upper bound". Even if it were reasonable to assume that the intrinsic HLC of the species CF_3CHO is equal to that of CF_3COF, the value would need to be multiplied by K_{hyd} to give H^*, the parameter required for deposition velocity estimation.

We suggest here an alternative procedure for estimating H^* for CF_3CHO, based on the use of available proxy data for its chlorinated analogue, chloral (CCl_3CHO). For CCl_3CHO, H^* has been reported as a function of temperature.[12] At 25 °C it is 3.44×10^5 M atm^{-1}. $H^*(CF_3CHO)$ can then be estimated from the following equation:

$$H^*(CF_3CHO)/H^*(CCl_3CHO) = \{H(CF_3CHO)/H(CCl_3CHO)\} \times \{K_{hyd}(CF_3CHO)/K_{hyd}(CCl_3CHO)\} \quad (9)$$

The estimation of $H^*(CF_3CHO)$ using eqn (9) relies on having sufficient data to derive the ratios:

$$H(CF_3CHO)/H(CCl_3CHO) \quad (10)$$

and

$$K_{hyd}(CF_3CHO)/K_{hyd}(CCl_3CHO) \quad (11)$$

For ratio (10) we suggest using as a surrogate the ratio of the HLC of CF_3CH_2OH to that of CCl_3CH_2OH, two oxygenated substances that do not form hydrates with water, so their reported HLCs are indeed "intrinsic" ones (H). For the purposes of this calculation, the H values were taken uncritically from the online compilation of HLCs by Sander.[13,14] Although there is considerable uncertainty in the data, warranting a more in-depth assessment of potentially available experimental and QSAR-derived values, here we adopt $H = 47.6$ M atm^{-1} for CF_3CH_2OH (originally from JPL recommendations) and 297 M atm^{-1} for CCl_3CH_2OH (average of the 3 values listed). Ratio (10) is therefore taken to be $47.6/297 = 0.16$.

For deriving ratio (11) there is also considerable uncertainty. In the case of CF_3CHO, there appears to be only a SPARC-derived K_{hyd} value, $(10^{4.22}) = 1.7 \times 10^4$ from Rayne and Forest.[15,16] Rayne and Forest state that this derived value is close to the one experimental data point available ($K_{hyd} = 10^{4.46} = 2.9 \times 10^4$) reported by Guthrie.[17] However, their conclusion is erroneous, since the experimental value reported by Guthrie[17] refers to the hydration of CCl_3CHO, not CF_3CHO. Guthrie merely *assumes* it to be valid also for CF_3CHO – in fact, it is taken from a literature review by Le Hénaff,[18] which shows that its true origin is a study by Gruen and McTigue,[19] which actually reports a value of 2.8×10^4.

For CCl_3CHO, apart from the above-mentioned value of 2.8×10^4, there are several other, sometimes greatly conflicting, values for K_{hyd}. Herold[20] reported a K_{hyd} value of >2500, according to Gruen and McTigue.[19] Bell and McDougall[21] studied CCl_3CHO hydrate dissociation at concentrations ranging from 0.0014 to 0.123 M in cyclohexane and derived a K_{hyd} value of 500. Baymak[22] reported an exceptionally low value for K_{hyd} of 25 for CCl_3CHO in aqueous solution, as measured by an electrochemical technique. Finally, in a textbook by Clayden *et al.*[23] a value of $K_{hyd} = 2000$ is listed, but the origin of this value is not stated.

Discounting some of these results (organic solvent medium for Bell and McDougall; outlier for Baymak), we will adopt the K_{hyd} value from Gruen and McTigue for CCl_3CHO together with that of Rayne and Forest for CF_3CHO. Applying eqn (9):

$$H^*(CF_3CHO) = 0.16 \times (1.7 \times 10^4/2.8 \times 10^4) \times 3.44 \times 10^5 \text{ M atm}^{-1} = 3.3 \times 10^4 \text{ M atm}^{-1}$$

This is likely to be an underestimate, since the hydration constant for CF_3CHO used here is lower than that for CCl_3CHO, which is contrary to the expectation that the greater electron-withdrawing effect of the fluorine atoms relative to chlorine, combined with their smaller size, and hence lesser steric hindrance towards nucleophilic attack, would suggest a larger K_{hyd} for CF_3CHO, than for CCl_3CHO.[23] Nevertheless, the main conclusion is that by adopting a range of HLC values of 0.96 to 13.17 M atm^{-1}, the latter based on $H(CH_3CHO)$ as an upper bound, PP23 likely underestimates this important parameter by several orders of magnitude.

It should be noted here that CF_3CHO hydrate is a weak acid, dissociating to $CF_3CH(OH)O^- + H^+$.[15,16] However, given its pK_a close to 10, dissociation would be negligible under most environmental conditions.[15,16] On the other hand, volatilization of the hydrate (unchanged) from aqueous solution (see below) might impact the *apparent* HLC, H^*.

2.2 The impact of wet and dry deposition of CF_3CHO

Given the variety and complexity of the parameterizations for wet and dry deposition, it is not immediately obvious what would be the impact of adopting, in AtChem2 with GEOS-Chem or other atmospheric models, the H^* value for CF_3CHO proposed here, which is greater by more than 4 orders of magnitude than those assumed in PP23, *i.e.* 0.96 and 3 M atm^{-1} (together with a value of 13.17 M atm^{-1} for acetaldehyde, taken as a upper bound proxy for CF_3CHO).

Nevertheless, the HLC is known to be a key parameter in estimating both wet and dry deposition and it is reasonable to assume that the far greater HLC would lead to enhanced wet and dry deposition velocities for CF_3CHO and hence, to a correspondingly reduced proportion of photolysis in the atmospheric fate of CF_3CHO, including any possible minor photolysis pathway leading to CF_3H formation.

Some insight into the impact of increasing the HLC from 13.17 M atm^{-1} to 3.3×10^4 M atm^{-1} can be gained from a generalized study by Bi and Isaacman-VanWertz,[24] which focused mainly on *wet* deposition. As can be seen in Fig. 5 of this paper, the overall timescale for wet deposition (averaged over periods with and without rainfall) declines as the HLC increases, plateauing at a minimum of roughly 100 hours when the HLC exceeds 10^5 M atm^{-1}. Assuming that the H^* value for CF_3CHO is greater than or equal to 10^4 M atm^{-1}, as proposed in this work, it is close enough to this low plateau that the overall wet-deposition lifetime may be taken to be ~100–200 hours, or 4–8 days. Using the recommended value of $k_{OH} = 5.8 \times 10^{-13}$ cm^3 per molecule per s at 25 °C,[25] and $[OH] = 1 \times 10^6$ molecule per cm^3,[26] leads to an average global lifetime for CF_3CHO with respect to OH reaction of 20 days. The relative importance of photolysis compared to OH reaction, as derived from Fig. 4 of PP23, is roughly 3 : 1, implying that the mean photolysis lifetime is about 7 days. Sulbaek Andersen *et al.*[2] estimated the atmospheric lifetime of CF_3CHO with respect to photolysis as 13 ± 4 days. Thus, the wet-deposition lifetime estimated here of 4–8 days, is similar to the mean lifetime due to reaction of CF_3CHO with the OH radical and photolysis. In comparison, the maximum HLC value adopted in PP23, (13.17 M atm^{-1}) would lead, by extrapolation of the data in Fig. 5 of Bi and Isaacman-

VanWertz,[24] to a wet-deposition lifetime of $>10^5$ hours (>11 years), making wet deposition completely insignificant.

Dry deposition may also be competitive with wet deposition but is highly dependent on season and ecosystem. Bi and Isaacman-VanWertz[24] also predicted general removal timescales for *dry* deposition, showing a decreasing trend with increasing HLC and reaching a minimum plateau for HLC $> 10^5$ M atm^{-1}, in a manner similar to wet deposition. They estimated that, in the particular case of a heavily forested area of the summertime south-eastern U.S., more soluble compounds have dry-deposition lifetimes of only about 7 hours (0.3 days). Furthermore, data presented in Table 1 of Zhang *et al.*[27] show that for compounds with HLCs similar to that proposed here for CF_3CHO, mean dry deposition velocities (V_d) are much greater than those assumed in PP23 for CF_3CHO (0.024–0.21 cm s^{-1}). For example, the mean V_d for H_2O_2 with an HLC of 8.7×10^4 M atm^{-1} (ref. 13) is 0.643 cm s^{-1}. This latter value refers to the North America domain, in which deposition is mainly to vegetation-covered land. However, dry deposition to water also needs to be considered, since water covers the greater part of the planet. It is not clear, from Fig. 3 of the ESI of PP23, if dry deposition to the oceans was assessed and included in the model used in PP23.

The potential importance of wet and dry deposition of CF_3CHO, compared to the conclusions of the PP23 study, raises the question of the fate of CF_3CHO, and indeed of its hydrate, in the terrestrial and oceanic environment. It is possible that the hydrates can react with OH in the aqueous phase, thus being a potential source of TFA. It is also possible that the hydrate can undergo biodegradation to trifluoroacetate ions.[28]

3. Atmospheric hydration of CF_3CHO and fate of the hydrate formed

In the first step of the wet deposition process, atmospheric gaseous CF_3CHO is taken up into cloud droplets and rainwater. Sulbaek Andersen *et al.*[29] performed studies to investigate the subsequent atmospheric fate of the hydrate thus formed, as well as its potential to arise also from the purely gas-phase reaction of CF_3CHO with water vapour. Sulbaek Andersen *et al.* observed that when CF_3CHO-air mixtures were bubbled through water, with a residence time estimated to be roughly 2 seconds (pHs ranging from 2 to 7), CF_3CHO was partially converted into the hydrate form. They also observed gaseous CF_3CHO reacting with water vapour to give the hydrate in smog chamber experiments, although it was suggested that the reaction occurred heterogeneously. An extremely low upper limit to the bimolecular rate constant for the homogeneous reaction was derived. Conversely, when mixtures of gaseous hydrate and air were left in the smog chamber for 22 hours, a 56% decay of the hydrate was observed, giving CF_3CHO in a yield of 100%. In this case too, a heterogeneous reaction was suspected. This thermal gas-phase reversion of the hydrate to the aldehyde was analogous to that reported for CCl_3CHO.[30] Based on the kinetic and product data from the smog chamber study it was concluded that the hydrate would be oxidized quantitatively in the atmosphere to TFA with a lifetime of approximately 90 days. This is a timescale considerably longer than the wet and dry deposition lifetimes suggested above based on the paper by Bi and Isaacman-VanWertz,[24] and it seems likely that re-incorporation into rain-cloud-seawater will be a significant atmospheric removal mechanism for the hydrate.

Recently Franco *et al.*[31] reported and modelled the analogous atmospheric processing of formaldehyde to formic acid, which was presented as a "previously unknown pathway" by de Gouw and Farmer.[32] The heterogeneous "processing" of CF_3CHO in hydrometeors to its hydrate, followed by desorption of the latter and its subsequent gas-phase oxidation to TFA was not included in the modelling in PP23. Granted, the inclusion of such a mechanism in the model would be hampered by the lack of quantitative characterization of the processes involved. In fact, other regional to global model studies on the atmospheric processing of CF_3CHO from specific HFOs have chosen to omit the wet and dry deposition of CF_3CHO (*e.g.*, Sulbaek Andersen *et al.*[33] Tewari *et al.*[34]).

4. Conclusions

We provide here a two-fold reason why the yield of CF_3H reported in PP23, may be greatly overestimated. The lower quantum yield for photolysis of CF_3CHO to give CF_3H and the greatly increased Henry's law coefficient for CF_3CHO proposed here, compared to the values used in PP23, would lead to a lower CF_3H yield on account of the smaller fraction of CF_3CHO undergoing photolysis relative to deposition and OH reaction.

If CF_3CHO is converted into its hydrate, in the atmosphere or after deposition to the Earth's surface, at a rate comparable to those for photolysis and reaction with OH radicals, the hydrate could be a substantial source of TFA. As suggested by Sulbaek Andersen *et al.*,[29] the hydrate could be released from cloud or rain water (*via* Henry's law partitioning or total evaporation of the hydrometeor) followed by atmospheric oxidation to TFA. This latter conclusion tacitly assumes that the gaseous hydrate will not revert to non-hydrated CF_3CHO on a shorter timescale than that required for oxidation. Alternatively, biotic or abiotic transformation of CF_3CHO and its hydrate in the terrestrial or oceanic environment, subsequent to deposition, may also lead to TFA.

Experimental data on K_{hyd} and H^* for CF_3CHO are urgently needed to settle some of these questions. Then further modelling with revised input parameters is warranted.

Data availability

No new primary research results were generated as part of this review. Alternative analysis and calculations are carried out as explicitly described in the manuscript text using the referenced source material.

Conflicts of interest

There are no conflicts to declare.

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References

1 J. B. Burkholder, R. A. Cox and A. R. Ravishankara, *Chem. Rev.*, 2015, **115**(10), 3704.
2 M. P. Sulbaek Andersen, S. Madronich, J. M. Ohide, M. Frausig and O. J. Nielsen, *Atmos. Environ.*, 2023, **314**, 120087.
3 IPCC, *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B. R. Matthews, T. K. Maycock, T. Waterfield, O. Yelekçi, R. Yu and B. Zhou, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2021, DOI: 10.1017/9781009157896.
4 M. R. McGillen, Z. T. P. Fried, M. A. H. Khan, K. T. Kuwata, C. M. Martin, S. O'Doherty, F. Pecere, D. E. Shallcross, K. M. Stanley and K. Zhang, *Proc. Natl. Acad. Sci. U. S. A.*, 2023, **120**(51), e2312714120.
5 M. P. Pérez-Peña, J. A. Fisher, C. Hansen and S. H. Kable, *Environ. Sci.: Atmos.*, 2023, **3**(12), 1767.
6 J. Campbell, A detailed investigation into CF_3CHO photolysis, PhD thesis, UNSW Sydney, 2022, , DOI: 10.26190/UNSWORKS/24197.
7 J. S. Campbell, K. Nauta, S. H. Kable and C. S. Hansen, *J. Chem. Phys.*, 2021, **155**, 204303.
8 M. P. Sulbaek Andersen and O. J. Nielsen, *Atmos. Environ.*, 2022, **272**, 118935.
9 R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, **4**, 1.
10 W. J. De Bruyn, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, *Environ. Sci. Technol.*, 1995, **29**(5), 1179.
11 C. George, J. Y. Saison, J. L. Ponche and P. Mirabel, *J. Phys. Chem.*, 1994, **98**(42), 10857.
12 E. A. Betterton and M. R. Hoffmann, *Environ. Sci. Technol.*, 1988, **22**(12), 1415.
13 R. Sander, *Atmos. Chem. Phys.*, 2023, **13**, 10901.
14 R. Sander, *Henry's Law Database*, https://www.henrys-law.org/henry/, accessed August 2024.
15 S. Rayne and K. Forest, *Nat. Preced.*, 2010, DOI: 10.1038/npre.2010.4520.1.
16 S. Rayne and K. Forest, *J. Environ. Sci. Health, Part A*, 2016, **51**(7), 579.
17 J. P. Guthrie, *Can. J. Chem.*, 1975, **53**(6), 898.
18 P. Le Hénaff, *Bull. Soc. Chim. Fr.*, 1968, 4687.
19 L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 1963, 5217.
20 W. Herold, *Z. Phys. Chem., Abt. B*, 1932, **18**(1), 265.
21 R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, 1960, **56**, 1281.
22 M. S. Baymak, *Electrochem. Sci. Adv.*, 2022, **2**(6), e2100074.
23 J. Clayden, N. Greeves and S. Warren, *Organic Chemistry*, Oxford University Press, 2nd edn, 2012, p. 135.
24 C. Bi and G. Isaacman-VanWertz, *Environ. Sci.: Atmos.*, 2022, **2**(6), 1526.
25 J. G. Calvert, A. W. Mellouki, J. J. Orlando, M. J. Pilling and T. J. Wallington, *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, 2011.
26 R. G. Prinn, J. Huang, R. F. Weiss, D. M. Cunnold, P. J. Fraser, P. G. Simmonds, A. McCulloch, P. Salameh, S. O'Doherty, R. H. J. Wang, L. Porter and B. R. Miller, *Science*, 2001, **292**, 1882.
27 L. Zhang, Z. He, Z. Wu, A. M. Macdonald, J. R. Brook and S. Kharol, *J. Environ. Sci.*, 2023, **127**, 264.
28 J. M. Fraser and L. S. Kaminsky, *Toxicol. Appl. Pharmacol.*, 1988, **94**(1), 84.
29 M. P. Sulbaek Andersen, A. Toft, O. J. Nielsen, M. D. Hurley, T. J. Wallington, H. Chishima, K. Tonokura, S. A. Mabury, J. W. Martin and D. A. Ellis, *J. Phys. Chem. A*, 2006, **110**(32), 9854.
30 K. B. Wiberg, K. M. Morgan and H. Maltz, *J. Am. Chem. Soc.*, 1994, **116**(24), 11067.
31 B. Franco, T. Blumenstock, C. Cho, L. Clarisse, C. Clerbaux, P.-F. Coheur, M. De Mazière, I. De Smedt, H.-P. Dorn, T. Emmerichs, H. Fuchs, G. Gkatzelis, D. W. T. Griffith, S. Gromov, J. W. Hannigan, F. Hase, T. Hohaus, N. Jones, A. Kerkweg, *et al.*, *Nature*, 2021, **593**(7858), 233.
32 J. de Gouw and D. Farmer, *Nature*, 2021, **593**(7858), 198.
33 M. P. Sulbaek Andersen, J. A. Schmidt, A. Volkova and D. J. Wuebbles, *Atmos. Environ.*, 2018, **179**, 250.
34 S. G. Tewari, J. P. Bell, N. Budgen, S. Platz, M. Gibbs, P. Newham and H. Kimko, *Front. Environ. Sci.*, 2023, **11**, 1297920.