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Temperature-dependent structure-activity relationship of OH + haloalkene rate coefficients under atmospheric conditions and supporting measurements

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1 Abstract:

2 Hydrofluoroolefins (HFOs) and related haloalkenes are a family of compounds, primarily man-made,
3 with many industrial applications. Gas-phase electrophilic addition of OH to the olefinic bond represents
4 the primary sink for these chemicals in the atmosphere. The degree and type of halogenation strongly
5 affect their chemical reactivity, leading to differing reactivities with the OH radical that have presented
6 a challenge for structure-activity relationships (SARs). Here, we investigate and extend the SARs to
7 estimate temperature-dependent OH reaction rate coefficients, $k(T)$, at tropospheric temperatures.

8 We considered two techniques: the group-additivity approach of Atkinson and co-workers and the recent
9 method of Tokuhashi and co-workers; we found the latter to make superior predictions for halogenated
10 olefins. We extended Tokuhashi *et al.*'s SAR to include more olefins and to predict temperature
11 dependencies.

12 We compared SAR predictions against new absolute $k(T)$ for two HFOs (3,3,3-trifluoropropene and
13 1,1,3,3-tetrafluoropropene) measured using the pulsed-laser photolysis–laser-induced fluorescence
14 technique from 212 to 373K. The Arrhenius expressions were determined as $k_{\text{OH}+\text{CF}_3\text{CH}=\text{CH}_2}(T) =$
15 $(8.86\pm 0.82)\times 10^{-13}\exp[(159\pm 26)/T]$ and $k_{\text{OH}+\text{CF}_2\text{HCH}=\text{CF}_2}(T) = (7.46\pm 0.34)\times 10^{-13}\exp[(365\pm 12)/T]$. The
16 measured $k(T)$ was predicted accurately between 200 and 400K using the modified Tokuhashi approach.
17 Our new measurements of the OH reaction rate coefficient with 3,3,3-trifluoropropene were in excellent
18 agreement with literature determinations. We represent the first reported $k(T)$ for
19 1,1,3,3-tetrafluoropropene.

20 Given that new HFOs enter the market frequently, such estimation techniques may be a helpful screening
21 tool for assessing their environmental impact before they are examined further and reach the mass–
22 production phase.

24 1. Introduction:

25 Following the Montreal Protocol and its amendments, ozone-depleting substances continue to be
26 replaced by new generations of substitutes, which are less harmful to the climate and the ozone layer.^{1,2}
27 In particular, the recent Kigali amendment is phasing out high global warming potential (GWP)

28 hydrofluorocarbons (HFCs).² Hydrofluoroolefins (HFOs), which are very short-lived fluorinated gases
29 with low GWPs, are substitutes that are increasing in use.³

30 HFOs have found many industrial applications as refrigerants, propellants, and foam-blowing agents.
31 Composed of fluorine, hydrogen, and an olefinic carbon backbone, they represent a subset of the broader
32 class of haloalkenes, which contain any combination of olefin and halogen substitution. Such olefins
33 have many additional uses as solvents, cleaning fluids, and feedstocks for polymers. Due to their
34 widespread usage, HFO emissions are increasing in the atmosphere, and atmospheric monitoring
35 programs are now detecting them.⁴ HFOs and related haloalkenes are primarily removed from the
36 troposphere via electrophilic addition of the OH radical to the double bonds within them. Accurate
37 knowledge of the OH reaction rate coefficient is valuable because it can be incorporated into
38 atmospheric models that assess their contribution to air pollution, stratospheric ozone depletion, and
39 global warming.¹

40 A large variety of haloalkenes are already in use and the global demand for efficient but environmentally
41 friendly cooling technologies is growing.⁵ It is likely that many new haloalkenes proposed as
42 replacements have yet to have their OH reaction rate coefficients measured. For initial consideration of
43 uses, it is therefore desirable to have reliable estimates of these rate coefficients; which is the main focus
44 of the present work.

45 Structure-activity relationships (SARs) have been used extensively to estimate reaction rate coefficients
46 by correlating the chemical structure of a species with its reactivity.⁶ From trends in available kinetic
47 data, SARs derive satisfactory predictions applicable to a broader set of chemicals for which rate
48 coefficients are unavailable. Similarly, the development and improvement of SARs are becoming
49 increasingly necessary as atmospheric chemical models become more explicit and complete.⁶
50 Furthermore, in the process of parameterizing the chemical reactivity that SAR-development entails, we
51 aim to improve the chemical understanding of the mechanism of the electrophilic addition of OH
52 radicals to alkenes.

53 We estimated room-temperature OH reaction rate coefficients of haloalkenes, k_{298} , from the AOPWIN
54 v1.92 module of the estimation programs interface EPI Suite^{7,8} based on the approach of Kwok and
55 Atkinson.⁹ We also applied the more recent method of Tokuhashi *et al.*¹³⁻¹⁷ to calculate k_{298} and extended
56 it to predict temperature-dependent rate coefficients, $k(T)$, between 200 and 400 K. We assume that the
57 addition reactions are at their high-pressure limit and thus the pressure is not a parameter that influences
58 the rate coefficients. We compared these calculations with new laboratory measurements of the absolute
59 OH reaction rate coefficients as a function of the temperature of two HFOs, $\text{CF}_3\text{CH}=\text{CH}_2$ (212–367 K)
60 and $\text{CF}_2\text{HCH}=\text{CF}_2$ (223–373 K), using the pulsed-laser photolysis–laser-induced fluorescence (PLP–

LIF) technique. The reaction of $\text{CF}_3\text{CH}=\text{CH}_2$ with OH has been studied previously at various temperatures,¹⁸⁻²³ whereas the rate coefficient of $\text{CF}_2\text{HCH}=\text{CF}_2$ with OH has never been reported to the best of our knowledge.

2. Methodology:

2.1. Structure-activity relationships (SARs) :

2.1.1. Literature methods:

In this section, we outline the existing methods to predict k_{298} from the structure of an olefin. We note that Tokuhashi's method¹³⁻¹⁷ and the implementation of Atkinson's SAR⁹⁻¹² by AOPWIN⁷⁻⁸ are both limited to room temperature (298 K).

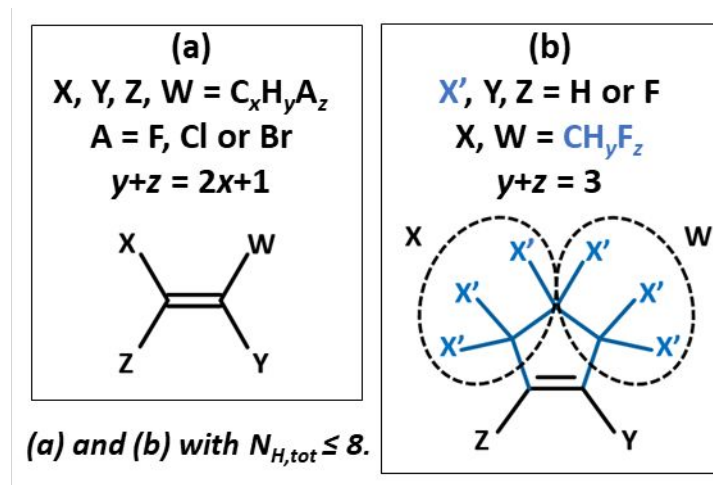


Figure 1: Schematic of the structure of the alkenes used in the models, with (a) being the description applied for acyclic alkenes where X, Y, Z, W substituents are defined by $\text{C}_x\text{H}_y\text{A}_z$ where $A = \text{F, Cl or Br}$ and where $y + z = 2x + 1$, where $x \geq 0$ and (b) referring specifically to the cyclic olefins containing H and F substitutions only, both (a) and (b) defined for molecules with a total hydrogen count, $N_{\text{H,tot}}$, of ≤ 8 . In structure (b), X', Z, and Y substituents can be either H or F atoms. The two groupings X and W are defined by splitting the cycle into two symmetrical chains, each possessing three X' atoms in the case of a cyclopentyl group. In Tokuhashi *et al.*'s recent work,¹⁷ only linear olefins, as in structure (a), are described, excluding Br substitutions and limited to values of $x \leq 2$.

2.1.1.1. Atkinson approach

The AOPWIN v1.92 program output for olefins includes estimations of the gas-phase hydroxyl radical

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3 82 reaction rate coefficients at 298 K.⁷⁻⁸ These estimations are built upon the work of Atkinson and co-
4
5 83 workers, with the most recent update described in Kwok and Atkinson's paper.⁹ This method estimates
6
7 84 the reactivity of a large number of alkenes, which themselves are part of a broader approach that also
8
9 85 predicts the reactivity of saturated organic molecules. For halogenated alkenes, the overall calculated
10
11 86 OH reaction rate coefficient is dominated by the reactivity of the C=C bond towards OH radical
12
13 87 electrophilic addition with generally negligible contributions from the H-abstraction channel.
14
15 88 Depending on the identity of the substituents, the reactivity of the alkene is expected to be affected by
16
17 89 the electron-withdrawing inductive effects, the electronegativity of the halogenated group(s), the
18
19 90 possible interplay between these groups and their respective positions. For a halogenated alkene of
20
21 91 formula X(Z)C=C(W)Y (see Structure (a) in Figure 1), the room temperature rate coefficient towards
22
23 92 the OH reaction is calculated as follows:

$$k_{298, \text{Atkinson}} \text{X(Z)C=C(W)Y} = k_{\text{base}} \times F(\text{X}) \times F(\text{Y}) \times F(\text{Z}) \times F(\text{W}) \quad (1)$$

24 94 where k_{base} is the base rate coefficient of the associated generic alkene, -C=C , -C=C- , >C=C , >C=C- or
25
26 95 >C=C< , and its stereoisomer (*cis* or *trans*), and $F(\text{X})$, $F(\text{Y})$, $F(\text{Z})$, $F(\text{W})$ are multiplicative constants that
27
28 96 are specific to a functional group (X, Y, Z, W being halogens or alkyl groups).⁹ For further details on
29
30 97 the method, readers are directed to the original papers from Atkinson¹⁰⁻¹² and Kwok and Atkinson,⁹ or
31
32 98 the website of the EPI Suite interface that implements AOPWIN.^{7,8}

33 99 For halogenated alkyl groups, i.e., allylic halogen substitutions, a constant value for " $F(\text{-Halogen})$ " of
34
35 100 0.76 is employed in Atkinson approach to describe the substitution effect.⁹ If halogen substitutions of
36
37 101 the alkenes are more distant than the allyl position with respect to the olefinic bond, these compounds
38
39 102 are treated as regular alkenes. Consequently, such an implementation becomes degenerate towards many
40
41 103 possible permutations on the alkyl group.

42 104 43 105 **2.1.1.2. Tokuhashi's method - Diagonal substituent factors:**

44 106 A method for estimating OH reaction rate coefficients of halogenated alkenes was more recently
45
46 107 developed by Tokuhashi and co-workers (see ¹³⁻¹⁷). In that work, the authors consider that a haloalkene's
47
48 108 reactivity is related to the identity of the substitution and the position of these substituents around the
49
50 109 double bond. The diagonal substitution pattern across the olefinic bond was found to be a critical
51
52 110 parameter that alters the rate coefficient.

53 111 In their previous work on halogenated ethenes,¹⁵ Tokuhashi and co-workers observed that the
54
55 112 experimentally determined rate coefficients for these compounds are determined not only by the type of
56
57 113 substituents attached to the double bond but also on the substituent on the opposite side of the olefinic

114 bond. By considering this substitution position, Tokuhashi *et al.*¹³⁻¹⁷ have developed a method that can
 115 reproduce the available experimental data within a factor of two, with a few exceptions.

116 Substituent factors are designed to account for the changes in the electron density in the π -orbitals, which
 117 are expected to be of primary importance in describing the reactivity of the double bond towards an
 118 electrophilic addition of OH. The calculated OH rate coefficient at room temperature is obtained by:

$$119 \quad k_{298, \text{Tokuhashi}} \text{X(Z)C=C(W)Y} = k_{\text{base}} \times F(\text{X-C=C-Y}) \times F(\text{Z-C=C-W}) \quad (2)$$

120 The base rate coefficient, $k_{\text{base}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,^{13,17} is that of the unsubstituted case. The
 121 terms $F(\text{X-C=C-Y})$ and $F(\text{Z-C=C-W})$ are the substituent factors for the structures shown in parentheses.
 122 The X-C=C-Y and Z-C=C-W represent diagonal positions (see Structure (a), Figure 1), as defined by
 123 Tokuhashi *et al.*¹³⁻¹⁷

124

125 **2.1.2. This work (modified Tokuhashi approach)**

126 In this section, our approach will be described as an updated and extended version of the Tokuhashi
 127 method described in section 2.1.1.2.¹³ In the original work of Kwok and Atkinson⁹ and that of Tokuhashi
 128 *et al.*,^{13,17} the rate coefficient for OH-addition to cycloalkenes is not estimated. In the AOPWIN program,
 129 in contrast, k_{298} are predicted for the presence of a ring by treating them as linear alkenes with a structure
 130 separated into two symmetrical chains on both sides of the double bond. Based on Equation 2, the OH-
 131 reaction rate coefficient of $\text{CF}_3\text{CF}=\text{CF}_3$ (structure #54, see Figure 2) would be identical to that of the
 132 cyclic perfluorocyclopentene (#63). However, the acyclic compound in this case has a much larger rate
 133 coefficient than the cyclic compound. Hence, the difference in reactivities may be a consequence of the
 134 ring strain, and/or the supplementary steric effects encountered in cyclic structures compared to linear
 135 geometries.²⁴ Our approach is speculative given the sparsity of experimental data for cyclic halogenated
 136 olefins, and we use a single additional factor F_{cycle} to account for the difference in reactivity. As new
 137 data become available, this factor may be expanded as a function of ring size.

138 Hence, the model built in the present work estimates k_{298} for the electrophilic addition reaction of OH
 139 with molecule X(Z)C=C(W)Y from the following formula:

$$140 \quad k_{298, \text{calc}} = k_{\text{base}} \times F(\text{X-C=C-Y}) \times F(\text{Z-C=C-W}) \times F_{\text{cycle}} \quad (3)$$

141 where $k_{\text{base}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is intended to represent the base-level reaction rate
 142 coefficient of electrophilic addition to the $>\text{C}=\text{C}<$ bond. The F -factors in Equation 3 include the
 143 substituent factors, $F(\text{X-C=C-Y})$ and $F(\text{Z-C=C-W})$ that account for the diagonal structure around the
 144 olefinic bond (see structures (a) and (b), Figure 1), and F_{cycle} that accounts for an olefin's cyclic structure.

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3 145 If alkenes are acyclic, F_{cycle} is 1. Because of the need to distinctly define each diagonal substitution
4 146 across the double bond in this method, we excluded rate coefficients reported for undefined
5 147 stereoisomers or a mixture of *E* and *Z* isomers from the training set.

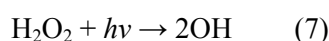
8 148 The calculated k_{298} values were optimized using a numerical solver that optimized the *F*-factor values
9 149 in order to minimize the relative difference between estimated and experimental results, defined as
10 149 $RE(\%)=100\times(k_{298,\text{calc}}-k_{298,\text{meas}})/k_{298,\text{meas}}$. The resulting optimized *F*-factors are presented in section 3.2.
11 150
12 150 Additionally, our SAR provides a method to estimate the temperature-dependent reaction rate
13 151 coefficient, $k(T)$, based on the values of the calculated k_{298} , and the Arrhenius equation, as presented in
14 152 section 3.4.
15 153
16 154

21 155 **2.2. Rate coefficient measurements of the reaction of OH with CF₃CH=CH₂ and** 22 156 **CF₂HCH=CF₂:**

23 157 **2.2.1. Apparatus Description:**

24 158 The rate coefficients for OH reaction with two HFOs, CF₃CH=CH₂ and CF₂HCH=CF₂, were measured
25 159 between 212 and 367 K, and 223 and 373 K, respectively, using a pulsed-laser photolysis–laser-induced
26 160 fluorescence (PLP–LIF) apparatus (Figure 2) described elsewhere.^{25,26}

27 161 The OH radicals were produced by photolysis of hydrogen peroxide (H₂O₂) or nitric acid (HNO₃) using
28 162 a pulsed KrF excimer laser (PLP) ($\lambda = 248$ nm, 25–85 mJ pulse⁻¹ cm⁻² in the reaction cell) inside a 200
29 163 cm³ Pyrex reactor:



32 166 The initial hydroxyl radical concentrations, $[\text{OH}]_0$, were varied in the ranges $(1.7\text{--}30.6) \times 10^{10}$ molecule
33 167 cm⁻³ for the reaction with CF₃CH=CH₂ and $(6.7\text{--}279.0) \times 10^{10}$ molecule cm⁻³ for the reaction with
34 168 CF₂HCH=CF₂ (see Equation S1). The output of an Nd:YAG pumped dye laser (Rhodamine 590) was
35 169 doubled and used to excite the Q₁1 line in the (1,0) band of the ($\text{A}^2\Sigma^+, v'=1$) ← ($\text{X}^2\Pi, v''=0$) transition of
36 170 OH radicals near 282 nm. The resulting OH fluorescence signals emitted from the ($\text{A}^2\Sigma^+, v'=1$) → ($\text{X}^2\Pi,$
37 171 $v''=1$) and ($\text{A}^2\Sigma^+, v'=0$) → ($\text{X}^2\Pi, v''=0$) transitions (308–316 nm) were detected by a photomultiplier
38 172 tube (equipped with a narrow band-pass filter centered at 309 nm (FWHM = 7.6 nm) to minimize the
39 173 detection of scattered light from the probe laser.^{25,27} Collisional quenching of the OH($^2\Sigma_1^+$) was
40 174 minimized by using helium or argon. The energies of both laser beams were measured at the exit of the
41 175 reaction cell.

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3 176 The resulting fluorescence signal from OH radicals detected by the PMT was integrated using a gated
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5 177 charge integrator over a fixed period. The delay between photolysis and probe laser pulses was varied
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7 178 from 10 μ s to 10 ms, and the fluorescence signal (S_t) from 100 probe laser pulses at 10 Hz was averaged
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9 179 for each delay time to obtain the temporal profiles of the OH radical signal, which is proportional to its
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11 180 concentration ($[\text{OH}]_t$), see Equation 9. We usually used about 10 delay times to construct an OH-decay
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13 181 profile. Under pseudo-first-order conditions in $[\text{OH}]$ ($[\text{HFO}] \gg [\text{OH}]$), the following relationship is
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15 182 obeyed:

$$\ln \left(\frac{[\text{OH}]_t}{[\text{OH}]_0} \right) = \ln \left(\frac{S_t}{S_0} \right) = - (k[\text{HFO}] + k_d)t = -k't \quad (9)$$

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19 184 The pseudo-first-order OH decay rate coefficients in the presence (k') and absence (k_d) of HFO reactant
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21 185 were measured. The OH radicals are lost through reaction with HFO, as well as reaction with the OH-
22
23 186 precursor (H_2O_2 or HNO_3) and diffusion out of the detection zone; the latter two losses were accounted
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25 187 for in the background removal rate coefficient, k_d .²⁵ $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$ concentration were
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27 188 varied over (0.19–65) and $(2.8\text{--}47) \times 10^{13}$ molecule cm^{-3} , respectively. Absolute second order rate
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29 189 coefficients, k (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), at a given temperature and pressure were obtained from the slope
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31 190 of the ($k'-k_d$) versus $[\text{HFO}]$ variation using a linear regression procedure. They are presented at selected
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33 191 temperatures for $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$ together with experimental conditions in Tables S1
34
35 192 and S2.

36
37 193 The mixture of the OH precursor, olefin, and bath gas was flowed through the reaction cell to avoid
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39 194 accumulating products in the reaction volume. Calibrated mass flow controllers were employed to
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41 195 quantify gases flowing into the system. The temperature of the bath gas was regulated by circulating a
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43 196 cooling or heating fluid through the outer jacket of the reactor and measured using a retractable
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45 197 thermocouple (212–373 K to within ± 0.1 K). The pressure was continuously measured in the reaction
46
47 198 cell with two calibrated pressure gauges (0–1000 Torr). Concentrations of $\text{CF}_3\text{CH}=\text{CH}_2$ and
48
49 199 $\text{CF}_2\text{HCH}=\text{CF}_2$ were monitored online at 298 K using a 1000 cm path-length Fourier transform infrared
50
51 200 (FTIR) spectrometer (1 cm^{-1} resolution, 500–4000 cm^{-1} range) located downstream of the LIF reactor.
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53 201 The integrated band strengths measured in this study (Figure S2 and S3, Table S3) were used to calculate
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55 202 the concentration in the reactor after correcting for pressure and temperature differences between the
56
57 203 LIF reactor and the FTIR cell.

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59 204

2.2.2. Chemicals:

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205 All the gases used were UHP certified to be >99.9995 % (Air Liquide) pure. A 50wt.% solution of H_2O_2

was obtained from Sigma-Aldrich and concentrated before use by bubbling purified air through it for several days. $\text{CF}_3\text{CH}=\text{CH}_2$ (3,3,3-trifluoropropene) and $\text{CF}_2\text{HCH}=\text{CF}_2$ (1,1,3,3-tetrafluoropropene) were purchased from SynQuest Labs (CAS: 677-21-4, purity 99%) and (CAS: 4556-24-5, purity 98%), respectively. Two mixtures were prepared (1% and 10% in He). Purified gas-phase nitric acid was obtained by dehydrating a high-purity nitric acid HNO_3 solution (70% in H_2O) through the dropwise addition in a 1:2 ratio with concentrated sulfuric acid H_2SO_4 (>95%). Care was taken to avoid NO_2 formation in this sample over time by maintaining it at $\leq 0^\circ\text{C}$ and preventing room air ingress; the purity was confirmed by IR spectrum analysis of the headspace.

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3. Results and discussion:

3.1. SAR training set:

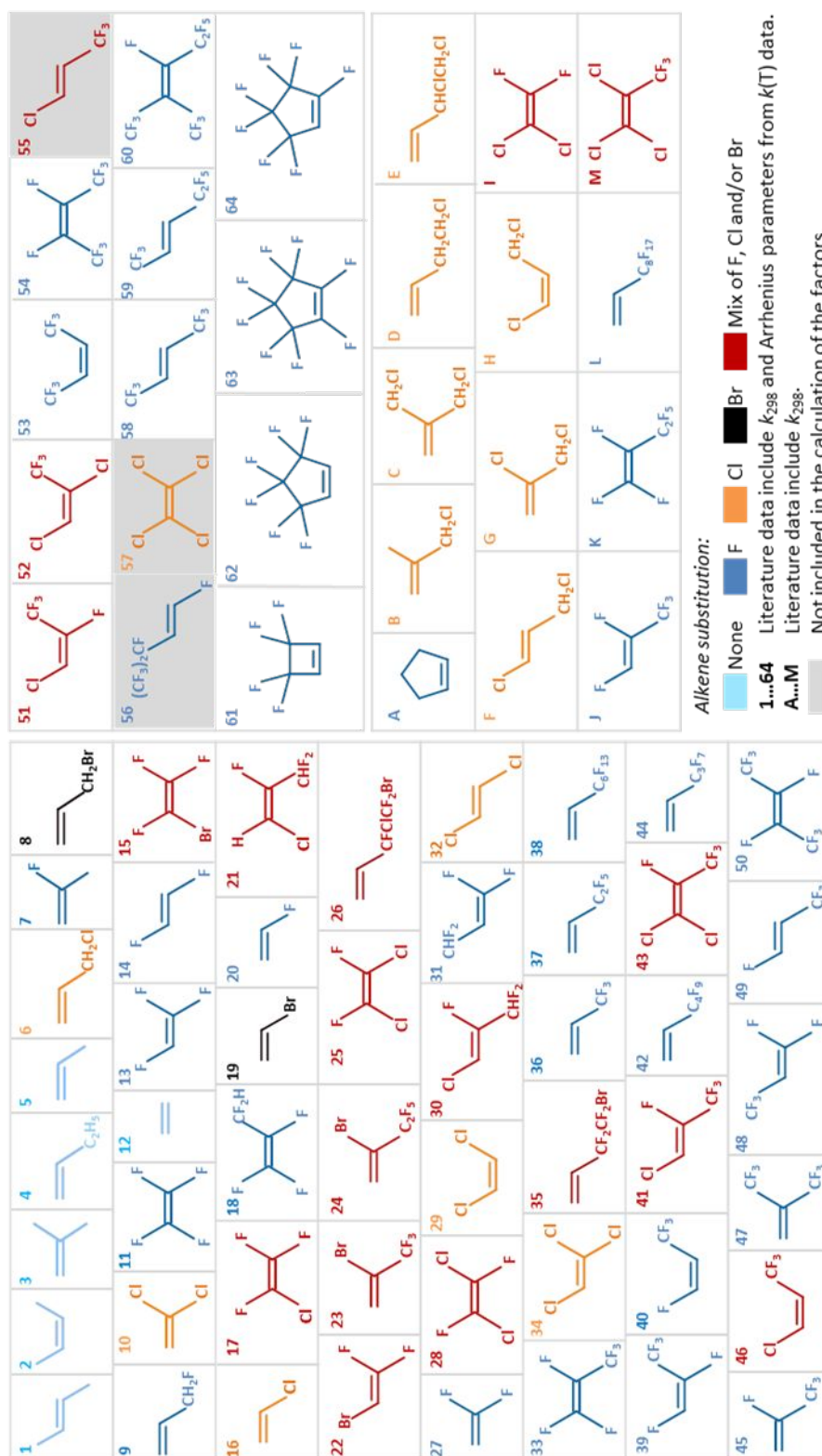
In this and the subsequent sections, we define the training set as those data points included in our multilinear regression analysis to derive the F -factors. The latter F -factors were optimized using a numerical solver that minimized the difference between the experimental and calculated (as defined in Equation 3) rate coefficients, as described in section 2.1.2. To test SAR performance and constrain fitting parameters, we compiled a comprehensive list of reaction rate coefficients for OH radical reactions with haloalkenes and alkenes for the training set. We used the latest version of the database of McGillen *et al.*²⁸ from which we obtained a total of 77 rate coefficients, 64 of which have been measured as a function of temperature (structures 1-64) and the remaining 13 determined at ~ 298 K (structures A-M) (Figure 2 and 3). We assume that all these data are in their high-pressure limit for an addition reaction. So far, very few alkenes have exhibited pressure dependence in their reaction with OH at pressures >100 Torr, and these appear to be limited to molecules with fewer heavy atoms such as ethene.²⁹ However, any rate coefficient not at its high-pressure limit would be expected to be an outlier in our correlation analysis. Furthermore, we excluded alkenes with large alkyl substituents because the OH radical could also abstract an H atom.³⁰

The compounds of the training set are presented together in a single Arrhenius diagram in Figure 3. Certain rate coefficients available in the literature show non-Arrhenius behavior, which is better described by $k(T) = A \exp(-B/T)(T/300)^n$. In some cases, i.e., for (*E*)- $(\text{CF}_3)_2\text{CFCH}=\text{CHF}$, (*Z*)-1,1,1,2,3,4,4,4-octafluorobut-2-ene, (*E*)-1,1,1,2,3,4,4,4-octafluorobut-2-ene, for simplicity, we refitted such data to an Arrhenius expression for the experimental temperature range (214 to 380K for (*E*)- $(\text{CF}_3)_2\text{CFCH}=\text{CHF}$ and 230-370K for the others). The worse discrepancy between the measured data point and the value from the Arrhenius fit is observed for (*E*)-1,1,1,2,3,4,4,4-octafluorobut-2-ene at $T=370$ K. In that case, the re-fitted values differ from the measurements by at most 13% for compound

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2
3 240 (*E*)-1,1,1,2,3,4,4,4-octafluorobut-2-ene over the range $T=230\text{--}370$ K. Although this results in a less
4
5 241 accurate fit to the individual measurements, we consider this to have a minor effect for all the cases
6
7 242 studied. The structures for each of the compounds considered in this study are presented in Figure 2,
8
9 243 which are placed in order of reactivity. The selected data are divided into three groups:

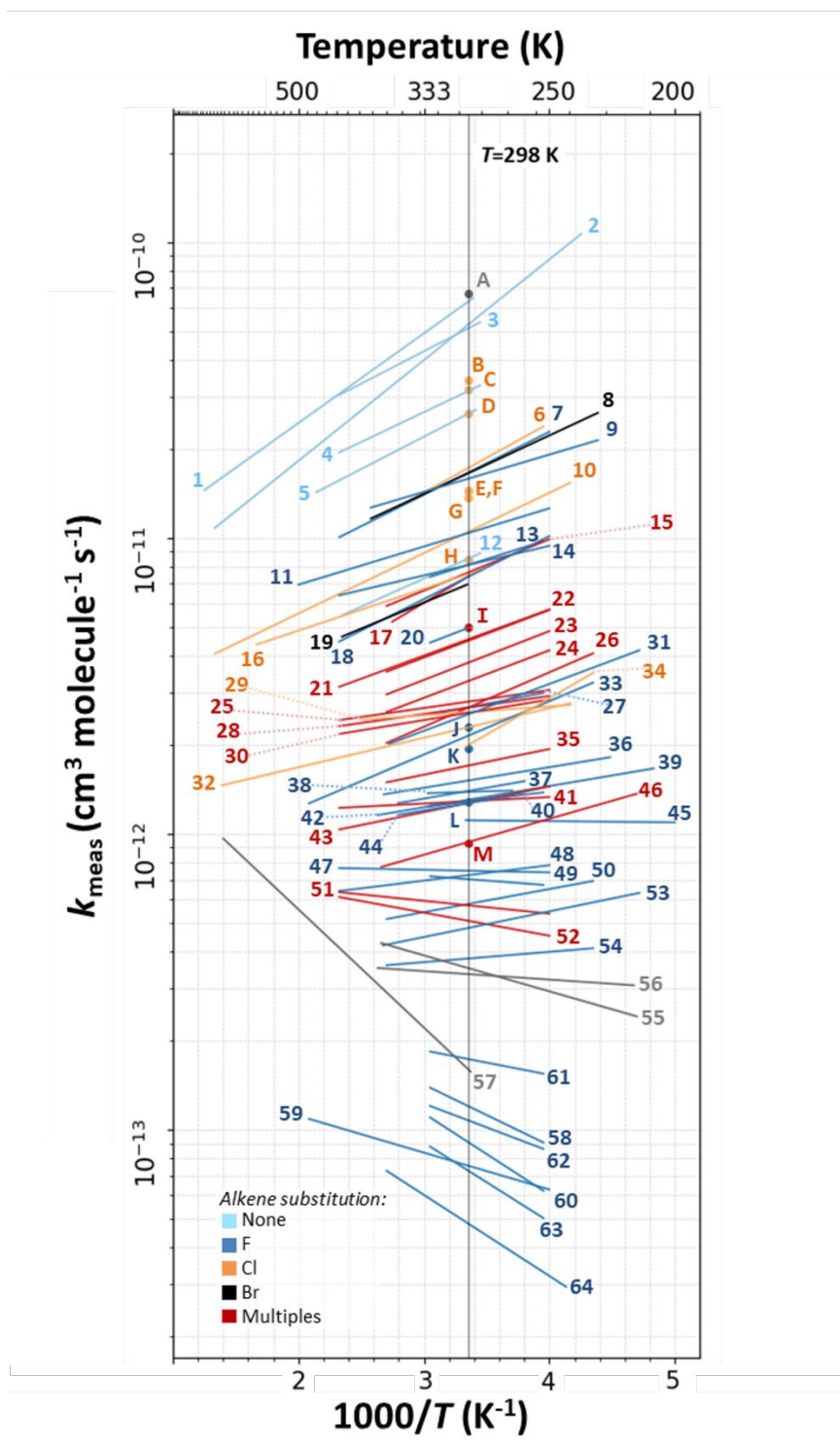
- 10 244 1. compounds with known Arrhenius parameters (numbers 1–64)
- 11
- 12 245 2. compounds with only room temperature measurements (letters A–M)
- 13
- 14 246 3. compounds not included in the training set (grey background, see details in section 3.4.)
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16
17 247 Since the SAR of Kwok and Atkinson as implemented in AOPWIN v1.92 includes almost all organic
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19 248 structures,⁷⁻⁹ no additional efforts were required to extend this SAR in the present work. By contrast, the
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21 249 SAR of Tokuhashi and co-workers is limited to haloalkene structures.¹⁷ We included additional alkenes
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23 250 and haloalkenes in the training set to extend this approach further. We opted not to include long-chain
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25 251 alkenes, where abstraction reactions are known to contribute to the overall reactivity.³⁰ Therefore, this
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27 252 SAR should be viewed as a quantification of the electrophilic addition reaction to the olefinic bond
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29 253 within a molecule rather than its overall reaction rate coefficient. However, extending this SAR to
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31 254 include hydrogen abstraction, similar to Kwok and Atkinson's approach,⁹ would be possible.
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256 **Figure 2:** Structures of the 77 molecules included in this study. Molecules with $k(T)$ data (1–64) and with only
 257 k_{298} data (A–M) are ordered by reactivity at 298 K.



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259 **Figure 3:** Arrhenius plots showing rate coefficients for all alkenes and haloalkenes included in this study. Data
260 were taken from the recent database of McGillen *et al.*²⁸ Dots represent measurements at room temperature only,
261 and lines represent temperature-dependent determinations.

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3.2. Performance of SARs at 298 K:

The optimized F -factors of Equation 3 included in the model are displayed in Table 1. The Tokuhashi *et al.* approach¹⁷ requires more fitting parameters than that of Kwok and Atkinson.⁹ This approach, therefore, requires more data with similar structures to train the corresponding F -factor. As assessed in section 3.6., by adding new diagonal substituent factors in this approach, the number of rate coefficients that can be estimated has been increased, especially for longer perfluoroalkyl substitutions.

Table 1: Substituent factors optimized for the diagonal structure around the olefinic bond from this work and that of Model 1 of Tokuhashi *et al.*¹⁷ The F -factors from this work are presented as defined in Equation 3. ^aFactors were optimized only from one experimental k_{298} data.

Diagonal substitutions across the double bond	Substituent factors (F)	
	This work	Tokuhashi <i>et al.</i> (2021) ¹⁷
H-C=C-H	2.39	2.348
H-C=C-F	1.87	2.041
H-C=C-Cl	2.21	2.218
H-C=C-Br	5.57	Not included
H-C=C-CH ₂ Cl	5.62	4.971
H-C=C-CH ₂ Br	7.32 ^a	Not included
H-C=C-CH ₂ F	6.69 ^a	5.395 ^a
H-C=C-CHF ₂	2.54 ^a	1.121 ^a
H-C=C-C _x H _y ($x \leq 2$)	9.14	7.561 for $x=1$
H-C=C-C _x F _y	5.93×10^{-1}	8.43×10^{-1} for $x=1$
H-C=C-C _x F _y X _z	8.57×10^{-1}	Not included
C _x H _y -C=C-C _z H _w ($x=z=1$)	2.64×10^{1a}	Not included
F-C=C-F	3.50	3.453
F-C=C-Cl	1.76	2.261
F-C=C-Br	2.28	Not included

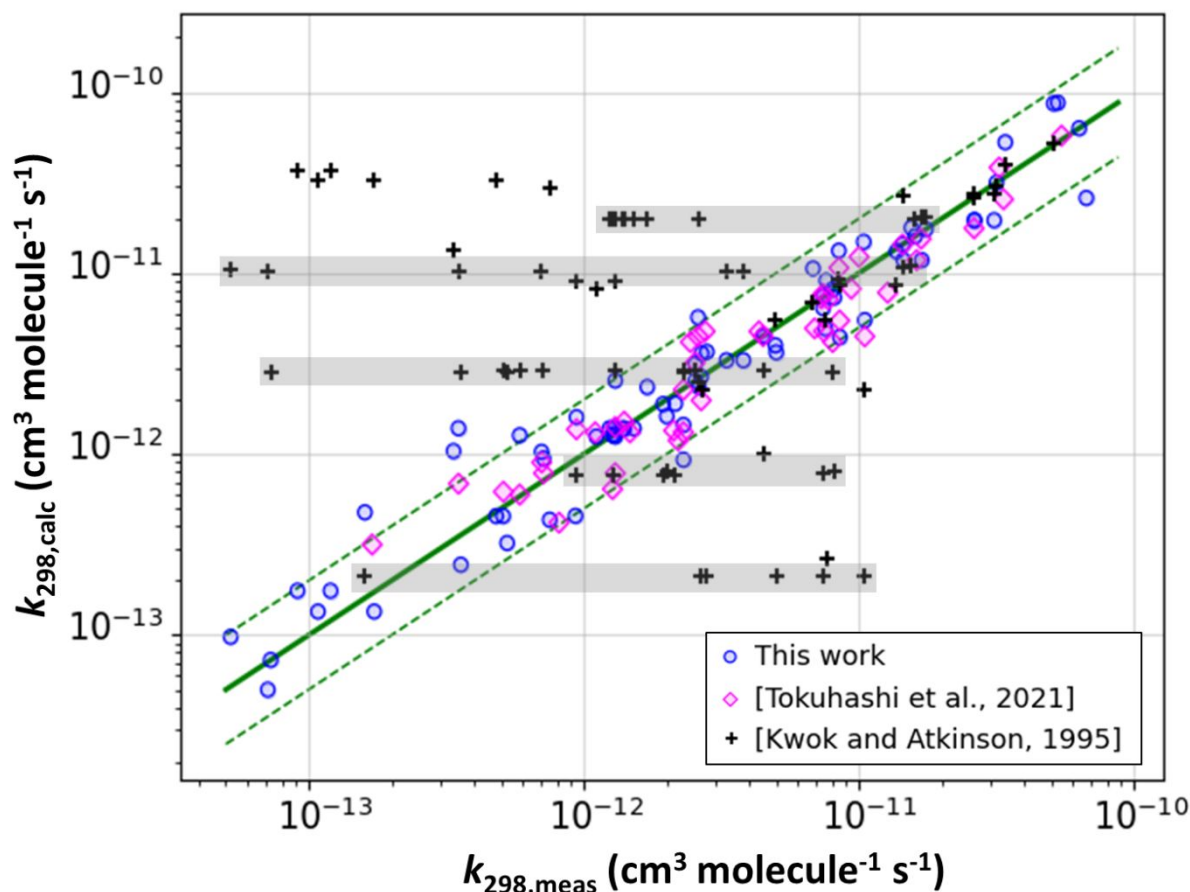
F-C=C-CHF ₂	1.69	2.109 ^a
F-C=C-C _x F _y	5.54 × 10 ⁻¹	3.84 × 10 ⁻¹ for x=1
Cl-C=C-Cl	9.04 × 10 ⁻¹	5.79 × 10 ⁻¹
Cl-C=C-CHF ₂	1.36	2.194 ^a
Cl-C=C-C _x F _y	7.20 × 10 ⁻¹	2.94 × 10 ⁻¹ for x=1
C _x F _y -C=C-C _x F _y	7.78 × 10 ⁻²	Not included
Cl-C=C-CH ₂ Cl	6.02 ^a	6.132 ^a
F _{cycle}	3.07 × 10 ⁻¹ (cyclic) 1 (acyclic)	Not included

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274 The performance of the SARs of Kwok and Atkinson,⁹ the SAR of Tokuhashi *et al.*,¹⁷ and our extension
 275 of the SAR of Tokuhashi *et al.* was assessed at 298 K. A comparison between calculated rate coefficients
 276 and experimental measurements is shown in Figure 4 for each of these methods. The SAR of Kwok and
 277 Atkinson,⁹ the original SAR formulation, was found to be notably less accurate than the other methods,
 278 as 64% of the training set predictions are under- or overestimated by more than 50%, with many outliers
 279 being up to 2 orders of magnitude larger or smaller than the measured values. For example, one estimate
 280 is 400 times larger than the measurement, i.e., for (*E*)-CF₃CH=CHCF₂CF₃ with $k_{\text{meas}} = 9.10 \times 10^{-14} \text{ cm}^3$
 281 $\text{molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{calc}} = 3.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There are several potential reasons for the
 282 discrepancy. It could be a limitation in the algorithm itself, demonstrating a high degree of degeneracy
 283 towards certain structural attributes. We define this degeneracy as various substitution patterns yielding
 284 identical rate coefficients (see Figure 4). Furthermore, the method provides the same estimates for rate
 285 coefficients measured to be 2 orders of magnitude apart from each other, *cf.* CF₂=CF₂ ($k_{\text{meas}} = 1.04 \times$
 286 $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) versus CCl₂=CCl₂ ($k_{\text{meas}} = 1.60 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) both of which are
 287 estimated to have a rate coefficient of $k_{\text{calc}} = 2.14 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As discussed in more detail
 288 in section 3.6, the predictions and measured values agree in our approach. The increased number of
 289 fitting parameters in the Tokuhashi method¹⁷ and our extended version affords the individual prediction
 290 of rate coefficients for specific isomeric structures, which is one of the reasons why degeneracy is lower
 291 in these approaches compared to the Atkinson method.⁹⁻¹²

292 We note that difficulties with multiple substituted haloalkenes have been recognized since the inception
 293 of this approach.⁹⁻¹² In addition, the training set available for the current implementation of the Kwok
 294 and Atkinson method⁹ was limited compared to the Tokuhashi approach¹⁷ presented here. Rate
 295 coefficients at room temperature, k_{298} , were well-predicted using the modified Tokuhashi approach, as

296 illustrated in Figure 4. Tokuhashi's SAR^{13,17} and our extended version show only minor differences, with
 297 80% and 77%, respectively, of cases being reproducible to within a factor of 2. Our approach to
 298 generalizing the SAR to include more haloalkenes and alkenes appears not to come at the cost of
 299 reducing its overall performance.



300
 301 **Figure 4:** SAR results and comparison with Tokuhashi predictions¹⁷ (magenta diamond) and AOPWIN^{7,8}
 302 calculations based on Kwok and Atkinson approach⁹ (black plus) at 298 K. Blue circles are predictions using our
 303 SAR model ($k_{298,calc}$). Green dashed and bold lines show the interval in which data calculated agree within a factor
 304 of 2 with measured data. The grey areas indicate identical predictions from AOPWIN as a consequence of the
 305 degeneracy in the SAR algorithm.

307 3.3. The relationship between k_{298} and E_a/R :

308 Next, we investigated the effect of temperature on alkene and haloalkene reaction rate coefficients. By
 309 comparing all temperature dependencies in a single Arrhenius diagram (see Figure 3), it is clear that the
 310 experimental temperature dependence factor (E_a/R) switches from a positive to a negative value as the

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3 311 rate coefficient at 298 K becomes larger. By correlating the experimental E_a/R with the $\ln(k_{298})$ (Figure
4 312 5), we found that the data could be fitted adequately using an inverse sigmoidal function for E_a/R ranging
5 313 from -784 K to +920 K, as:

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$$\ln\left(\frac{k_{298}}{2.7 \times 10^{-10}}\right) = \frac{-8.6}{\left[1 + \exp\left(\frac{-300 \text{ K} - \frac{E_a}{R}}{363 \text{ K}}\right)\right]} \quad (10)$$

16 315 where $\ln(k_{298})$ is the natural logarithm of the room temperature rate coefficient k_{298} in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,
17 316 and E_a/R is the Arrhenius activation energy in Kelvins, both of which are measured properties. The
18 317 remaining values represent optimized fitting parameters. Equation 10 is a parametrization function and
19 318 does not provide physical meanings for the parameters. Reactions with the lowest activation energies
20 319 possess rate coefficients close to their collision limits, resulting in a lower limit in E_a/R factors.

25 320 Although it should be remembered that the exact size of the collision rate coefficient will vary depending
26 321 on several parameters such as the size or the polarizability of the molecules involved. Nevertheless, the
27 322 probability of collision between the OH radical and the olefinic bond is unlikely to change drastically
28 323 within the training set.

32 324 Conversely, the less reactive compounds will possess the highest E_a value. It is intuitive to expect a limit
33 325 to which a given selection of halogenated substitutions can withdraw electrons from the olefinic bond,
34 326 e.g., in perfluoroolefins. Indeed, similar E_a/R values are seen for the less reactive molecules in this study.
35 327 Hence, the lower bound of the fit is assumed to be equal to the lowest measured value of E_a included in
36 328 this training set.

40 329 These upper and lower bounds ($(E_a/R)_{\min} = -784 \text{ K}$ and $(E_a/R)_{\max} = +920 \text{ K}$) therefore bracket the range
41 330 of values that we encountered in this training set. In the following steps of the calculation, for k_{298} larger
42 331 than $7.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and smaller than $2.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the calculated E_a/R
43 332 factors were forced to be equal to the upper and lower bounds of the fit respectively (Figure 6).

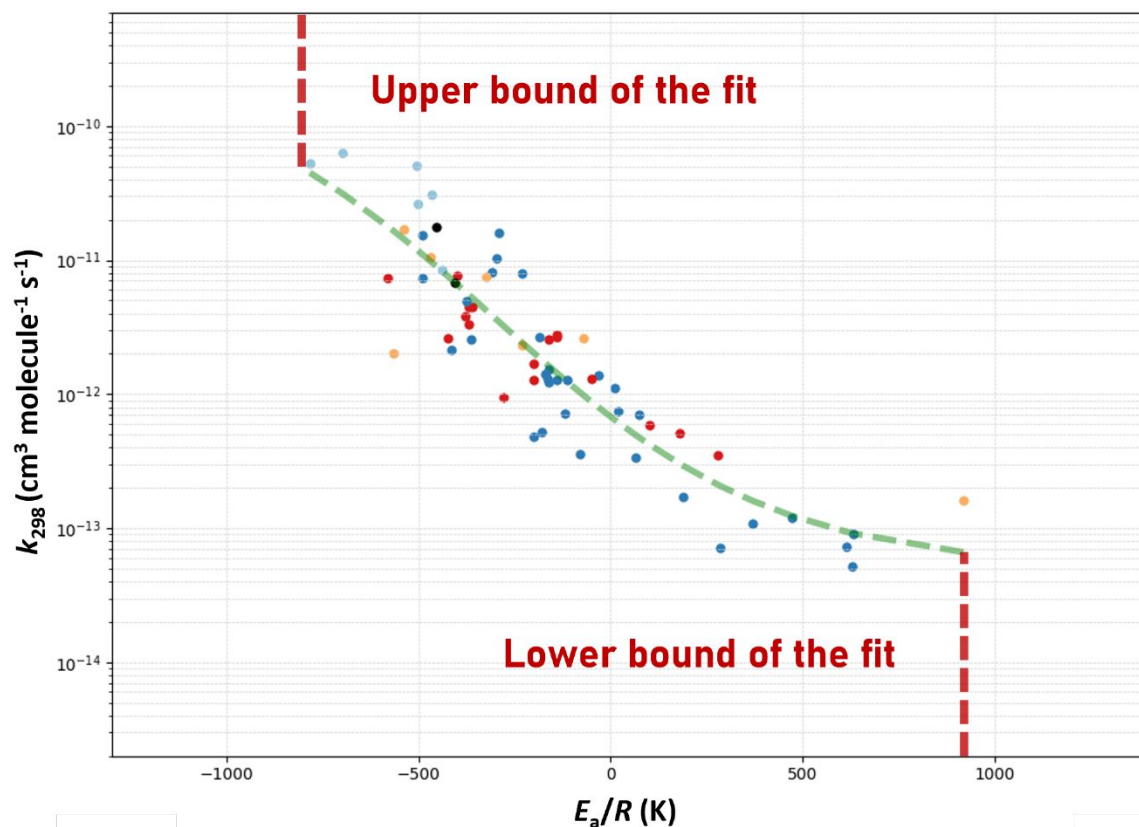


Figure 5: Inverse sigmoidal fit of k_{298} vs. E_a/R for all the 77 molecules included in this study and described in Figure 2.

3.4. Extension and performance of SAR for temperature dependence between 200 and 400 K:

The A -factor (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) has been calculated to extend the room temperature predictions to temperature-dependent ones. As seen in Table S4 and Figure S4, A -factor in our training set can range from $1.98 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $9.42 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hence, to account for its variation, the A -factor was retrieved using the estimated k_{298} (Equation 3) and the estimated E_a/R factor (Equation 10) using the equation:

$$A = k_{298} \exp\left(\frac{E_a}{298 \times R}\right) \quad (11)$$

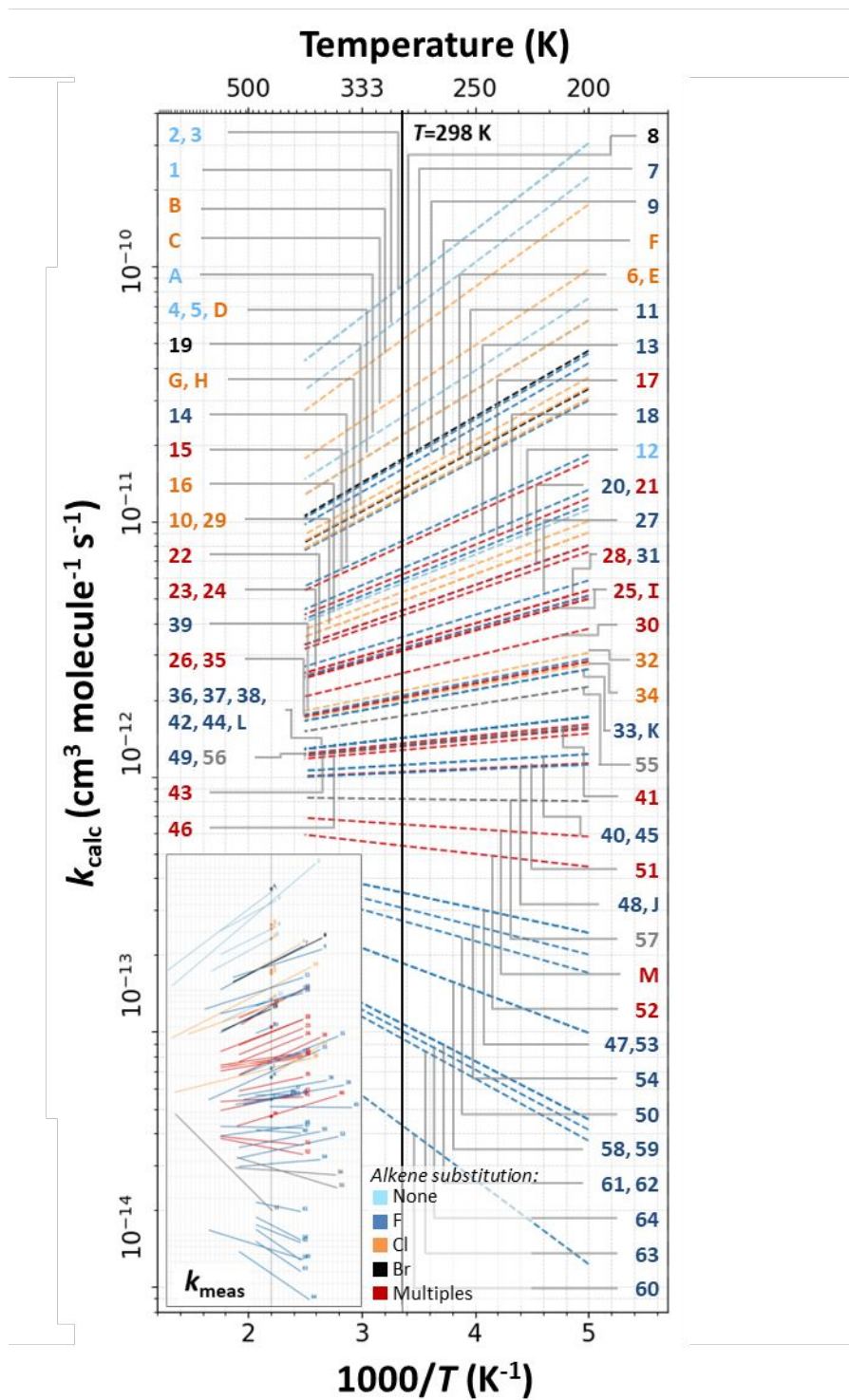
Then, Arrhenius parameters and $k(T)$ can be estimated over the temperature range of this study (200–400 K); the results are plotted in Figure 6. The agreement between measurements and calculations $k_{\text{calc}}(T)$ is quantified from the ratio relative to the measured values $k_{\text{meas}}(T)$, defined as $k_{\text{calc}}/k_{\text{meas}}$ when $k_{\text{calc}} > k_{\text{meas}}$ and $k_{\text{meas}}/k_{\text{calc}}$ when $k_{\text{meas}} > k_{\text{calc}}$, in Figure 7. In general, temperature-dependence is well-predicted using this method. Most (~84%) of the predicted rate coefficients are within a factor of two of

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3 350 the experimental values throughout the temperature range of 200 to 400 K, as presented in Figure 8.
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5 351 Three notable exceptions are $\text{CCl}_2=\text{CCl}_2$, $(E)\text{-CHCl=CHCF}_3$, and $(E)\text{-(CF}_3)_2\text{CFCH=CHF}$, where the
6 predicted rate coefficients are higher than those measured. These compounds were excluded from the
7 352 fitting procedure as they demonstrated no apparent improvement when optimizing the F -factors. All
8 353 three of these molecules possess a high degree of halogenation, with two of them containing chlorine.
9 354 Tokuhashi *et al.*¹⁷ have observed previously that chlorination results in worse predictions. It can either
10 355 be because of a mechanistic difference that this SAR does not adequately describe chlorinated molecules
11 356 or due to some significant uncertainties and disagreements in the experimental data. We are not yet able
12 357 to understand the exact reason for this behavior.
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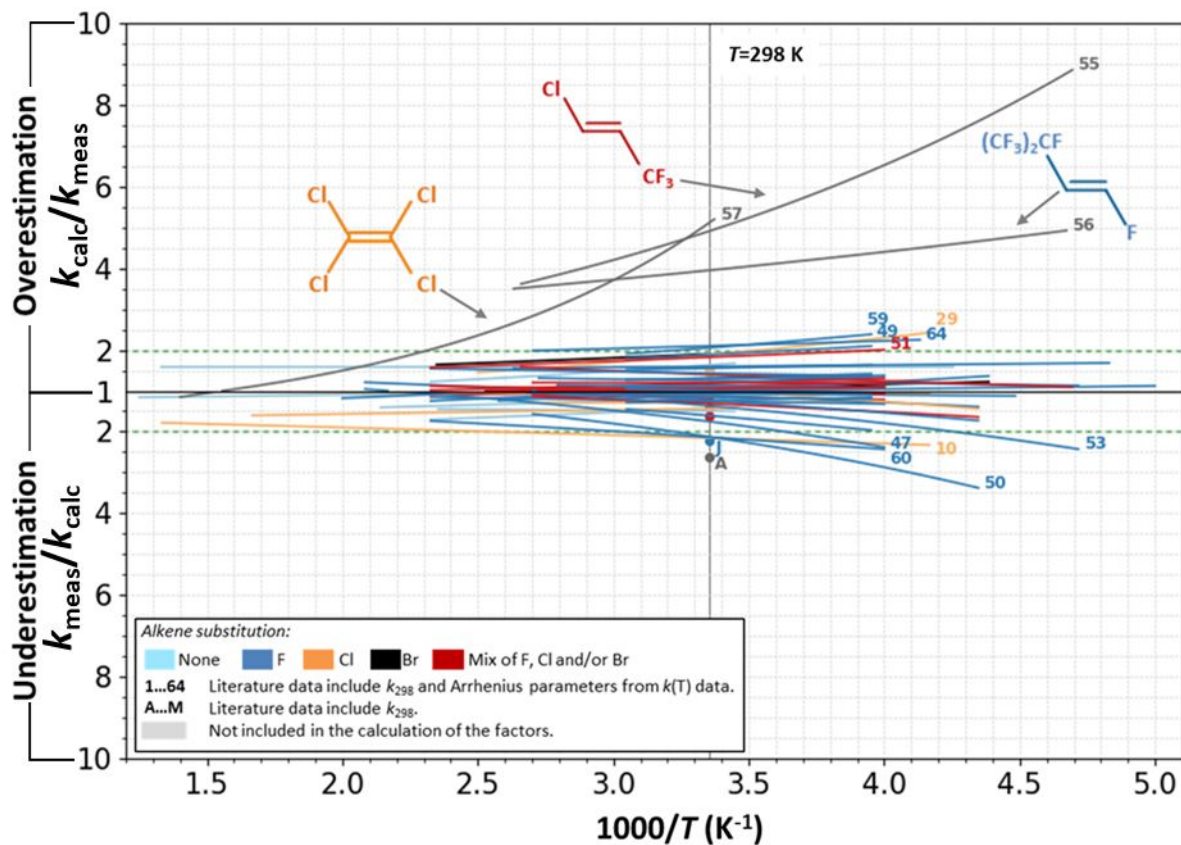
14 359 For highly halogenated compounds, multiple halogen substitutions and the specific bulkiness of chlorine
15 360 substitutions close to the reactive center (i.e., the olefinic bond) may contribute to the steric strain and
16 361 steric shielding that is encountered in the electrophilic addition.³¹ Furthermore, since these are
17 362 electrophilic addition reactions, we expect the electron withdrawal in the π -orbitals to have an important
18 363 effect on the overall rate coefficients. Specific combinations of halogen substitutions within a sidechain
19 364 may also influence reactivity. In the example of $(E)\text{-(CF}_3)_2\text{CFCH=CHF}$, the $(\text{CF}_3)_2\text{CF-}$ substitution may
20 365 have a more potent electron-withdrawing effect than the generic $\text{CF}_2\text{X-}$, to which we have assigned it.
21 366 Evidence for such an influence comes from the resonance and field parameters which are notably
22 367 different from the straight-chain perhalogenated substitutions,³² and which could be responsible for the
23 368 low reactivity of $(E)\text{-(CF}_3)_2\text{CFCH=CHF}$ towards OH. However, further theoretical work and
24 369 measurements are required to better understand the mechanisms of these reactions.

25 370 There is also the possibility that there may be some mechanistic differences for some of the reactions
26 371 contained within our dataset. This would explain why some rate coefficients are poorly predicted using
27 372 this SAR approach, since one of the main assumptions of this work is that all reactions considered here
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375 **Figure 6:** Experimental data (inset) and predictions of $k_{\text{calc}}(T)$ over the studied temperature range (200–400 K) in
 376 dashed lines using our SAR model. Experimental values are plotted from Arrhenius parameters McGillen *et al.* in
 377 bold lines.²⁸



378
 379 **Figure 7:** Ratio between measured and calculated rate coefficients over the temperature range of this study, is
 380 defined as $k_{\text{calc}}/k_{\text{meas}}$ when $k_{\text{calc}} > k_{\text{meas}}$ and $k_{\text{meas}}/k_{\text{calc}}$ when $k_{\text{meas}} > k_{\text{calc}}$. Green dashed and bold lines showing the
 381 interval in which data calculated agree within a factor 2 with measured data.

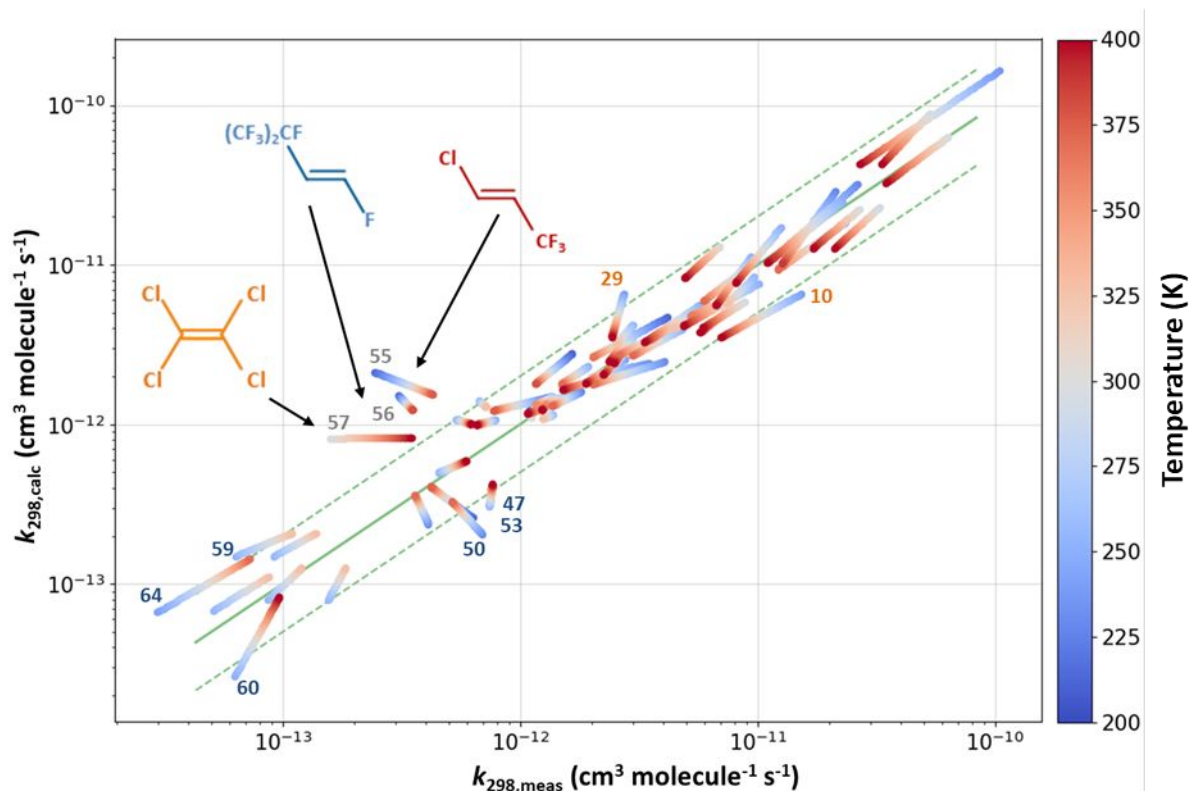


Figure 8: Calculated OH rate coefficients versus measured OH reaction rate coefficients as a function of temperature over 200–400K. The bold green line represents the perfect agreement between prediction and measurements. The dashed lines identify the range within which calculations and measurements agree within a factor of 2 on either side.

3.5. Measurements of the temperature dependence for the reaction rate coefficients of OH with $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$:

To test the SAR for predicting the temperature dependence, we determined the Arrhenius parameters and k_{298} for the reaction of OH with $\text{CF}_2\text{HCH}=\text{CF}_2$ between 223 and 373 K using our PLP–LIF setup. There are no experimental data available for this reaction. In addition, we measured the established rate coefficient for OH reaction with $\text{CF}_3\text{CH}=\text{CH}_2$ (212–367 K).

The measured values of the OH reaction rate coefficient as a function of temperature for the two selected HFOs, $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$, are provided in Tables S1 and S2, respectively, together with the experimental conditions. The pseudo-first-order decay rate coefficients of the OH fluorescence signal k' (s^{-1}), are plotted against the concentration of the HFO (in molecule cm^{-3}), yielding second-order plots, examples of which are shown in Figure 9. The slopes of the lines give the OH reaction rate coefficients k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) based on Equation 9. The reported uncertainties in the

rate coefficient determinations reflect the statistical uncertainties (2σ at 95% CI) from the uncertainty-weighted linear least squares fit of these data. The overall systematic errors of the measurements were estimated to be $<15\%$, including statistical error in k' ($<6\%$) and temperature (1%), and the estimated uncertainty in the concentration of HFO ($\sim 10\%$) and pressure ($\sim 6\%$). Flow rates and concentrations of gases were varied from one run to another to test the reproducibility of our results. The use of nitric acid or hydrogen peroxide as precursors for OH radicals displayed no noticeable difference in the measured rate coefficients. The linearity in the second-order plots indicates that the pseudo-first-order assumption remains valid in our experimental conditions.

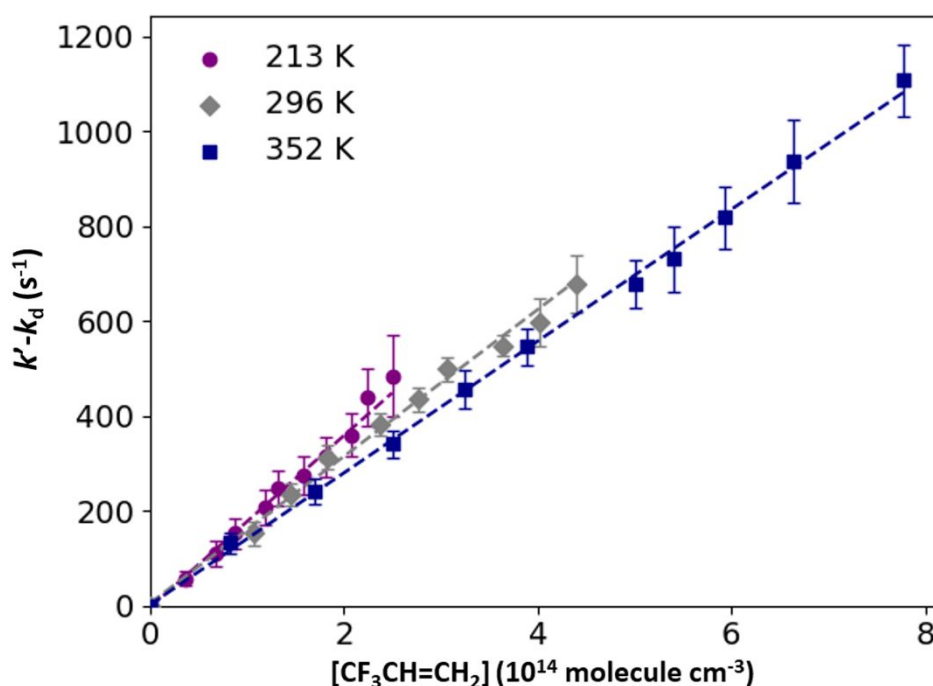


Figure 9: Representative plots of the dependence of the pseudo-first-order rate coefficient (k') on $[\text{CF}_3\text{CH}=\text{CH}_2]$ at three temperatures measured using the PLP-LIF apparatus. Plotted uncertainties represent statistical errors (2σ at 95% CI).

The temperature-dependence of the reaction rate coefficients for $\text{CF}_3\text{CH}=\text{CH}_2$ between 212 and 367 K and $\text{CF}_2\text{HCH}=\text{CF}_2$ between 223 and 373 K were well represented by a simple Arrhenius expression (see Figure 10). Both reactions exhibit negative temperature dependencies. To obtain the Arrhenius parameters, we employed an uncertainty-weighted linear least squares curve-fitting routine to the logarithm of the temperature-dependent rate coefficient data, $\ln(k_{298})$, as a function of inverse temperature, using the reported statistical uncertainties of the experimental data. The parameters from this work and the literature are presented in Table 2, and the Arrhenius plots are shown in Figure 10.

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3 421 The fits of our experimental data are defined as follows:
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$$k_{\text{OH} + \text{CF}_3\text{CH}=\text{CH}_2}(T) = (8.4 \pm 1.3) \times 10^{-13} \exp\left(\frac{161 \pm 12}{T}\right) \quad (12)$$

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$$k_{\text{OH} + \text{CF}_2\text{HCH}=\text{CF}_2}(T) = (7.6 \pm 1.2) \times 10^{-13} \exp\left(\frac{365 \pm 6}{T}\right) \quad (13)$$

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15 425 where the stated uncertainties represent the combined absolute and statistical errors (2σ at 95% CI) of
16 426 the measurements. We compare our results for OH reaction with $\text{CF}_3\text{CH}=\text{CH}_2$ with the measurements
17 427 and the associated uncertainties of Tokuhashi *et al.*,¹³ Orkin *et al.*,¹⁸ and González *et al.* in Figure 10.²²
18 427 The plotted uncertainties of k for the literature data represent only statistical errors. Our results are in
19 428 excellent agreement with the data from Orkin *et al.*,¹⁸ and only slightly different from those of González
20 429 *et al.*²² and Tokuhashi *et al.*¹³ at lower temperatures. To the best of our knowledge, we are the first to
21 430 report the rate coefficients for reaction with $\text{CF}_2\text{HCH}=\text{CF}_2$. Compared to $\text{CF}_3\text{CH}=\text{CH}_2$, the reactivity of
22 431 $\text{CF}_2\text{HCH}=\text{CF}_2$ is higher, with a larger negative temperature dependence. This was also anticipated by
23 432 the relationship between k_{298} and E_a/R (see Figure 5). We have extended the minimum temperature for
24 433 which data are available in the literature, from 250 to 212 K, in OH rate coefficient determinations for
25 434 the reaction with $\text{CF}_3\text{CH}=\text{CH}_2$.¹³
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33 436 The parameters predicted from the model are in good agreement with the measured values (Figure 10
34 437 and Table 2), with k_{298} underpredicted for $\text{CF}_3\text{CH}=\text{CH}_2$ by only 7% and overpredicted for $\text{CF}_2\text{HCH}=\text{CF}_2$
35 438 by 24%. One of the diagonal substituent factors of the newly measured $\text{CF}_2\text{HCH}=\text{CF}_2$, $F(\text{F}-\text{C}=\text{C}-\text{CF}_2\text{H})$,
36 439 was trained with only one other compound in the model, which explains the lower accuracy compared
37 440 with the more studied $F(\text{H}-\text{C}=\text{C}-\text{CF}_3)$ present in $\text{CF}_3\text{CH}=\text{CH}_2$. To improve the model, we then re-
38 441 evaluated the F -factors, including k_{298} for $\text{CF}_2\text{HCH}=\text{CF}_2$ we measured in this work, and, as expected,
39 442 notable improvements can be observed (see red/green plots in Figure 10).
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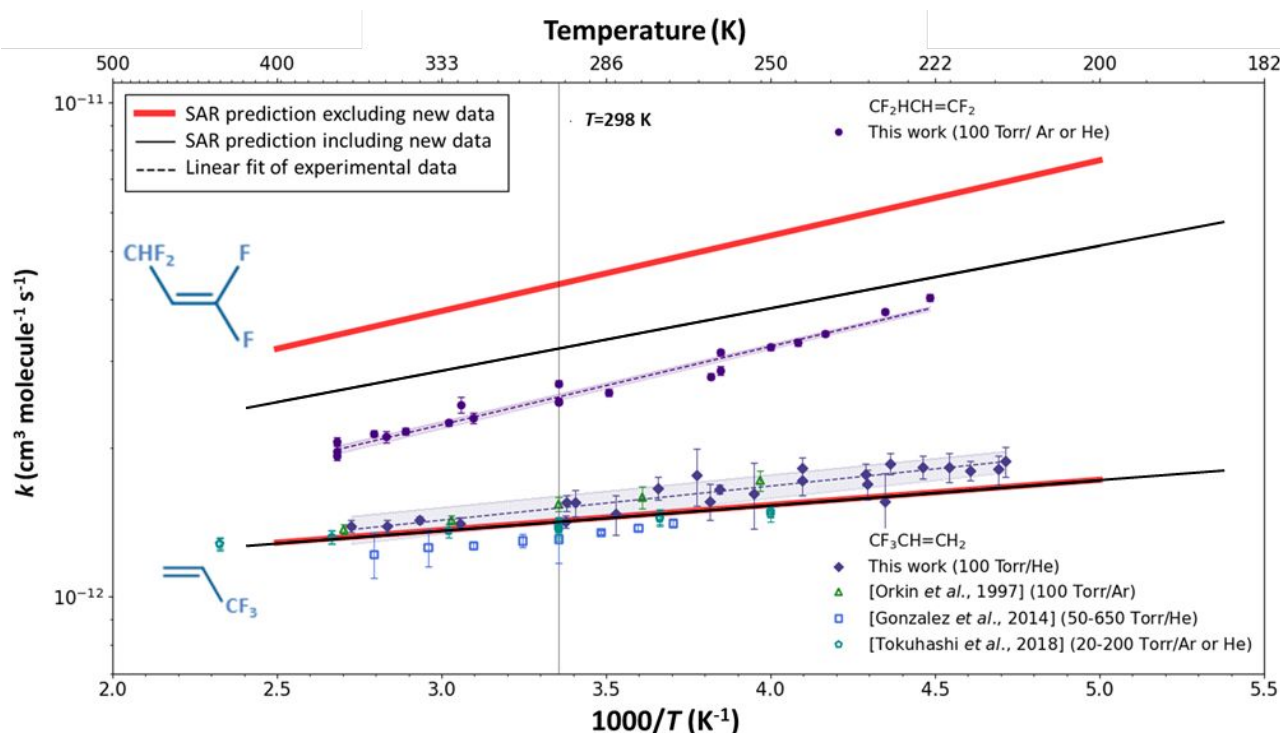


Figure 10: Arrhenius plots on a log scale showing the experimental measurements of the $k(T)$ as a function of inverse temperature, $1000/T$, for the reaction of OH radicals with $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$ measured in this work, compared to the literature.^{13,18,22} SAR predictions from the model without including the new measurements presented in this work are plotted in red, while the updated version that includes the new data is plotted in black. A notable improvement in the prediction of OH rate coefficient for the reaction with $\text{CF}_2\text{HCH}=\text{CF}_2$ is observed, whose diagonal factors were constrained by only one previous measurement.

Table 2: Arrhenius parameters for reactions of OH with $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$ compiled from this work and previous studies.^{13,18-23} For $\text{CF}_3\text{CH}=\text{CH}_2$, the recommendation of Arrhenius parameters results from the fit including data of this work and that of Orkin *et al.*,¹⁸ while k_{298} is a weighted average of all the rate coefficients reported in the literature. P is the total pressure of the carrier gas (He or Ar) and reactive compound. The quoted error bars are those of the authors. ^aFP: flash photolysis, RF: resonance fluorescence, RR: relative rate methods. ^bReported values for A , E_a/R , and k_{298} in the table are the SAR predictions when including new measurements for $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{HCH}=\text{CF}_2$. For comparison, the values of $(A, E_a/R, k_{298})$ predicted from the SAR before adding the new measurements are $(1.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 351 \text{ K}, 4.28 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for $\text{CF}_2\text{HCH}=\text{CF}_2$ and $(9.61 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 117 \text{ K}, 1.43 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for $\text{CF}_3\text{CH}=\text{CH}_2$.

Molecule	A (10^{-13} cm ³ molecule ⁻¹ s ⁻¹)	E_a/R (K)	k_{298} (10^{-12} cm ³ molecule ⁻¹ s ⁻¹)	T (K)	P (Torr)	Technique ^a	Reference
CF ₃ CH=CH ₂	9.60	116	1.42	200–400		Calculations ^b	This work
			1.51	298		Calculations	(Tokuhashi <i>et al.</i> , 2021) ¹³
	8.86 ± 0.82	159 ± 26	1.47 ± 0.25	212–367	100	PLP–LIF	This work
	8.28 ± 0.7	183 ± 26	1.52 ± 0.02	252–370	100	FP–RF	(Orkin <i>et al.</i> , 1997) ¹⁸
	7.65 ± 0.26	165 ± 10	1.31 ± 0.14	263–358	50–650	PLP–LIF	(González <i>et al.</i> , 2015) ²²
	10.6 ± 0.20	80 ± 10	1.40 ± 0.01	250–430	20–200	FP, PLP–LIF	(Tokuhashi <i>et al.</i> , 2018a) ¹³
			1.36 ± 0.25	296	700	RR	(Andersen <i>et al.</i> , 2005) ¹⁹
	8.86 ± 0.71	160 ± 24	1.40 ± 0.67				Recommendation
CF ₂ HCH=CF ₂	12.0	290	3.17	200–400		Calculations ^b	This work
	7.46 ± 0.34	365 ± 13	2.55 ± 0.18	223–373	100	PLP–LIF	This work

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465 3.6. Discussion of the SAR:

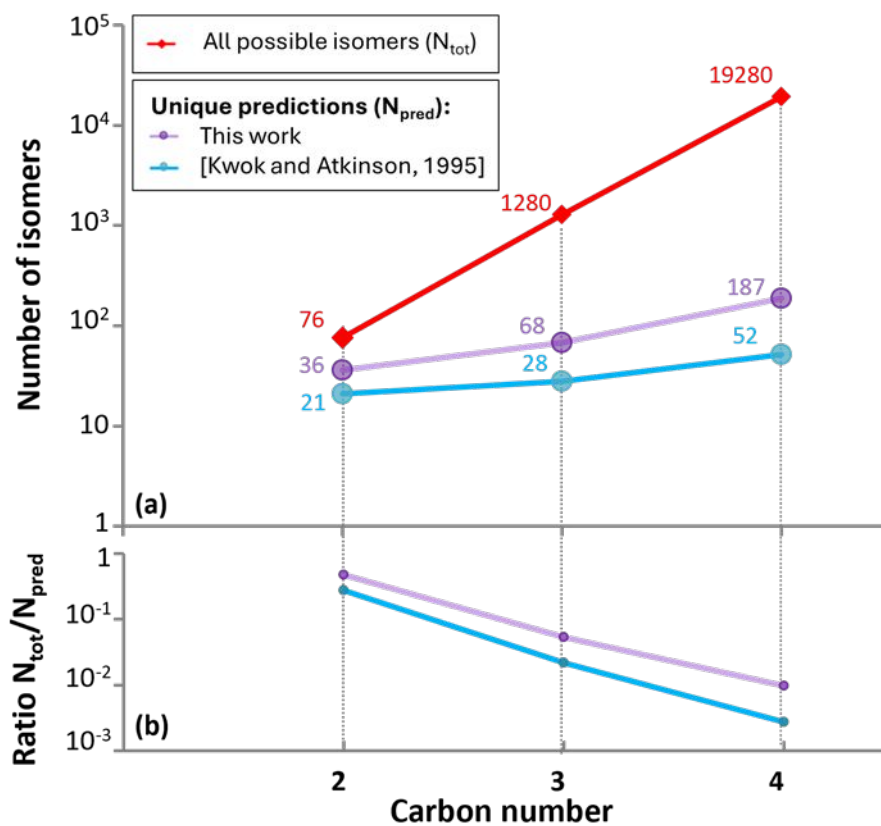
466 In this section, we discuss the degeneracy in the predictions from our SAR and other existing methods
 467 as the number of isomers increases. We begin by enumerating all isomers of alkenes, N_{tot} , and
 468 haloalkenes containing C, H, F, Cl, and Br up to a carbon number of 4. We obtained N_{tot} using a set of
 469 Markush structures generated in MarvinSketch version 22.5.0, ChemAxon
 470 (<https://www.chemaxon.com>). Since AOPWIN outputs distinctively H-abstraction and OH-addition
 471 reaction rate coefficients, to test the degeneracy of this method with regards to the electrophilic addition,
 472 we filtered this output to exclude the contribution of H-abstraction reaction channels in this section and
 473 only use OH addition reaction rate coefficients. Taking this into account, we computed OH electrophilic
 474 addition reaction rate coefficients, k_{add} , for all the possible isomers using the AOPWIN program. We
 475 eliminated duplicates to obtain the number of unique predictions, N_{pred} , for each carbon number.
 476 Similarly, we enumerated all the unique predictions of k_{298} that can be obtained with the diagonal factors
 477 given in this work. The comparison between the number of existing isomers and the number of unique
 478 predictions from each approach is presented in Figure 11. It is noted that within these enumerations,
 479 optical isomers will be present, and this form of isomerization is not expected to impart a change to the
 480 rate coefficient.

481 There are many possible structures with all combinations of halogens and alkenes (Figure 11). So far,
 482 the substituted ethenes alone constitute 76 isomers. As the number of carbons increases, the number of
 483 isomers increases exponentially, many of which are of potential interest in various applications. It would
 484 be impractical to measure each one or even calculate them all with theory. SARs provide a rapid way to

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3 485 estimate all these possibilities. Since it is a simplification, we can expect uncertainties in these
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5 486 predictions (Figure 11, Panel a). We observed significant degeneracy in the predictions of AOPWIN
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7 487 (see trends of similar k -values in Figure 4), although in this case, the k -values include both the OH
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9 488 addition and the H-abstraction pathways. Here, we only compare the OH electrophilic addition rate
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11 489 coefficient values, and we observe an important degeneracy again in the estimations of AOPWIN
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13 490 (Figure 12). For example, at a carbon number of 2, there are 76 isomers and, in the best case, 36 unique
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15 491 predictions are obtained from this SAR. But as the carbon number increases, the number of unique
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17 492 predictions grows slowly relative to the number of possible isomers (Figure 11, Panel b). For clarity, we
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19 493 only present our SAR predictions together with those of AOPWIN as our algorithm is only an extension
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21 494 of the approach of Tokuhashi *et al.*,¹⁷ and hence the level of degeneracy and distribution of predictions
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23 495 is similar.

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25 496 Our description above raises the question: how simple is too simple? Inspecting the currently available
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27 497 dataset, one can observe that the dataset of reaction rate coefficients is quite evenly distributed (Figure
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29 498 12). Based on the available data in the training set, there does not seem to be a dominant mode in the
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31 499 rate coefficient distribution, overall, it looks almost continuous. The estimation space of our approach
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33 500 appears to be more uniformly distributed compared to the AOPWIN program, which has several clusters
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35 501 of degenerate predictions. For example, the clusters 56 and 82 (x-axis) out of the 100 k -data groups in
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37 502 Figure 12 contain the highest frequencies of predictions from AOPWIN, meaning that there are many
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39 503 estimates having the same rate coefficient, even though there are no or few experimental data in this
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41 504 range. This highlights both the problem of degeneracy and inaccuracy when using a SAR. This work
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43 505 improves upon previous methods since it appears to reproduce and cover the entire distribution
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45 506 uniformly, consistent with the pattern of the experimental data.

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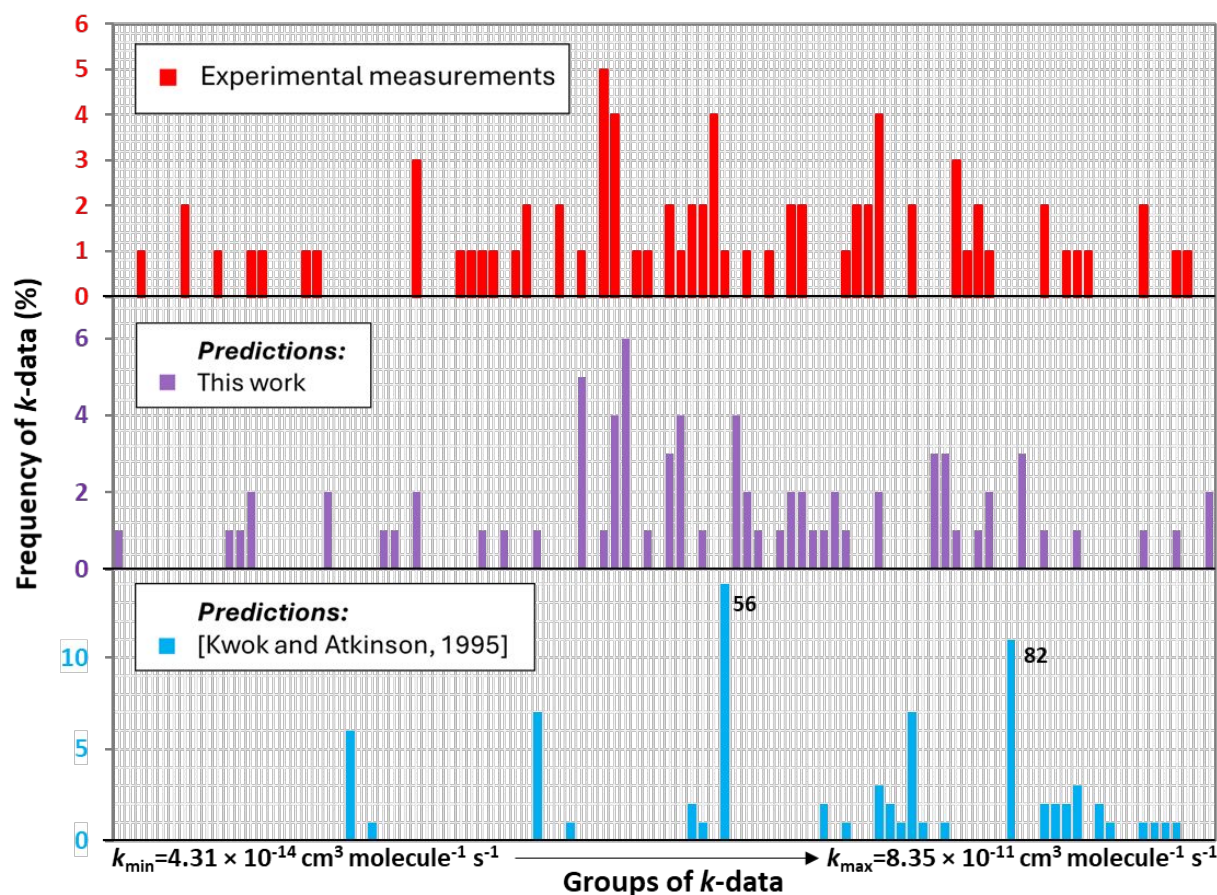


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509 **Figure 11:** Panel a: Number of possible olefinic isomers from the combination of H, F, Cl, and Br substitutions at
510 carbon numbers between 2 and 4, N_{tot} , in relation to the number of unique predictions, N_{pred} , obtained with the
511 approaches of Kwok and Atkinson⁹ obtained from AOPWIN and this work. Panel b: Ratio between N_{tot} and N_{pred} .

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515 **Figure 12:** Histograms of the available kinetic data for the OH reaction with alkenes of interest. Upper panel: the
516 measured rate coefficients, Middle panel: values calculated from this work, Lower panel: values calculated with
517 the approach of Kwok and Atkinson⁹ outputted from AOPWIN. Rate coefficients are binned into 100 groups of
518 evenly distributed k_{298} -rate coefficients ranging from the minimum k_{298} through to the maximum.

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520 3.7. Atmospheric implications:

521 Most of the haloalkenes of this training set are short-lived, and thus they are not well mixed in the
522 troposphere. Their lifetimes depend strongly on the location and time of their emission.^{33,34} An average
523 tropospheric lifetime calculation would not be accurate for all cases. By estimating reaction rate
524 coefficients with this method, one can then evaluate the tropospheric lifetime of the compound of interest
525 using the approach of Brioude *et al.*³³ Consequently, rather than focus on the tropospheric lifetime of
526 each compound, we explore the potential of SARs in their use as a screening tool. Rapid and
527 straightforward estimation of the OH reaction rate coefficient for a large number of haloalkenes is
528 possible using this approach, allowing scientists, industries, and policymakers to select more
529 environmentally friendly product candidates conveniently.

4. Summary and Conclusions:

In this work, we developed a method to predict the Arrhenius parameters of the OH addition reaction rate coefficients of haloalkenes and related compounds. For this purpose, we used literature data for the OH kinetics of hydrofluoroolefins (HFOs) and related haloalkenes, constituting the training set of this study. From the structure-activity relationship (SAR) of the OH rate coefficients of this training set, a trend was observed between reactivity, structure, and activation energy. The more reactive compounds ($k_{298} \sim 10^{-12}$ – 10^{-10} cm³ molecule⁻¹ s⁻¹) have a predominantly negative temperature dependence, while less reactive compounds ($k_{298} \sim 10^{-12}$ – 10^{-14} cm³ molecule⁻¹ s⁻¹) display a generally positive temperature dependence. This is consistent with the expectation that the barrier for a reaction hinders reactivity for many compounds. Our method to calculate room-temperature reaction rate coefficients, k_{298} , is in good agreement with measurements as well as previous approaches developed by Tokuhashi *et al.*¹⁷ and Kwok and Atkinson,⁹ as more recently implemented in the AOPWIN program, as described in Lim's paper.^{7,8} The extended method we present to predict $k(T)$ over the temperature range 200–400 K is the first temperature-dependent calculation method to predict the kinetics of OH-addition to haloalkenes. The overall performance of this new approach was found to be satisfactory, as 90% of the estimated Arrhenius parameters agree within a factor of 2 for the 77 compounds examined. Our method provides an excellent starting point for estimating the temperature-dependent OH electrophilic addition rate coefficient for a wide range of halogenated alkenes as a multiplication of three F -factors developed in this work.

This approach is built upon the simplest possibility that these F -factors are proportional to the reactivity of the double bond. The multiplicative substituent factors, $F(X-C=C-Y)$ and $F(Z-C=C-W)$, may relate to, amongst other possible factors, the electron density of the π -orbital of the double bond of the compounds. The lower the value of the diagonal substitution factor, the lower the electron density, and the higher the diagonal substitution factor, the larger the reactivity. Additional steric effects could be involved for the cyclic structures compared to the linear structures, which could change their reactivity. These effects are captured by the additional multiplicative F_{cycle} factor. We observe a commonality among all the alkenes we consider, suggesting that the mechanism is essentially the same without abrupt changes within the training set. There are potential exceptions in the case of certain chlorinated compounds. We interpret the common pattern in the training set to mean that the electrophilic OH oxidation of each of these alkenes is essentially similar.

We also report measurements of the OH reaction rate coefficient as a function of temperature of two HFOs, CF₃CH=CH₂ (212–367 K) and CF₂HCH=CF₂ (223–373 K), obtained using the PLP–LIF technique. Our $k(T)$ measurements for CF₃CH=CH₂ are in good agreement with those reported in the literature, with the range of temperature range being extended in this study. Measurements of

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3 564 $\text{CF}_2\text{HCH}=\text{CF}_2$ kinetics are the first available to date and are in good agreement with the predictions
4 565 obtained from our SAR. The measurements of the latter compound helped refine the parameterization
5 566 of the CF_2H functionality, which was poorly represented before.
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8 567 These predictions represent an improvement in predicting the rate coefficients of haloalkene degradation
9 568 with the OH radical. The value of this work lies in advancing our ability to easily and quickly estimate
10 569 the rate coefficient for OH reactions with at least 291 haloalkenes, among which 214 compounds have
11 570 no experimental data reported so far. A significant improvement has been observed in reducing
12 571 degeneracy in the estimates and increasing the variety of predictable structures compared to previous
13 572 existing methods. This provides a tool that industries and policymakers can easily use to select the most
14 573 reactive molecules among the different possible compounds that could be implemented as new
15 574 substitutes to help avoid atmospherically persistent emissions and estimate their potential to produce
16 575 local ozone.
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23 **Supplementary Material:**

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26 **Excel data file:** DATA-SI.csv and .xlsx with all the data for reaction rate coefficients and Arrhenius
27 parameters from existing measurements and calculations from this work, Tokuhashi and co-workers¹³⁻
28 ¹⁷ and the AOPWIN program^{7,8}.
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31 **Figure S1:** Schematic diagram of the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF)
32 experimental setup.
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35 **Table S1:** Experimental conditions and parameters of the absolute rate measurements of the reaction of
36 OH radicals with $\text{CF}_3\text{CH}=\text{CH}_2$ using the pulsed-laser photolysis–laser-induced fluorescence (PLP–LIF)
37 setup.
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40 **Table S2:** Experimental conditions and parameters of the absolute rate measurements of the reaction of
41 OH radicals with $\text{CF}_2\text{HCH}=\text{CF}_2$ using the pulsed-laser photolysis–laser-induced fluorescence (PLP–
42 LIF) setup.
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45 **Figure S2:** Typical Beer-Lambert plot showing the integrated band strength (IBS) as a function of
46 $\text{CHF}_2\text{CH}=\text{CF}_2$ concentration, at the wavenumber range used to obtain $[\text{CHF}_2\text{CH}=\text{CF}_2]$ in OH kinetic
47 analysis.
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51 **Figure S3:** Typical Beer-Lambert plot showing the integrated band strength (IBS) as a function of
52 $\text{CF}_3\text{CH}=\text{CH}_2$ concentration, at the wavenumber range used to obtain $[\text{CHF}_2\text{CH}=\text{CF}_2]$ in OH kinetic
53 analysis.
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56 **Table S3:** $\text{CHF}_2\text{CH}=\text{CF}_2$ and $\text{CF}_3\text{CH}=\text{CH}_2$ integrated band strengths, S_{int} , measured at wavenumber
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3 ranges relevant to the atmospheric window using manometrically prepared mixtures in He, ideal gas
4 and Beer-Lambert laws.
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7 **Table S4:** Results of the $k(T)$ predictions using the model with factors in Table 1.
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9 **Figure S4:** Reaction rate constant at room temperature k_{298} as a function of the Arrhenius A -factor.
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18 **Acknowledgments:**
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