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REGULAR ARTICLE

Global warming potential predictions for hydrofluoroethers with two carbon atoms

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Abstract Global warming potentials are predicted using computational chemistry and thermodynamics approaches for four hydrofluoroethers where no data have previously been available. We also compare results with the same methodology for six other species. We combine predictions of radiative forcing values from density functional theory computations at the B3LYP/6-31g* level of theory with previous experimentally determined or newly estimated hydroxyl radical-hydrogen abstraction rate constants to obtain these global warming potentials. We find that many of the HFEs studied have lower global warming potentials than the hydrofluorocarbons and chlorofluorocarbons they may soon replace, although other environmental and technical issues may need to be addressed first.

Keywords Radiative forcing · Hydrofluoroethers · Quantum chemistry · Global warming potentials · GWP

1 Introduction

Hydrofluoroethers (HFEs) are a class of compounds which have recently been the focus of intense attention as replacement materials for chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs) [1–33]. While there have been 33 US patents filed for the use of HFEs in the past 20 months [34,35], relatively little information is known about their physical properties or environmental impacts. The main impetus for their potential introduction into widespread industrial use is that the HFE class of compounds has been postulated, and in some cases proven, to have lower global warming potentials (GWPs) than the HFCs they would replace.

GWPs can be calculated relative to the reference CO_2 information when one knows kinetic rates of attack of the species i by hydroxyl radical in the troposphere combined with infrared spectroscopy using the following equation [36–38]:

$$\mathrm{GWP}_i = \frac{\int_0^{\mathrm{TH}} a_i[x_i(t)]\mathrm{d}t}{\int_0^{\mathrm{TH}} a_{\mathrm{ref}}[x_{\mathrm{ref}}(t)]\mathrm{d}t} \quad (1)$$

where TH is the time horizon for GWP the species will be considered over, a_i is the radiative forcing due to a unit increase in atmospheric concentration, and $[x_i(t)]$ is the time-dependent concentration of a pulse of species i.

Equation (1) can be transformed to use atmospheric lifetime, τ, instead of integrating the concentration of the species over time:

$$\mathrm{GWP}_i = \frac{a_i \int_0^{\mathrm{TH}} \mathrm{e}^{-t/\tau}\mathrm{d}t}{\mathrm{AGWP}_{\mathrm{CO_2}}(\mathrm{TH})} \quad (2)$$

where atmospheric lifetime is denoted as:

$$\tau_{\mathrm{lifetime,R}} = \tau_{\mathrm{lifetime,CH_3CCl_3}} \frac{k_{\mathrm{OH+CH_3CCl_3(277\,K)}}}{k_{\mathrm{OH+R(277\,K)}}} \quad (3)$$

In this work, we use the AGWPs at 20, 100 and 500 year time horizons (THs) for the CO_2 reference species previously introduced by Wuebbles [39].

Atmospheric lifetimes of species can be obtained by multiplying the global atmospheric lifetime of the well-characterized reference compound, CH_3CCl_3, by the ratio of the OH reaction rate constant at 277 K for CH_3CCl_3 to the one for a new species [40,41]. In this work, the data from

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DeMore et al. [42] gives 6.686×10^{-15} cm^3 molecule^{-1}s^{-1} [40] for the rate constant of CH_3CCl_3. For the atmospheric lifetime of the reference compound, we use a value of 5.7 years [43].

This paper uses Eqs. (1)–(3) combined with radiative forcing results from density functional theory reported in our earlier work [34] and expanded here to compute GWPs for ten HFEs using either experimentally determined rate constants or ones derived following Urata's work [28]. Computational chemistry for this application is particularly desirable due to the fact that some of these potential replacement compounds may not have been synthesized and purified yet. The result is an expanded database of GWPs to allow for comparisons between alternatives being contemplated in industrial applications. Currently, GWPs at some time horizon using experimentally based information have been reported for only three of the possible HFEs described in this work.

2 Methodology

The Gaussian98 [44] suite of programs and subroutines were used for all quantum mechanical calculations in this work. All rotameric structures were optimized at the B3LYP/6-31g* level to be local minima as evidenced from frequency calculations at the same level leading to zero negative eigenvalues from the Hessian matrix. Prior to using the 6-31g* frequencies in the radiative forcing calculations or equilibrium constant estimations, they were scaled by a factor of 0.9613 as this scaling factor was demonstrated by Scott and Radom to yield the best agreement with observed vibrational frequency peaks from experiments for this method and basis set combination [45]. In our earlier work on some of the species considered here, we demonstrated that moving to larger basis sets did not improve the radiative forcing predictions compared to modeled results, justifying the small basis set used in this work [34]. Bond dissociation energies were computed with optimized structures at both the B3LYP/6-31g* and (RO)B3LYP/6-311g** levels as discussed later.

For some of the chemical species, there are four possible rotameric forms. In order to report a theoretical result for radiative forcing that would most represent experimental or modeled results, one would like to know the weightings for the canonical ensemble for each rotameric form present in a sample. This allows one to weight the relative contribution to radiative forcing through:

$$a_{\text{total}} = \sum_i a_i f_i \tag{4}$$

where a_i is the radiative forcing in W m^{-2} ppbv^{-1} of rotamer i and f_i is the weighting factor. It should be noted that these units indicate the energy in watts that 1 ppbv of a chemical would adsorb of energy passing through a square meter of atmosphere parallel to the earth's surface.

In order to estimate the equilibrium constants, K_{eq}, for each rotameric pair, we relied heavily on the equations detailed in Ochterski [46]. However, we used scaled 6-31g* frequencies in all ZPE, thermal correction, and entropic equations. For low vibrational frequencies which were identified to be hindered rotors, we used the tables of Pitzer and Gwinn [47] combined with rotational barrier heights calculated at the B3LYP/6-31g* level to estimate entropy calculations instead of assuming the harmonic oscillator approximation. For all calculations where temperature was an input parameter, we assumed a temperature of 277 K because this is the average tropospheric temperature where these species are evaluated for their global warming potentials. It should be noted that there are no effects of temperature on radiative forcing as one moves from 298 K where the computations were done to 277 K. Likewise, kinetic rates at 298 K are nearly identical to those at 277 K so the temperature dependences in this work are very weak. However, we have chosen to report our results at 277 K to be consistent with other researchers.

Radiative forcing was obtained following our previously described method [34,35]. Briefly, the method of Pinnock et al. [48] using binned cross-sectional areas was combined with the theoretical procedure described by Papasavva et al. [49], to predict a_i from:

$$a_i = \sum_k A_k F(\upsilon_k) \tag{5}$$

where a_i is the radiative forcing, A_k is the predicted infrared intensity and $F(\nu_k)$ is the binned radiative forcing from Pinnock's work. We assumed the harmonic oscillator approximation for the lowest frequency modes here as the $F(\nu_k)$ values in the frequency ranges for these species are so small that corrections to the radiative forcing through hindered rotor estimates are not justified. While the atmospheric window between 700 and 1,500 cm^{-1} [50–52] is typically used, in this work, we expand the work of Elrod [53] and Papasavva [49] to encompass the lower frequency contributions down to 0 cm^{-1}.

A short discussion on the accuracy of radiative forcing values generally shows that, even from the best modeled results using experimental data, results would differ by about 14% [54,55]. Other work suggests errors may be as much as 25% [56]. This shows that quantum chemical-based predictions of radiative forcing that are within 14–25% of experimental data will confirm that the theoretical results are of equivalent quality as results from models using experimental data.

Rate constant measurements or estimates are needed in order to predict the atmospheric lifetime through Eq. (3) to get GWPs. Arrhenius expressions are available for only four of the 1,1-HFEs (CH_3OCF_3, CH_3OCHF_2, CHF_2OCHF_2 and

CF_3OCHF_2) in the JPL compendium of kinetic data [57]. For CH_3OCF_3, the JPL database reports the Arrhenius parameter A to be 1.5×10^{-12} cm^3 molecule^{-1} s^{-1} and E_a/R to be equal to 1,450 K. Similarly, we used the JPL data for A equaling 6.00×10^{-12} and E_a/R being 1,530 K for CH_3OCHF_2. The reported values are 1.10×10^{-12} and 1,830 for CHF_2OCHF_2, and 4.60×10^{-13} and 2,040 for CF_3OCHF_2. Because the JPL is the source of the highest quality of data for kinetic information, we chose to use their values instead of other results. Our previous work [35] summarizes more extensively the other data not used due to the existence of JPL data. It should be noted that no new experimental data has become available since the JPL data set was published that would lead to different kinetic values.

While this work is concerned with HFEs, we include dimethyl ether (DME) because it is a 1,1-ether and may reveal some interesting trends compared to the rest of the species in this work. Atkinson et al. recently reviewed the kinetic measurements of others [58–66] and recommended Arrhenius constants of A and E_a/R to be 5.7×10^{-12} cm^3 molecule^{-1} s^{-1} and 215 in the 230–300 K range [67].

There are no Arrhenius parameters available for CH_3OCH_2F, although its rate constant has been estimated to be 1.92×10^{-13} at 298 K by Urata et al. [28] using a neural network derived empirical correlation between bond dissociation energies (BDEs) and rate constants for fluorinated hydrocarbons and ethers. The work of Urata et al. built upon the previous work of Chandra et al. [68], and we will refer to both the works that used essentially the same methodology. For three other HFEs, there are no estimates or measurements of rate constants for hydrogen abstraction by hydroxyl radical. These species include CH_2FOCH_2F, CH_2FOCHF_2 and CH_2FOCF_3; we have expanded Urata's methodology to estimate rate constants for these reactions using computed BDEs.

A brief description of Urata's methodology and testing is needed before we describe how we applied computational chemistry to estimate rate constants. In their work, they used a training set of reaction rate constants for fluorine-containing compounds to develop an empirical correlation using neural network procedures. They found they could predict rate constants accurately through the following equation:

$$k(T) = \left(\frac{8\pi k_b T}{\mu}\right)^{1/2} \left(\sigma_R^o\right)^2 \times \sum_i \gamma_i \exp\{(A + B \times \mathrm{BDE}_i)/\mathrm{RT}\} \qquad (6)$$

where k_b is Boltzman's constant, μ is the reduced mass of the reacting species, γ_i is the number of equivalent C–H bonds of type i in the reacting molecule, and σ_R^o is the intrinsic reaction radius for the OH radical, which was taken to be 1.5×10^{-8} cm. Chandra et al. [68], found that A and B were −43.2254 and 0.4828 kcal/mol, respectively, for hydrogen atoms on carbons adjacent to the oxygen ether linkage, which includes all hydrogen atoms in this work. The authors also note that if the considered molecule has several nonequivalent hydrogen atoms, the total rate constant should be calculated as the sum of the individual rate constants from each C–H site. In contrast to the constants reported above, Urata et al. [28] did a refit using the neural network method and obtained values of −29.3864 and 0.3471 for A and B, respectively.

Chandra's and Urata's works report the ratio of their estimated values to experimental ones, k_{est}/k_{exp}, in Table 2 where Chandra et al. report this ratio to range between 0.53 for CCl_3CH_3 to 1.94 for CF_3CHFCF_3 for 31 non-ether species. Similar results are reported in Table 3 for 19 HFEs where the correlative method performs less reliably in a quantified manner with ratios ranging between 0.69 and 5.91. The average ratio for this class of reactions is 1.59. To put this in context, the average experimental error in the JPL database for kinetic results is about 1.1–1.3 for most of the HFEs [57]. The refitting of the empirical constants by Urata et al. leads to a range of k_{est}/k_{exp} of 0.22–6.17 with a larger data set of rate constants.

In this work, BDEs were predicted at the B3LYP/6-31g* level by removing each hydrogen atom from a parent rotamer and then reoptimizing the structure to find the resulting radical species. Energies were then computed by summing this energy, including other temperature-dependent terms for the resulting radical, with that for hydrogen and then subtracting the energy and thermal terms for the parent rotamer. Similar calculations were done using recalculations and extensions of the (RO)B3LYP/6-311g** energies originally used by Chandra et al. and Urata et al.

3 Results and discussion

For the parent rotamer species, we follow the nomenclature of Ulic and Oberhammer [27]. For the BDE determinations and identifying which rotameric form was used and which hydrogen atom was removed, we create our own system as there are no guidelines available for HFEs on this issue. We first list the rotameric form of the parent species and then re-list that name with a minus sign and a signifier of which hydrogen was removed. For example, a synclinal–synclinal form of CH_2FOCHF_2 could have three different hydrogen atoms removed, as shown in Table 2. For example, one could remove the antiperiplanar hydrogen from the end that has two hydrogen atoms, leading to our nomenclature of (sc, sc)–(sc–ap, sc). This indicates that the (sc, sc) rotamer was the starting species and that the hydrogen was then removed from the (ap) position on the first (sc) end.

Table 1 A comparison of radiative forcing values in $\mathrm{W\ m^{-2}\ ppbv^{-1}}$ for each rotameric form of a chemical to the weighted canonical averaged value when thermodynamic equilibrium considerations are included

Species	Form	Weight	a	Form	Weight	a	Form	Weight	a	Form	Weight	a	Total a	Previous a
CH_3OCH_3	only 1	1.0	0.0657										0.0657	0.020[a]
CH_3OCH_2F	(sc)	0.9991	0.1500	(ap)	0.0009	0.1525							0.1500	
CH_3OCHF_2	(sc)	0.0432	0.1925	(ap)	0.9568	0.2103							0.2095	
CH_2FOCH_2F	(sc, sc)	0.8868	0.2453	(sc, −sc)	0.1132	0.2207							0.2425	
CH_3OCF_3	only 1	1.0	0.2433										0.2433	0.310[a] 0.190[b] 0.198[c1] 0.172[c2]
CH_2FOCHF_2	(sc, sc)	0.0288	0.2996	(sc, −sc)	0.2770	0.3003	(ap, sc)	0.6942	0.3145				0.3101	
CHF_2OCHF_2	(ap, ap)	0.0885	0.4454	(ap, sp)	0.7675	0.4843	(sc, sc)	0.1270	0.3758	(sc, −sc)	0.0170	0.4339	0.4662	0.570[a] 0.430[d] 0.592[e] 0.400[f]
CH_2FOCF_3	only 1	1.0	0.3255										0.3255	
CHF_2OCF_3	(sp)	0.7622	0.4415	(ap)	0.2378	0.4695							0.4482	0.600[a] 0.405[d] 0.410[g] 0.424[c1] 0.407[c2]
CF_3OCF_3	only 1	1.0	0.4782										0.4782	

Weighting factors are determined from equilibrium thermodynamic calculations at 277 K

[a] [69] ab initio, B3LYP/6-311++g(3df,3pd), narrow band model using 30 × 100 $\mathrm{cm^{-1}}$ bands, cloudy sky

[b] [6] Pinnock's narrow band model, 750–2,000 $\mathrm{cm^{-1}}$

[c] [81] (a) cloudy sky, uniform profile, line-by-line, (b) cloudy sky, line-by-line, atmospheric lifetime accounted for, uniform profile

[d] [9] cloudy sky, Pinnock's narrow band model

[e] [82] 700–1,500 $\mathrm{cm^{-1}}$, clear sky, line-by-line, uniform vertical profile

[f] [70] cloudy sky, line-by-line, Pinnock's method

[g] [7] cloudy sky, narrow band model, cloudy sky

We include a supplementary information section with this paper that summarizes much of the intermediate results and provides computational input files with the optimized geometries at the B3LYP/6-31g* level for the parent species studied. Figures showing each rotameric form and the nomenclature used in Table 2 are also included. While we do not include *z*-matrices for the radicals formed after a hydrogen atom has been removed, we include figures showing how the BDE was found for all the possible combinations.

Using our previously described method for estimating weighting factors for contributions from different rotameric forms [34], we used thermodynamic calculations of Gibb's free energies, including hindered rotor contributions to appropriate vibrational modes for entropic considerations, to report the weightings in Table 1. For four of the species, CH_3OCH_3, CH_3OCF_3, CH_2FOCF_3 and CF_3OCF_3, there is only one rotameric form possible and the weighting factor is 1.0. A temperature of 277 K was used for all weighting factors because this is the most prevalent temperature in the troposphere where global warming potentials are evaluated.

First, we compare our weighted average radiative forcing values to the individual rotameric forms. We find the largest difference between a weighted average value to an individual rotamer value to be for CHF_2OCHF_2 where the value is 0.4662 $\mathrm{W\,m^{-2}\,ppbv^{-1}}$, but one rotamer with the (sc, −sc) form has a value of 0.3758, leading to a difference of about 19%. The other differences between one rotameric form and the weighted average are much smaller with values ranging from 1.7% for CH_3OCH_2F to 9% for CH_2FOCH_2F. This implies that the additional computational and analytical expenses required to determine the weighting factors using hindered rotation barriers is not justified as one expects errors in radiative forcing of about 25% for even the best results [56]. This is similar to our finding in our previous work for other 1,1-HFEs [34].

The results here indicate that the differences in radiative forcing values among different rotameric forms are very similar to each other. For CH_3OCH_2F, the values are 0.1500 and 0.1525, a difference of only 2%. The difference is slighly larger for CH_3OCHF_2, with a difference of 8%. A difference of

10% is seen for CH_2FOCH_2F, 12% between the highest and lowest values for CH_2FOCHF_2, 22% for CHF_2OCHF_2 and only 6% for CHF_2OCF_3. We find here that there are never differences of more than 22% for the highest and lowest radiative forcing values among the rotameric forms for any single species. If one compares this to the expected 25% differences among experimentally based values, then one sees that computing all the different rotameric forms does not significantly affect the results.

The weighted forcing value is also often dominated by only one of the rotameric forms. For cases where only two rotameric forms are possible, two of them are dominated by one form with weights greater than 96%. For CHF_2OCF_3, there is a 76–24% split among the forms, but again, the radiative forcing values are only different by 6% in this case. For the two species where three or more rotamers are possible, one form dominates with weightings greater than about 70%. So, with radiative forcing values so similar and now with only one rotamer dominating, the weighted radiative forcing values do not differ much from the single rotamer weighted most. Future research will be needed to see if these trends remain true as one moves to larger species where more varied and larger rotameric forms are possible.

Values of radiative forcing from previous experimental measurements, modeling work and density functional theory calculations are shown in Table 1 in comparison to our reported values for each rotamer and the final weighted values. It should be noted that the radiative forcing results for superscripts ii through vii all involve experimentally measured absorption cross sections combined either with Pinnock's narrow band model [48] or a line-by-line analysis. Our work and that of Good and Francisco are both based on Pinnock's narrow band model. Where Good and Francisco used only ten gross bins for their analysis, we use the full range of narrow bins laid out by Pinnock. Good and Francisco [69] used high-level B3LYP calculations with the 6-311++G(3df, 3pd) basis set and a narrow band model using 30 separate $100\,\text{cm}^{-1}$ bands to predict cloudy sky radiative forcing values. Our smaller basis set using a more refined band model with $10\,\text{cm}^{-1}$ bands appears to give results in better agreement with other work, as discussed next.

Looking at CH_3OCF_3 where two other groups have modeled results, we find our value of 0.2433 to be closer to the 0.190, 0.198 and 0.172 found by previous researchers compared to Good and Francisco's value of 0.310. Likewise, their value of 0.570 for CHF_2OCHF_2 is higher than the two previous modeling results for cloudy sky radiative forcing which our value of 0.4662 is closer to. A direct comparison to Imasu's work reporting clear sky radiative forcing values is not possible as it is more than a simple scaling issue to convert between the two measures. For CHF_2OCF_3, our reported value of 0.4482 compares favorably to the four values clustered between 0.405 and 0.424, while Good and Francisco's work with a value of 0.600 is higher. In general, our values are close to and within the 25% error expected in radiative forcing values, indicating that our results for the six HFEs where no radiative forcing values are available will be accurate and that our value for CH_3OCH_3 will be valid as well.

Now that we have investigated how predicted values for radiative forcing compare to modeled values using experimental data, we turn to the consideration of kinetic estimations using Urata's method. There is more kinetic data available for reactions with hydroxyl radical for this class of compounds than there are data on radiative transfer values. However, there are still four species where there have been no previous experimental measurements for rate constants. In Table 2, we report the past experimental values and a brief discussion here justifies which experimental values were used for comparison with our predicted results and those using Urata's method. For CH_3OCH_3, Atkinson et al. [67], have aggregated published results from other researchers and have added this species to their growing high-quality database of atmospheric chemistry kinetics, with a rate constant of $2.62 \times 10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$. Likewise, the JPL database of Sander et al. [57], reports a value of 3.54×10^{-14} for CH_3OCHF_2, 1.16×10^{-14} for CH_3OCF_3, 2.38×10^{-15} for CHF_2OCHF_2 and 4.89×10^{-16} for CHF_2OCF_3. These values are used for comparison because they have been through a rigorous selection and validation process for inclusion in the databases. Other individual measurements from laboratories are not compared to in this work.

Urata et al. did not determine all possible rotameric forms or different H-removal sites from the parent HFEs in their previous work, so we recomputed all their values in this work. We also scaled the frequencies for the 6-31g* calculations to account for zero point energy and thermal corrections to the energy, but used unscaled frequencies for the higher level 6-311g** calculated results. Like the previous work of Chandra et al. we also used the theoretically exact -0.5000 hartrees for the energy of the H atom.

In the subsequest paragraphs discussing kinetic estimates from both Chandra et al.'s and Urata et al.'s work we have recalculated their rate constants using their bond dissociation energies. We have also calculated rate constants using our own work and the two different computational methodologies already discussed. It should be noted that we were able to recalculate Chandra's rate constants using their BDEs and empirical parameters. However, we were unable to obtain the rate constants in Urata's paper with the refitted empirical values using the same equations and their reported BDEs. The reason for this is hypothesized to be an incorrectly reported empirical parameter in their work as the methods of Chandra and Urata are the same. This issue will relate to why Urata's work appears less robust compared to the experiment in this work compared to their publication. We have used their

Table 2 Bond dissociation energies in kcal mol^{-1} for all possible rotameric conformations of parent species and the resulting radical species at the B3LYP/6-31g* and (RO)B3LYP/6-311g** levels of theory along with rate constant estimations following Urata, et al.'s, empirical correlation compared to experimental values in cm^3 molecule^{-1} s^{-1}

Species H-removed	Forms	B3LYP/6-31g* BDE 298.15 K (kcal mol^{-1})	B3LYP/6-31g* k 298.15 K (cm^3 molecule^{-1} s^{-1})	(RO)B3LYP/6-311g** BDE 298.15 K (kcal mol^{-1})	(RO)B3LYP/6-311g** k 298.15 K (cm^3 molecule^{-1} s^{-1})	k exp (cm^3 molecule^{-1} s^{-1})
CH_3OCH_3	only 1	95.17	3.05×10^{-12}	95.60	2.14×10^{-12}	2.62×10^{-12}[a]
CH_3OCH_2F	(sc)–(sc)	95.66	3.29×10^{-13}	97.34	8.34×10^{-14}	
	(sc)–(ap)	97.06	2.09×10^{-13}	97.89	1.06×10^{-13}	
	(ap)–(sc)	93.53	3.72×10^{-12}	94.52	1.66×10^{-12}	
CH_3OCHF_2	(sc)–(sc−sc)	98.61	2.90×10^{-14}	100.58	5.80×10^{-15}	3.54×10^{-14}[b]
	(sc)–sc	97.65	6.31×10^{-14}	98.67	2.75×10^{-14}	
	(sc)–ap	98.12	8.64×10^{-14}	99.10	3.87×10^{-14}	
	(ap)–(ap)	102.04	1.76×10^{-15}	104.29	2.82×10^{-16}	
	(ap)–(ap or sc)	98.79	7.49×10^{-14}	99.94	2.93×10^{-14}	
CH_2FOCH_2F	(sc, sc)–(ap)	99.17	3.67×10^{-14}	101.33	6.32×10^{-15}	N/A
	(sc, sc)–(sc−sc, sc)	97.68	1.24×10^{-13}	99.65	2.47×10^{-14}	
	(sc,−sc)–(sc,−sc−ap)	97.11	1.97×10^{-13}	98.70	5.37×10^{-14}	
	(sc,−sc)–(sc,−sc−sc)	96.39	3.54×10^{-13}	98.18	8.19×10^{-14}	
CH_3OCF_3	only 1	99.40	4.48×10^{-14}	100.64	1.63×10^{-14}	1.19×10^{-14}[c]
CH_2FOCHF_2	(sc, sc)–(sc-(−sc), sc)	99.23	1.72×10^{-14}	98.71	2.62×10^{-14}	N/A
	(sc, sc)–(sc, sc−sc)	97.76	5.71×10^{-14}	101.53	2.63×10^{-15}	
	(sc, sc)–(sc−ap, sc)	96.66	1.40×10^{-13}	99.76	1.11×10^{-14}	
	(sc,−sc)–(sc−sc,−sc)	100.24	7.54×10^{-15}	102.56	1.14×10^{-15}	
	(sc,−sc)–(sc,−sc−sc)	97.99	4.73×10^{-14}	100.05	8.81×10^{-15}	
	(sc,−sc)–(sc,−sc−ap)	99.61	1.26×10^{-14}	101.89	1.97×10^{-15}	
	(ap, sc)–(ap−ap, sc)	102.05	1.72×10^{-15}	104.70	1.99×10^{-16}	
	(ap, sc)–(ap, sc−ap)	98.81	2.42×10^{-14}	100.77	4.91×10^{-15}	
	(ap, sc)–(ap, sc−sc)	98.49	3.14×10^{-14}	100.73	5.05×10^{-15}	
CHF_2OCHF_2	(ap, ap)–(ap−ap, ap)	101.57	5.07×10^{-15}	103.92	7.45×10^{-16}	2.88×10^{-15}[d]
						2.52×10^{-15}[e]
	(ap, sp)–(ap, sp–sp)	100.87	4.45×10^{-15}	105.64	9.18×10^{-17}	
	(ap, sp)–(ap−ap, sp)	102.90	8.57×10^{-16}	103.42	5.57×10^{-16}	
	(sc, sc)–(sc, sc−sc)	100.55	1.16×10^{-14}	102.73	1.96×10^{-15}	
	(sc,−sc)–(sc,−sc (−sc))	99.28	3.26×10^{-14}	101.32	6.21×10^{-15}	
CH_2FOCF_3	(sc)–(sc−sc)	98.66	2.69×10^{-14}	102.12	1.61×10^{-15}	N/A
	(sc)–(sc−ap)	97.09	9.69×10^{-14}	100.30	7.13×10^{-15}	
CHF_2OCF_3	(sp)–(sp)	101.06	3.80×10^{-15}	103.48	5.29×10^{-16}	3.4×10^{-15}[f]
						4.16×10^{-16}[g]
	(ap)–(ap)	100.71	5.03×10^{-15}	102.65	1.04×10^{-15}	
CF_3OCF_3						N/A

[a] [67]
[b] [57]
[c] [2]
[d] [71]
[e] [73]
[f] [83]
[g] [72]

reported empirical parameters in this work even though we were unable to reproduce their rate constants with their BDEs.

For CH_3OCH_3, there is only one rotameric form of the parent species and only one radical that can be formed, regardless of which hydrogen atom is removed. This leads to an estimate of the reaction rate of 3.05×10^{-12} using the B3LYP/6-31g* BDEs compared to a value using the ROB3LYP/6-311g** results of 4.97×10^{-13}. It should be noted that when we use Chandra's empirical parameters we get a rate constant of 2.14×10^{-12}. Regardless, our value differs from the experimental value of Atkinson by a factor of 1.16, while our recomputation is in agreement with the experimental value. Urata's original best comparison has a factor of 0.19 and Chandra's had a factor of 0.82 compared to the experimental rate constant.

There is only one rotameric form and one radical form for CH_3OCF_3 where our predicted rate constant using the B3LYP/6-31g* BDEs leads to an overestimate of k by a factor of 3.86. In contrast, Urata's more expensive ROB3LYP/6-311g** BDEs lead to an overestimate of the rate constant by a factor of 1.05 using our recalculations with their empirical parameters, and Chandra's is a factor of 1.42 higher than experiment.

For the rest of the HFEs where kinetic data are available, we compare each rotameric form to the overall experimental rate in order to judge trends in predictive ability that would be confounded by not using the statistically weighted rate constant values. We find for CH_3OCHF_2 that our errors for the rate constant compared to experimental values have factors of 0.82, 1.78, 2.44, 0.05 and 2.12 for $k_{\mathrm{est}}/k_{\mathrm{exp}}$ for the five different BDEs. Using the weighted canonical values yields a predicted rate constant that is a factor of 2.29 higher than the experiment. In contrast, the ROB3LYP results using Urata's methodology leads to factors of 0.12, 0.36, 0.57, 0.01 and 0.52 for the different rotameric forms, respectively. The total canonically weighted rate constant is predicted to be 0.55 that of the experimental value. In all cases, the lower level basis set without using the spin restricted calculations leads to poorer agreement with experiment. In Table 4 of their work, Urata et al. report results for this species with BDEs of 97.73 and 96.64 for two of the three possible hydrogen abstractions from the two possible rotameric forms. They did not report which rotameric forms were considered, however. Their rate constants were reported to be 1.924×10^{-13} for this reaction using some non-weighted average for the rotamers. As they most likely computed only results for hydrogen abstraction from the (sc) form of this species, which is weighted by 0.9991 as shown in Table 1 from thermodynamic analyses, their results are comparable to those of our work using a fully weighted value. They were not able to do this comparison in their original work because the experimental data were not readily available at that time, only being available during a conference presentation and not published by Sander et al. until after Urata's publication. Chandra et al.'s, empirical constants with the ROB3LYP results give a rate constant that is different from experiment by only 0.89 when the weighted ensemble is used.

The accepted experimental value for the CHF_2OCHF_2 hydroxyl radical hydrogen abstraction reaction is 2.38×10^{-15}. Our predictions at the B3LYP/6-31g* level using Urata's empirical fitting parameters lead to overestimates by factors of 2.13, 1.87, 4.86 and 13.71, with one underestimate by a factor of 0.36 compared to this value. The weighted rate constant value is a factor of 2.84 higher than the experimental one. Again, our recalculations using Urata's ROB3LYP/6-311g** proposed method lead to underestimates of the rate by factors of 0.49, 0.09, 0.33, 0.98 and one overestimate by a factor of 2.24. The weighted average is a factor of 0.54 of that of the experimental value. Our BDEs with their methodology range from 98.71 to 104.70 kcal mol^{-1}. While Urata et al. did not compute all four rotamers or the five possible radicals that could be reasonably formed from those parent species, they report a BDE of 103.45 with a rate constant that is an underprediction by a factor of 0.72. It is unclear where their final value for BDE is derived from as they did not fully investigate this species. Regardless, our recomputations using their methodology show that the larger basis set consistently underpredicts rate constants while the smaller 6-31g* basis set we have chosen overpredicts them. Chandra et al.'s, empirical constants lead to underestimates similar to those of Urata with a weighted rate constant that is a factor of 0.40 of the experimental value.

For CHF_2OCF_3, Urata reported a BDE of 104.27 kcal mol^{-1}, leading to a rate constant that was underpredicted by a factor of only 0.94 compared to experiment. On the other hand, our recalculations for both possible hydrogen abstractions leads to BDE predictions of 101.05 and 100.71, which then leads to overpredictions of the rate constant by factors of 7.76 and 10.29 compared to the experiment. These results for both rotamers lead to rate constants that are overpredictions by factors of 1.52 and 2.48, leading to better agreement than the lower level calculations. Chandra et al.'s, rate constants are overpredicted by only 1.08 and 2.13, with the best agreement to experiment.

Based on all of these comparisons to the past available experimental data, we find that except for one species, the 6-31g* BDEs lead to poorer agreement to experimental rate constants compared to both Chandra's and Urata's works. We were hoping the lower level calculations would lead to accurate results and save computational time on future larger species, but that hypothesis was not valid based on the data in this work. In general, Chandra's empirical constants led to the best agreement with experimental rate constants. It was also plausible to refit the empirical constants to reproduce rate constant data using the smaller basis set BDEs. That effort led to some improvement in predictive ability, but did

Table 3 A summary of rate constant estimations with a new empirical fit of Urata's model parameters using only the species in this work compared to Urata's previous results and experiment

Species	*k* predicted using weighted ensemble (cm^3 molecule^{-1} s^{-1})	*k* expt. (cm^3 molecule^{-1} s^{-1})	τ (years)
CH_3OCH_3	2.14×10^{-12}	2.62×10^{-12}	0.015[a]
CH_3OCH_2F	3.39×10^{-13}	N/A	0.112
CH_3OCHF_2	3.14×10^{-14}	3.54×10^{-14}	1.077[a]
CH_2FOCH_2F	4.29×10^{-14}	N/A	0.888
CH_3OCF_3	1.63×10^{-14}	1.16×10^{-14}	3.285[a]
CH_2FOCHF_2	1.15×10^{-14}	N/A	3.314
CHF_2OCHF_2	4.78×10^{-16}	2.38×10^{-15}	16.013[a]
CH_2FOCF_3	8.75×10^{-15}	N/A	4.355
CHF_2OCF_3	6.51×10^{-15}	4.89×10^{-16}	77.935[a]
CF_3OCF_3	N/A	N/A	

The results in this table use the (RO)B3LYP/6-311g** BDEs. Atmospheric lifetimes are reported last, using experimental data where available or our new empirical fit for other species

[a] Using experimental rate constant data from JPL

not improve the results to be better than using Chandra's constants. Now that we have compared these results, we can use our weighted rate constants to predict rate constants for the species where no experimental results are available.

In Table 3, we compare our rate constant predictions using weighted canonical ensembles from thermodynamic data at the 6-31g* level but using the (RO)B3LYP/6-311g** BDEs to for all species compared to experiment. It should be noted that we are using the *A* and *B* values from Chandra et al. in this work because this led to the smallest error compared to experiment of all combinations discussed so far.

There are five species where experimental kinetic data are available. We see our prediction for CH_3OCH_3, where there is only one rotameric form and only one radical form, is a factor of 0.82 lower than experiment. For CH_3OCHF_2, our result is 0.89 times the experiment. For CH_3OCF_3, our results differ from the experiment by a factor of 1.41. For CHF_2OCHF_2, our prediction is low with a factor of 0.4. Finally, for CHF_2OCF_3, we are a factor of 1.33 higher than the experiment. With our thoroughness of calculating all of the rotameric forms and all of the radicals formed while using weighted canonical ensembles, we conclude our results are within a range from 0.4 to 1.41 that of experiment for this set of 1,1-HFEs. Again, one can consider that the JPL recommends their experimental values to be within factors of about 1.10–1.15 of their reported correlation. For this reason, we can expect that the methodology used in this work will probably be within a factor of 2 for kinetic predictions compared to experiment for species where no experimental data are available to estimate atmospheric lifetimes for HFEs. Atmospheric lifetime is a scaled representation of the rate constant for a particular species compared to that of a well-characterized surrogate, as discussed in Eq. (3). If a rate constant is underpredicted by a factor of 2, the resulting atmospheric lifetime would also be off by the same factor of 2. This is why we use experimental data in this work when it is available.

We calculate atmospheric lifetimes using the weighted rate constants for each species using Eq. (3), and the results are reported in Table 3. We should note that our previous work shows that rate constants were not a strong function of temperature moving from 298.15 K where the measurements were done to 277 K where atmospheric lifetimes are estimated because of low activation energies [35]. Hence, we use rate constants at 298.15 interchangably with those at 277 K. In Table 3, we see trends in atmospheric lifetimes similar to those from our earlier work where the atmospheric lifetime decreases as the number of hydrogen atoms available for hydroxyl radical attack increases. We obtained peer reviewed atmospheric lifetime values for CHF_2OCHF_2 from Myhre et al. [70], and for CHF_2OCF_3 from Good, et al. [69]. The atmospheric lifetime of Myhre and co-workers was reported to be 11.3 while our reported value was 16.0. In this case, Myhre et al. used the kinetic data of Garland et al. [71], and Hsu and DeMore [72], averaging the kinetic rates of these two groups. Myhre's publication appeared in 1999 and there had been updated rate constants by Orkin et al. [73] and Wilson et al. [74] that the JPL [57] used in their updated values that we followed. For the CHF_2OCF_3 species, Good and co-authors used the single published information of Hsu and DeMore [75], while the JPL has used other reported rate information from the same paper but recalculated using the CHF_3 reference rate constant given in the JPL evaluation [57]. Again, we chose to follow the JPL's

Table 4 Final GWPs at the 20, 100 and 500 year time horizons for dimethyl ether and the 1,1-HFEs

Species/TH	20	100	500	20	100	500
	This work			Past modeled values		
CH_3OCH_3	4	1	0			
CH_3OCH_2F	49	15	5			
CH_3OCHF_2	515	158	49			
CH_2FOCH_2F	492	150	47			
CH_3OCF_3	1,493	458	143	1,300[a]	360[a]	130[a]
				2,200[b]	656[b]	202[b]
CH_2FOCHF_2	1,919	589	184			
CHF_2OCHF_2	8,448	3,617	1,132	9,760[b]	5,720[b]	1,830[b]
				10,700[c]	6,300[c]	2,000[c]
CH_2FOCF_3	2,226	688	215			
CHF_2OCF_3	10,885	10,637	4,589	11,800[b]	14,000[b,d]	9,120[b]
				10,137[e]	12,015[e]	7,596[e]
CF_3OCF_3	N/A	N/A	N/A			

It should be noted that GWP values based on the estimated kinetic rates may vary by a factor of two due to the spread of expected errors in kinetic predictions

[a] Past modeled work for GWP from Orkin et al. [76]

[b] Past modeled work for GWP from Good et al. [69]

[c] Past modeled work for GWP by Myhre et al. [70]

[d] This value was originally listed as 1,400 in the publication, but is probably a typographical error due to the magnitude of the values at 20 and 500 year THs

[e] Past modeled work for GWP by Christidis et al. [7]

recommendations on kinetics as they have been rigorously justified. There are no other reported atmospheric lifetimes for any of the 1,1-HFEs in the open literature.

GWPs were calculated using Eq. (2) using either kinetic data where available or using Chandra's methodology and BDEs calculated at the (RO)B3LYP/6-311g** level of theory. These GWPs are reported in Table 4. For the first time, GWPs are available for CH_3OCH_2F, CH_2FOCH_2F, CH_2FOCHF_2 and CH_2FOCF_3. A comparison of our earlier work [35] shows that including the relative weighting for radiative forcing using thermodynamic considerations does not affect the results significantly, at least for these small 1,1-HFEs. The additional work is not justified.

There are some obvious trends that we have commented on before in our radiative forcing work [34], which is that radiative forcing increases as the number of C–F bonds on an HFE increase. Likewise, decreasing the number of C–H bonds increases the atmospheric lifetime and leads to larger global warming potentials. Using our approach here, it is not possible to estimate the GWP for CF_3OCF_3 since one cannot estimate the disappearance rate through hydroxyl radical attack of hydrogen. Instead, this HFE will persist in the environment until it reaches the stratosphere and can be destroyed by photolysis.

A discussion on the expected differences among different approaches for GWP values is needed at this point of the discussion. First, it should be noted that GWPs are typically reported to whole number values and ranges for errors on the reported values are generally not given.

There are previously reported GWPs outside of our own work [35] for only three of the 1,1-HFEs. Orkin et al. [76] reported values of 1,300, 360 and 130 at the 20, 100 and 500 year time horizons for CH_3OCF_3. Good et al. [69] reported GWPs of 2200, 656 and 202. The variations between the two groups highlight that differences in GWPs from different models and researchers can be almost a factor of 2 from each other. Our value using the JPL kinetic data and our radiative forcing value predict the GWP to be 1,493, 458 and 143 at the different THs, placing our values between the two previously reported ones.

There are two different GWP sets reported for CHF_2OCHF_2. Good et al. [69] report values of 9,760, 5,720 and 1,830, while Myhre et al. [70] report 10,700, 6,300 and 2,000 in their work. Our values are somewhat lower, with values of 8,448, 3,617 and 1,132. These predictions are within the factor of 2 comparison for the previously discussed species, indicating we have acceptable agreement to both sets of values. GWPs of 11,800, 14,000 and 9,120 were reported for CHF_2OCF_3 by Good et al. [69]. Christidis et al. [7], reported slighly lower values of 10,137, 12,015 and 7,596. Our values are 10,855, 10,637 and 4,589, using the updated JPL database for kinetics and atmospheric lifetime. Again, we are within the range of previously reported values.

Some final comments on expected errors can be made regarding the work done on the species where no previously measured kinetic data are available. In our discussion on kinetics, we pointed out that the kinetic estimates in this work may be different from experiment by a factor of about 2. In addition to these contributions to differences in final GWP values, the expected errors compared to experimentally determined and modeled radiative forcing values will be less than 40% based on the limited results presented here for 1,1-HFEs. Our largest percent difference in radiative forcing was 40% for CH_3OCF_3, but 16% for CHF_2OCHF_2 and 10% for CHF_2OCF_3. The effect of the kinetic estimate on GWP varies depending on whether the atmospheric lifetime is shorter or longer than that of the reference species, CO_2, highlighted in Table 4 where the shortest atmospheric lifetimes lead to decreases in GWPs as TH is increased. This is in contrast to CHF_2OCF_3 where GWPs increase from 20 to 100 years and then decrease again as one moves to the 500 year time horizon. A simple approximation for estimating errors ignores these nonlinear effects, leading to GWPs that could be as low as 0.3 times the values in our table if the kinetics are underpredicted by a factor of 0.5 and radiative forcing is underpredicted by a factor of 0.6, to 2.8 times higher for the other extreme.

It is possible to put the GWPs reported in Table 4 in better context by comparing them to values for HFCs which need to be replaced to meet the Kyoto Protocol requirements and to values for CFCs which are under phase-out because of the Montreal Protocol. HFC-23 is fluoroform, CHF_3, which is used in semiconductor manufacturing, as a refrigerant, and as a fire extinguishant. The reported GWPs for this chemical are 11,700, 9,100 and 9,800 at the three time horizons [77]. All of the GWPs reported in this work are lower than these, although CHF_2OCF_3 is similar in magnitude, indicating it may not be a good choice for applications to replace HFC-23, but the other 1,1-HFEs may be acceptable.

CFC-11 is CCl_3F and is a gas that has been used as a blowing agent. While many replacements have already been found [78,79], HFEs may be considered here as well. Using intermediate data from Christidis et al. [7], one can obtain GWPs for this species of 5,326, 4,274 and 1,544 at the 20, 100 and 500 year THs, respectively. Only one of the species reported in this work has GWP values larger than this species, which is CHF_2OCF_3. This indicates that replacing CFC-11 with all but one of these alternative species may be desirable from a GWP-only standpoint. Other technical issues may need to be resolved.

It is useful to keep in mind that the Kyoto Protocol requires a reduction of GHG emissions by 5.2% over the first span of implementation. One way to quantify this is to switch to new technologies that reduce GWP by this amount or larger while also monitoring the total emission rates of any new gases released. A consideration of the Inventory of US Greenhouse Gas Emissions and Sinks: 1990–2000 [77] shows that many of the commonly used HFCs that must be reduced have GWPs that range from 140 to about 6,000 at the 100 year TH. This means that 1,1-HFEs with fewer than three fluorine atoms, if they meet all other technological, safety, toxicity and economic criteria, can replace all but two of the HFCs listed in that reference, HFC-134a and HFC-152a.

Bivens and Minor [80] did a thorough review of some of the other important issues regarding HFEs several years ago. For example, they showed a general rule of thumb for flammability predictions using the ratio of the number of fluorine atoms divided by the sum of the number of hydrogen and fluorine atoms in a species. Values of 0.67 or 0.70 or higher are expected for compounds which are not flammable. In the cases of the 1,1-HFEs here, only CHF_2OCHF_2, CH_2FOCF_3, CHF_2OCF_3 and CF_3OCF_3 satisfy this criteria. One would not use bis(trifluoromethyl) ether as a replacement material because its atmospheric lifetime would be too long and its GWP too large. Likewise, CHF_2OCF_3 is not desirable due to its large GWP. This leaves two species that are good candidates for replacing HFCs and CFCs based on only the criteria of GWP and flammability. Clearly, much more information is needed about these HFEs and their interactions with existing chemicals before one can judge their suitability for replacing individual HFCs.

This work highlights the fact that even for the small class of 1,1-HFEs, some of them are clearly unacceptable replacements for existing chemicals that are being phased-out worldwide by the Montreal and Kyoto Protocols. More information about technical performance, including heat capacities, heats of vaporization, water solubilities to determine mobility in the environment and the possibility for removal from the troposphere through rain-out, octanol–water partitioning coefficients to identify bioaccumulative capacities and toxicity information are all needed before one can rationally begin designing replacement materials for HFC- and CFC-replacement uses.

4 Conclusions

We predicted GWPs for the entire class of 1,1-HFEs, thus populating a larger database for this emerging class of industrial compounds. We found again for these small species that inclusion of thermodynamic considerations to estimate weighting values for the canonical ensemble did not significantly change our results. We also commented on the fact that some HFCs which these HFEs may replace already have lower GWPs and it would be detrimental to switch to these compounds.

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