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Assessment of theoretical methods for the study of hydrogen abstraction kinetics of global warming gas species during their degradation and byproduct formation
(IUPAC Technical Report)*

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Abstract: Global climate change is a major concern as it leads to an increase in the average temperature of the earth's atmosphere. The existence and persistence of some gaseous species in the atmosphere contribute to global warming. Experimental techniques are used to study the kinetics and degradation of global warming gases. However, quantum mechanical methods are also useful for the kinetic and radiative forcing study of global warming species and can precede experimental investigations. Research has also been targeted to develop more adapted procedures using ab initio and density functional theory (DFT) methods. This report provides a global perspective, in simplified manner, of the theoretical studies of the degradation of gas species in the atmosphere with an emphasis on the hydrogen abstraction kinetics of global warming gas species during their degradation and byproduct formation. En route, the results obtained from these studies are analysed and compared with experimental data where available. Our analyses indicate that the theoretical predictions are in agreement with experimental findings but the predicted parameters are dependent on the method being used. Theoretical methods are used to predict the thermodynamic parameters of reactions, and, with relevance to this report, the global warming potential (GWP) index can also be calculated. This report can be useful for future investigations involving global warming gaseous species while providing suggestions on how computations can fill in data gaps when experimental data are unavailable.

Keywords: ab initio methods; degradation; density functional theory; experimental methods; global warming potential; global warming species; hydrogen abstraction; IUPAC Physical and Biophysical Chemistry Division; kinetics.

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CONTENTS

1. INTRODUCTION

Our planet Earth and its environment have different cycles that are involved in sustaining a clean and green world and, *a priori*, if these cycles are disturbed, sustainability cannot be maintained [1,2]. There are reports indicating that the temperature of our climate is increasing [3–5], and this rise in temperature is commonly termed as "global warming". It is worth noting that, in 1975, Dr. Wallace Smith Broecker coined the term "global warming" in his publication in *Science* [6]. Industrial revolution has enhanced global warming, although there is evidence that it started long before [7]. The term "global warming" is very important and has migrated from reports of research to being in the content of elementary science textbooks. Global warming is commonly used as the theme for news headlines, discussions, meetings, and conferences. Interestingly, global warming is also one of the components of political campaigns.

It is generally recognized that global warming can have adverse effects on the environment [8], living species [9], and the global economy [10]. These have led to an international attempt to reduce the emission of global warming gases. One major step was the near-implementation of the Kyoto Protocol [11] where almost all countries agreed to control the emissions of six compounds and their derivatives that are associated with global warming. These six compounds are carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

To begin this technical report, it is essential to understand the origin of global warming [12–14]. Solar radiation passes through our atmosphere and then encounters the earth where it is either absorbed or is reflected back into space due to the albedo effect. Some energy may have been already reflected by aerosols in the atmosphere on the way in. The escape of heat from the earth at some wavelengths of infrared radiation is possible, as there are a few compounds in the earth's atmosphere that can absorb significant thermal radiation in the range 700–1250 cm^{-1}. This creates a window, termed as the "atmospheric window", through which heat from the earth can be transmitted into space. Therefore, the earth has a natural way of balancing and maintaining its temperature, if this window is kept open. However, there are natural and anthropogenic compounds that can absorb radiation in the range of 700–1250 cm^{-1}. These compounds and their derivatives have the ability to prevent the dissipation of thermal radiation from the earth. The absorption of radiation by gaseous species is related to radiative forcing. The latter is defined as a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the earth's atmosphere [15]. The compounds which can absorb radiation in the range of 700–1250 cm^{-1} are known as global warming species, and indices have been set up for their classifications. The first index is the relative instantaneous radiative forcing (RIRF) [16]. In this index, the RIRF of carbon dioxide is arbitrarily set at 1, and the RIRFs for other gases are set relative to this value. A second index was proposed by Lashof and Ahuja [17], and this is termed as the global warming potential (GWP):

$$\mathrm{GWP} = \frac{\int_o^t a_i(t)C_i(t)\,dt}{\int_o^t a_{\mathrm{ref}}(t)C_{\mathrm{ref}}(t)\,dt} \tag{1}$$

where a_i is the radiative forcing due to a unit increase in atmospheric concentration of the i^{th} species, $C_i(t)$ is the time-dependent concentration of a pulse of the i^{th} species. The corresponding quantities for a reference gas, usually carbon dioxide, are in the denominator. Some data for six global warming species are collected in Table 1.

Table 1 Relative contributions to global warming of six gases.

Gas	Atmospheric lifetime/year[a]	Relative instantaneous radiative forcing[a]	Global warming potential
CO_2	50–200	1	1
CH_4	12	43	21[b]
N_2O	120	250	310[b]
HCFC-22	12	13 000	1600[c]
CFC-11	60	15 000	3400[c]
CFC-12	195	19 000	7100[c]

[a] Ref. [18].
[b] Ref. [19].
[c] Ref. [20].

Experimental methods have been used to study the global warming species, in particular, the kinetics of their reactions and degradation rates and pathways [21–28] with other atmospheric species, including their branching ratios through competitive channels [29]. Advances in computational science and computer technology have made impacts in the research of chemical kinetics. Over the years, researchers have been in search of practical tools for the kinetic studies of chemical reactions. In the context of this report, in the last two decades, although theoretical methods are used to study global warming and model species [30–76], understanding of the interactions of these species with other components in the atmosphere and their degradations has been challenging due to competitive reactions and non-ambient atmospheric conditions [77,78]. Theoretical methods have also been used for modeling the fate of global warming and model species and calculation of atmospheric lifetime, radiative forcing, and GWP [79–91]. In view of the increasing applications of theoretical methods for studying the kinetics of global warming and model species, research has been devoted to validating and improving the accuracy of predictions from computational methods [92–103]. A critical analysis of the literature indicates that the number of published quantum mechanical computations dealing with greenhouse gas degradation kinetics lags behind the wealth of experimental data. This drives us towards the goals of this technical report. The primary goal is to provide a global perspective of the quantum chemical methods that can be used to predict kinetic parameters. Another goal is to provide a critique of these methods with regards to greenhouse gases by comparing theoretical predictions with experimental data. The last goal is to recommend computational procedures that can potentially be used for future investigations involving global warming gas species while reducing the expense and time needed to obtain the same data through experimental methods.

2. COMPUTATIONAL METHODS

Computational methods consist of algorithms implemented in codes for computer processing. These algorithms are based on theories that include classical, quantum, and statistical mechanics and other aspects of molecular physics, chemical physics, and physical chemistry [104]. These algorithms are progressing with the pace of computational power, and in general, research is driven towards reducing computational time while increasing and maintaining accuracy [105]. Computational methods are used to predict, among others, the structure, kinetics, and thermodynamic parameters of chemical systems. Computational methods are broadly classified as molecular mechanics (MM) [106], semi-empirical [107], ab initio [108], and density functional methods [109]. However, in relation to this report, the last two methods are more important, and these methods will be discussed in detail.

2.1 Quantum mechanical methods

Quantum mechanical methods are useful in the characterization of the structure, thermodynamic, and spectroscopic parameters of chemical systems. These methods aim to obtain a solution of the Schrödinger equation (SE) [110]. A first attempt in solving the SE is the application of the Born–Oppenheimer approximation where the nuclear and electronic motions are decoupled [111,112]. Nuclei are considered almost stationary, and therefore the electronic SE is left to be solved. The electronic SE can be solved for hydrogen-like systems, while approximate methods are used for systems containing more than one electron. Quantum mechanical methods for solving the SE are generally classified as ab initio or density functional methods.

The ab initio methods are based on the molecular orbital (MO) approach [113], and a first step in solving the electronic SE using an ab initio method is to have a mathematical approximation for the wave function, which is done by using basis sets [114]. A basis set consists of mathematical functions from which the wave functions are constructed. The wave functions for a system represent the distribution of electrons. MOs are taken as a linear combination of atomic orbitals (LCAO) [115]. The choice of the functions is one of the factors that affect the accuracy of computations. In practice, a compromise is involved between the resources (time, memory, and speed) available, and the required accuracy.

The simplest ab initio method is the application of the Hartree–Fock (HF) theory [116]. In the HF method, a system is reduced to a series of one-electron wave functions where each electron moves in an average field due to the other electrons. The equations are solved iteratively until self-consistency is achieved, and hence this approach is commonly called the Hartree–Fock self-consistent field (HF-SCF) method [117]. The HF-SCF method enjoys the advantage of being computationally inexpensive, and energy prediction is an upper bound of the exact energy. In the HF-SCF computations, the two-electron integrals, namely, coulombic and exchange integrals, have to be evaluated [118–120].

The Møller–Plesset (MP) perturbation theory [121] considers the HF wave function and energy as the unperturbed system and evaluates configuration-interaction (CI) using the Rayleigh–Schrödinger (RS) perturbation theory [122]. There are different MP methods depending on the order of perturbation expansion, but the second-order MP theory (MP2) is commonly used [123]. A disadvantage of the MP method is that the computation converges slowly for heavy elements, and this can lead to inaccurate energies [124]. The problem of convergence is reduced with the coupled cluster (CC) methods [125,126]. The CC methods start with the HF method and construct multi-electron wave functions making use of the exponential cluster operator to account for CI. The coupled-cluster with single and double excitations (CCSD) [127] and coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) [128] are common CC methods. In the context of gaseous kinetics, quadratic configuration interaction with single and double excitations with perturbative triple excitations, QCISD(T), has been used as a higher level of theory [129].

It is known that the wave function for an N-electron system depends on 3N coordinates. However, electron density, integrated over N-1 coordinates, is the square of the wave function and therefore depends on three coordinates only [130]. Density functional theory (DFT) [130,131] is based on the principle that electron density can be a functional that determines the ground-state electronic energy, and thus the DFT methods aim to formulate the proper functionals [132]. It is generally known that for the DFT method, basis set convergence is fairly rapid compared with the MP2 method. However, the DFT method with the popular B3LYP functional [133] has difficulties in modeling transition-state structures and computation of activation energies [134,135]. In order to account for these difficulties, functionals such as BB1K [136], MPWB1K [137], and BMK [138] were developed for accurate computations of equilibrium parameters and activation energies of radical hydrogen abstraction and transfer reactions. In 2008, Zhao and Truhlar presented two hybrid meta-exchange correlation functionals, namely, M06 and M06-2X [139]. They recommended the M06-2X functional for applications involving main-group thermochemistry and kinetics. Recently, Wheeler and Houk [140] assessed the integration grid errors arising from the use of the popular but older DFT functional. They studied a set of 34 organic reactions and reported the better performance of the M06 suite of functionals.

Apart from these computational methods, other theoretical procedures are available for computations and each one is generally suitable and adapted for a particular problem. Some examples include the G1–G4 methods [141–145] based on the Gaussian theory, the complete basis set (CBS) [146] and complete basis set radical (CBS-RAD) methods [147]. These composite methods build upon a molecular structure optimized at a lower level of theory and then use the optimized structure for higher-level energy calculations with larger basis set computations. This improves the accuracy of energy predictions compared to lower levels with smaller basis sets.

Computational thermochemistry deals with the prediction of thermochemical properties, and these parameters are useful for understanding chemical reactions. Different approaches have been proposed to improve the accuracy of the computations of thermochemical properties, and some of them are the Weizmann-*n* method [148,149], high-accuracy extrapolated ab initio thermochemistry (HEAT) method [150], correlation consistent composite approach (ccCA) [151], multireference correlation consistent composite approach (MR-ccCA) [152], and the focal-point approach [153–155]. Focal-point analysis is a more effective approach, and it has been applied successfully in studies related to hydrocarbons [156,157]. Focal-point analysis is not based on a black-box approach and provides practical means to overcome the incompleteness of basis sets used in ab initio computations to calculate energy with a series of systematically improved basis sets while extrapolating to the basis set limit.

2.2 Rate constants of elementary steps

In order to understand the degradation of global warming species, it is important to have the kinetic parameters of the degradation reactions. Computational methods are used to estimate the heat of reaction, Gibbs energy change of reaction, and, more importantly, the activation energy with high accuracy. Rate constants for an elementary step of a reaction are also calculated using computational methods. The rate constants for a bimolecular reaction are calculated using conventional transition-state theory (TST) [158–161] with the Wigner tunneling coefficient [158,162] or with the small curvature tunneling (SCT) approximation [163–165]. It should be noted that at the lower temperatures encountered in the atmosphere, the SCT method is more accurate and must be used. According to the standard Eyring TST, the rate constant, *k*, is obtained as

$$k = \Gamma \cdot \frac{k_B T \sigma}{h} \frac{Q_{TS} N_A}{Q_1 Q_2} \cdot e^{\left(\frac{-\Delta E_a}{RT}\right)} \tag{2}$$

where k_B is the Boltzmann constant; *h* is Planck's constant, *T* is the temperature; *R* is the ideal gas constant; N_A is the Avogadro constant; Q_{TS}, Q_1, and Q_2 are the total partition functions of the transition state and reactants, respectively; ΔE_a is the activation barrier for the reaction; σ is the structure symmetry factor for the reaction; and Γ is the tunneling coefficient. The total partition function *Q* is the product of the electronic, vibrational, translational, and rotational partition functions.

Rate constants are computed from thermodynamic parameters using standard equations [166]. In the context of atmospheric reactions, Runge et al. [167] proposed a combination of quantum chemistry and quantum dynamics to calculate the rate constant of gaseous reactions. Theoretical methods to treat gaseous reactions should be able to accommodate a large number of degrees of freedom while being computationally tractable. In order to address these concerns, Runge et al. [167] developed a semi-classical flux-flux autocorrelation function (SCFFAF) approach attached to an ab initio parametrization of a simplified Hamiltonian (NDDO).

3. APPLICATIONS OF THESE METHODS AND RELATED STUDIES

3.1 Studies relevant to this report

Over the years, quantum mechanical methods have been used for the direct theoretical study of the hydrogen abstraction kinetics of degradation and byproduct formation of global warming species. Most of the theoretical studies have been focused on exploring the thermodynamic parameters, activation energies, and rate constants, and understanding reaction mechanisms and the more relevant GWPs of gaseous species. Some studies have also been directed to improve theoretical predictions. The following section intends to provide examples from a spectrum of the different studies relevant to this report. It is worth pointing out at this stage that previously most of the studies were based on experiments but then there was a paradigm shift towards experimental/theoretical investigations to reach a situation where, lately, only theoretical studies are being used.

The hydrogen abstraction from methanol by the methyl radical was studied using the HF/3-21G and MP4SDQ/6-31G(d,p)//MP2/6-31G methods [30]. Two reaction channels were investigated, $CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$ and $CH_3OH + CH_3 \rightarrow CH_3O + CH_4$. These reactions were studied over a range of temperatures, and it was found that the quantum tunneling effect is of importance at low temperatures. The hydrogen abstraction from the hydroxyl group was found to dominate over that from the methyl group at low temperatures. This is in contradiction with previous findings of the electron spin resonance experiments on the methyl radical in solid methanol. The contradiction was explained based on the possibility of hydrogen bonding in condensed phases, which blocks the reaction site for the hydrogen abstraction from the hydroxyl group. Hydrogen abstraction from 2-propanol by hydroxyl radical was studied using MP2/6-31G(d) with scaling of the correlation energy [35]. The calculated rate constants for the combined hydrogen atom abstractions were in good agreement with the available experimental data.

Dobbs and Dixon [31] predicted the geometry of the transition state of the reaction $Cl^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HCl$ using the MP2 level of theory and TZ+2P basis set. Higher-order computations using QCISD and QCISD(T) as well as CCSD and CCSD(T) levels were also carried out. They reported the classical barrier height as 37.24 kJ·mol^{-1} (MP2), and this value decreased to 20.38 kJ·mol^{-1} with zero-point correction at the QCISD(T) level. Importantly, the CCSD(T) results were within 0.42 kJ·mol^{-1} of the QCISD(T) results. The calculated activation energy of the reaction was higher in comparison with experiment by about (4.18–5.44) kJ·mol^{-1}. The calculated rates were found to be in reasonable agreement with experimental data for temperatures greater than 300 K. The B3LYP functional, unlike the BLYP functional, was found to be successful in locating the transition state. However, the uncorrected zero-point barrier height was calculated to be 6.47 kJ·mol^{-1} at the B3LYP level, which is low. The rate constants for the CH_2F_2 + OH hydrogen abstraction reaction were investigated using the variational transition state [48]. A dual-level approach to direct dynamics was employed using the interpolated optimized corrections method. The computations using the QCISD(T)/6-311G(2df,p)//QCISD/6-311G(d,p)[QCISD/6-31G(d)]///PM3 and the CCSD(T)//MP2/cc-pVTZ///PM3 methods reproduced quite well the experimental rate constants at temperatures from 500 to 250 K, and slightly overestimated them from 250 to 210 K. The classical energy barrier was reported to be (24.3 or 21.3) kJ·mol^{-1}, respectively. Coote [99] reported the reliable theoretical procedures for the calculations of electronic structure information in seven hydrogen abstraction reactions: $CH_2X^{\bullet} + CH_3Y \rightarrow CH_3X + CH_2Y^{\bullet}$ for (X,Y) = (H,H), (F,H), (Li,H), (Li,F), (CN,H), (OH,H), and (OH,CN). A comparison of the methods to calculate the enthalpies and barriers of these reactions led to the conclusion that the MPW1K/6-311+G(3df,2p) combination of method and basis set provided excellent low-cost performance and the RMP2/6-311+G(3df,2p) also performed very well.

Partially fluorinated ethers have been of interest as substitutes for CFCs, and previously, only experimental studies based on spectroscopic methods were considered. These studies have been directed to their general pattern of reactivity and degradation [168,169]. Wallington et al. [168] used pulse radiolysis transient UV absorption spectroscopy to study the ultraviolet absorption spectra and kinetics of $CF_3CH(^{\bullet})OCH_2CF_3$ and $CF_3CH(OO^{\bullet})OCH_2CF_3$ radicals at $T = 296$ K. The results were discussed with respect to the atmospheric chemistry of $CF_3CH_2OCH_2CF_3$, and the instantaneous forcing was calculated as 0.35 $W{\cdot}m^{-2}$. The GWP of $CF_3CH_2OCH_2CF_3$ was estimated as 0.019 for a 20-year horizon using an atmospheric lifetime of 114 days for the reaction of the fluoroether with OH radical. Orkin et al. [169] used flash photolysis resonance fluorescence to measure the rate constants of the reactions of OH radicals with the fluorinated ethers, namely, CHF_2–O–CHF_2 and CF_3CH_2–O–CH_2CF_3 over the temperature range from 277 to 370 K. The atmospheric lifetimes were estimated to be 24.8 and 0.3 years for these ethers, respectively. Their GWPs were estimated to be 1.75 (CHF_2–O–CHF_2) and 0.021 (CF_3CH_2–O–CH_2CF_3) for a 20-year horizon. Further, they suggested that the inclusion of an ether linkage in a fluoroalkane does not decrease the C–H bond strength as it does for simple hydrocarbons or that other factors may be important in determining reactivity patterns. In 1992, Cooper et al. [170] were perhaps among the first to use ab initio and semi-empirical methods to study the rate of hydrogen atom abstraction by a hydroxyl radical. They investigated reactions of fluorinated ethers with hydroxyl radical when these reactions were not yet studied experimentally. They estimated the energy of the highest-occupied MOs of fluorinated ethers, which they related to the rate of reaction. They found that the atmospheric lifetimes for fluorinated ethers range from 7.3 (CH_3OCH_2F) to 85 days (CHF_2OCF_3).

Good et al. [171] used experimental and theoretical methods to understand the atmospheric oxidation of CF_3OCH_3, CHF_2OCHF_2, and CHF_2OCF_3. These compounds are oxidized to trifluoromethyl formate, and then CF_3OCH_3 is further oxidized to carbonyl difluoride and carbon dioxide, while CHF_3OCHF_2 and CHF_2OCF_3 are converted to carbonyl fluoride only. Infrared spectroscopy was used for characterizing the species, and the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) method was used for computations. The main outcome of this work was that the major product of the degradation of these fluorinated ethers was found to be carbonyl fluoride, and the half-life of the latter was taken to be of the order of days.

Isoprene is one of the most abundant hydrocarbons emitted by the terrestrial biosphere. Lei et al. [172] studied the Cl-O_2-isoprene peroxy radicals arising from C-initiated oxidation of isoprene. The CCSD(T)//B3LYP/6-31G(d) level of theory indicates that the chloroalkenylperoxy radicals are about (163–176) $kJ{\cdot}mol^{-1}$ more stable than the separated reactants. These results help one to understand the reaction pathways and final distributions of the Cl-isoprene reaction system. The CF_3CCl_2O radical is known to decompose via two important channels, namely, C–C bond breakage and Cl elimination. Singh et al. [173] studied the decomposition of the CF_3CCl_2O radical. They calculated the thermal rate constants using canonical transition-state theory (CTST), and they reported the rate constants for the C–C bond breakage and Cl elimination as 6.7×10^6 s^{-1} and 1.1×10^8 s^{-1} at $T = 298$ K and 1 atm. These channels have an energy barrier of (36.0 and 27.2) $kJ{\cdot}mol^{-1}$, respectively. It is known that the degradation of global warming species such as halocarbons can proceed by reactions with ozone. Francisco and Maricq [174] reported the degradation of HFCs and their interactions with ozone where they made it clear that HFC degradation products are not detrimental to the environment. Although HFCs contribute to global warming, they have shorter atmospheric lifetimes than CFCs and FCs. Hayman and Derwent [175] described some degradation channels of hydrofluorochlorocarbons (HCFCs) and HFCs when they react with ozone. They also calculated the photochemical ozone creation potential (POCP) of these compounds as an index of atmospheric chemical reactivity. The PCOPs of HCFCs and HFCs confirmed that they make a negligible contribution to photochemical ozone production. However, HCFCs can still contribute to stratospheric ozone depletion. Further, they have high GWPs with strong radiative forcing and long atmospheric residence times. Apart from these degradation channels, organic compounds such as ethane, trichloroethene, and chloroform are known to degrade by thermal decomposition [176].

An important rate-limiting reaction for the degradation of halocarbons is known to be through hydrogen abstraction by hydroxyl radicals. Chandra et al. [177] studied the kinetics of hydrogen abstraction reactions of CF_3CHO, CF_2ClCHO, $CFCl_2CHO$, and CCl_3CHO with OH radicals. All the species, including TS structures, were optimized at the MP2/6-311G(d,p) level. Thermodynamic parameters, namely, activation energies and heats of reaction, were calculated from single-point computations at the QCISD(T)/6-311G(d,p) level. This theoretical kinetic study was further supported with rate constants calculated using TST with the inclusion of tunneling effects. The close relationship between the calculated and available experimental parameters is summarized in Table 2.

Table 2 The calculated rate constants, activation energies, enthalpies of reaction, and *A* factor. Computations were done at QCISD(T)/6-311G(d,p).

	Rate constant per molecule/($cm^3 \cdot s^{-1}$)		Activation energy/($kJ \cdot mol^{-1}$)	ΔH/($kJ \cdot mol^{-1}$)	A factor × 10^{12}/$cm^3 \cdot molecule^{-1} \cdot s^{-1}$)
		Experimental			
CF_3CHO	9.5×10^{-14}	5.5×10^{-13}[a]	7.1 (5.9)[b]	–92.5	26.4
		1.1×10^{-12}[b]			
CF_2ClCHO	2.8×10^{-13}	7.0×10^{-13}[a]	6.7	–92.0	15.9
$CFCl_2CHO$	6.0×10^{-13}	1.1×10^{-12}[a]	6.3	–92.9	32.6
CCl_3CHO	5.7×10^{-13}	1.6×10^{-12}[a]	6.3	–87.9	31.0
		1.6×10^{-12}[b]	(5.0 ± 0.8)[b]		(50.2 ± 8.4)[b]
		1.8×10^{-12}[c]			

[a] Ref. [178].
[b] Ref. [179].
[c] Ref. [180].

Fluorinated ethoxy radicals degrade by C–C bond breakage; Somnitz and Zeller [181] studied this type of bond breakage for CF_3CF_2O, CF_3CFHO, and CF_3CH_2O radicals. These radicals were studied using the B3LYP/cc-pVTZ(+1) method for geometry optimization, and the critically important energy barriers were computed using a modified G3(MP2) theory. They reported the rate constants for β-scission of the radicals with C–C bond breakage as (1.1×10^4, 5.7×10^6, 7.4×10^{-5}) s^{-1} for CF_3CFHO, CF_3CF_2O, and CF_3CH_2O, respectively, at 1 atm and $T = 300$ K. The energy barriers ($kJ \cdot mol^{-1}$) for the thermal decomposition are (32.2, 50.6, and 100.0) $kJ \cdot mol^{-1}$ for CF_3CF_2O, CF_3CFHO, and CF_3CH_2O, respectively.

It is generally known that the degradation of HCFCs also occurs by reactions with hydroxy radicals. However, the reactions of CFCs are slower compared to their chlorine analogues; they build up in the atmosphere, and hence, contribute to global warming. There are experimental studies that were carried out to investigate reactions of other chlorinated and fluorinated species with hydroxy radicals. These studies aimed to obtain the rate constants of reactions as these are used to estimate the half-lives of these compounds. However, theoretical studies are lagging. Fontana et al. [182] used the G2 level of theory to obtain the rate constants of reaction of hydroxy radicals with small molecules, such as methane and trifluoromethane, to large molecules, such as halogenated ethanes and methyl esters. They also explained the higher reactivity of HCF_2OCF_2H compared to CF_3OCF_2H by the presence of a hydrogen atom at the reaction center that increases the reaction rate by an electrostatic stabilization of the TS. Table 3 summarizes the predicted rate constants and corresponding experimental values [183–186].

Table 3 Predicted parameters for reactions with hydroxyl radical at T = 298 K.

Reactant	Calculated rate constant/ ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)	Experimental rate constant/ ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)	Classical barrier/ ($kJ \cdot mol^{-1}$)
CF_3H	2.40×10^{-16}	2.4×10^{-16}	34.31
CF_3CF_2H	2.52×10^{-15}	1.9×10^{-15}	25.56
CF_3OCF_2H	4.07×10^{-16}	4.2×10^{-16}	28.54
HCF_2OCF_2H	5.04×10^{-15}	$2.3–5.1 \times 10^{-15}$	22.76
CH_4	6.30×10^{-15}	6.3×10^{-15}	27.61
CCl_3CH_3	8.10×10^{-15}	9.9×10^{-15}	23.85
CF_3OCH_3	2.06×10^{-14}	1.0×10^{-14}	19.29

$CF_3CHClOCHF_2$ and $CF_3CHFOCHF_2$ degrade when they react with OH radical or a Cl atom. Yang et al. [187] studied these reactions using B3LYP/6-311G(d,p) and G3(MP2) levels and interpolated single-point energies (ISPEs). They found that these compounds degrade via two hydrogen abstraction channels leading to four possible products, namely, $CF_3CHClOCF_2$, $CF_3CClOCHF_2$, $CF_3CHFOCF_2$, and $CF_3CFOCHF_2$. They also calculated the rate constants, branching ratios, and Arrhenius expressions of the $CF_3CHClOCHF_2/CF_3CHFOCHF_2$ + OH/Cl reactions. The total rate constants calculated from the sum of the individual rate constants and branching ratios are in good agreement with the experimental data. An outcome from this research is that the substitution of Cl by F decreases the reactivity of $CF_3CHClOCHF_2$ towards OH and Cl.

Ma and Schobert [96] used the ground-state thermochemical properties such as reaction enthalpy, broken bond energy, and formed bond energy to estimate the activation energy of hydrogen abstraction reactions involving hydrocarbons. Two different empirical methods were proposed with the largest average standard error being 2.68 $kJ \cdot mol^{-1}$ for the activation energy of the reactions considered. An accurate benchmark calculation of the reaction barrier height for hydrogen abstraction by the hydroperoxyl radical from methane was undertaken using the CCSD(T) level and the triple-ζ (cc-pVTZ) basis set [101]. The barrier heights required adjustments when compared with other commonly used approaches.

There have been experimental studies related to the kinetics [188,189] and GWP [190,191] of sulfur-containing compounds. However, theoretical study has been ignored for sulfur-containing compounds except for the work of Papadimitriou et al. [190], Bruska and Piechota [192], and Xu et al. [193]. Bruska and Piechota [192] studied sulfur(VI) fluoride and its hydrogen derivatives using DFT methods as implemented in the $DMol^3$ code and the double-numerical quality basis set with polarization functions. The results of infrared spectra simulations confirmed that it is the fluorine atoms that play a crucial role in the greenhouse effect of SF_6. The absorption bands of SH_6 and SCl_6 are outside the atmospheric window while for $SF_{6-n}H_n$ there are more absorption bands with reduced intensities as compared to SF_6. Xu et al. [193] studied the molecular structures and energetics of $SF_5CF_3/SF_5CF_3^-$ species using nine hybrid and pure DFT (BLYP, BHLYP, B3LYP, BP86, B3P86, LSDA, B3PW91, BPW91, and KMLYP) and DZP++ basis sets. The potential energy surface of the anion has three minima, and one of the minimum structures is closely related to the neutral SF_5CF_3. The electron affinity ranges from 1.59 to 3.00 eV with the value of 1.59 eV from the KMLYP functional to be more reliable compared to the other functional investigated. The computed infrared intensities indicate that SF_5CF_3 may be an effective greenhouse gas, but may not have as long a half-life as SF_6 due to its reactions with electrons.

Sulfuryl fluoride (SO_2F_2) is a greenhouse gas and has the potential of being a radiative forcing agent. In order to obtain the potential climatic impact of SO_2F_2, Papadimitriou et al. [190] did a combined experimental and theoretical study of atmospheric loss processes and lifetimes of SO_2F_2. They reported the rate coefficients of the gas-phase reactions of OH and Cl with SO_2F_2. Computations for optimization and frequencies were done at the MP2/6-31++G(d,p) level, and absolute electronic energies were obtained using DFT and CCSD(T) methods. The functionals used were B386 and B3PW91. The computed thermochemistry for the OH and Cl reactions with SO_2F_2 indicates that the most likely bimolecular reactions are highly endothermic, and the formation of stable OH or Cl adducts with SO_2F_2 is unlikely. The low chemical reactivity of SO_2F_2 is confirmed both experimentally and theoretically. Further, they predict the GWP of SO_2F_2 to be 4780 over a 100-year time horizon.

3.2 Global warming potential

Apart from the theoretical studies targeting the kinetics involving global warming gas species, a relevant parameter for this report is the theoretical determination of GWP. The latter (GWP) is a useful parameter for characterizing species contributing to global warming. Previously, this parameter was determined from degradation rates and infrared vibrational spectroscopy but recently, theoretical approaches have been used to estimate GWPs. Papassavva et al. [76] used ab initio computations of vibrational frequencies and infrared intensities to calculate the GWP of CF_3CH_2F. The calculated harmonic frequencies using MP2/6-31G(d,p) method agreed with the experimentally observed frequencies below 800 cm^{-1}. The calculated absolute intensities were in good agreement (better than 10 %) with the limited experimental measurements previously reported. Blowers et al. [194] used the B3LYP/6-31G(p) level of theory in combination with the cloud sky model [195] to estimate radiative forcing for hydrofluoroethers (HFEs). This work provides radiative forcing values for 25 compounds after validating the method with 27 HFEs and should serve as a useful database. They also described how molecular structure can be manipulated to reduce environmental impacts due to global warming. Blowers et al. [196] estimated the gas-phase heat capacities of nine HFEs containing two carbon atoms (CH_3OCH_2F, CH_3OCHF_2, CHF_2OCHF_2, CH_3OCF_3, CH_2FOCHF_2, CHF_2OCHF_2, CH_2FOCF_3, CHF_2OCF_3, and dimethyl ether) using the B3LYP/6-31G(d) method. They found close agreement with experimental values for the two HFEs and a good agreement over a wide temperature range for dimethyl ether.

Table 4 summarizes the predicted gas-phase heat capacity values and available literature values for the compounds investigated.

Table 4 The predicted gas-phase heat capacity values and available literature ($J{\cdot}K^{-1}{\cdot}mol^{-1}$).

Species	$C_p°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	Experiment $C_p°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	Empirical $C_p°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$
CH_3OCH_3	64.98	65.56[a]	65.65
CH_3OCH_2F	71.55		73.47
CH_3OCHF_2	77.70		77.55
CH_2FOCH_2F	77.91		81.29
CH_3OCF_3	89.62		69.19
CH_2FOCHF_2	86.06		85.37
CHF_2OCHF_2	96.78	98.16[b,c]	89.44
CH_2FOCF_3	96.48		77.01
CHF_2OCF_3	108.03	105.35[d]	81.08
CF_3OCF_3	116.52		72.72

[a] Ref. [197].
[b] Ref. [198].
[c] Ref. [199].
[d] Ref. [200].

Theoretical prediction of GWP is important, and in their reports, Blowers et al. [201,202] described the use of a DFT method (B3LYP/6-31G(d)) and kinetic rate data to estimate GWPs for HFEs. They compared their data obtained with available literature data and described how molecular structure can be changed to reduce the warming effect. Recently, Blowers and Hollingshead [203] used B3LYP/6-311G(d,p) for initial geometry optimization of fluoromethanes and methane and reported that the CBS-RAD composite energy method should be a better procedure to obtain energies. They successfully applied purely computational methods, for the first time, to correlate the computed and experimental GWPs of methyl fluoride species. The thermodynamics and kinetics of five hydrogen abstraction reactions from hydrocarbons were studied, and in this benchmark research, two composite methods (CBS-QB3 and G3B3) and two DFT methods, MPW1PW91/6-311G(2d,d,p) and BMK/6-311G(2d,d,p), were explored [204]. All four methods were successful in describing the thermochemical properties such as enthalpy change, entropy change, and barrier of the reactions.

Bravo et al. [205] calculated the infrared spectra, radiative efficiencies (REs), and GWPs of HFEs and hydrofluoropolyethers (HFPEs). The molecular structures were first optimized using the B3LYP/6-31G(d,p) method. They determined accurately the REs using the scaled wavenumbers of the C–F stretching vibrational mode [206]. They found that quantum mechanical methods over-predicted the REs unless an empirical correction is applied. In general, theoretical studies to calculate radiative forcing, GWP, and atmospheric indices are lagging with respect to the ongoing experimental investigations [207–209].

4. CONCLUSIONS AND RECOMMENDATIONS

This technical report gives an exposé of the theoretical methods that are commonly used to study global warming gas species. Although the studies involving theoretical methods are fewer than experimental investigations, this report gathers selected theoretical studies that are in the peer reviewed literature, with an emphasis on hydrogen abstraction kinetics, to highlight how more information can be evaluated for additional global warming gas species. We have also referred readers to the estimation of radiative efficiencies, radiative forcing values, the calculation of GWP, and the Weizmann-*n* and focal-point approaches.

After an analysis of a broad range of theoretical studies involving atmospheric species, we are recommending the following towards future studies directed towards kinetics of global warming gas species and their byproduct formation:

(1) Ab initio methods are appropriate for understanding the reactions or degradation of gaseous species. However, the suitability of a particular ab initio method is still questionable. The CBS-RAD method [142] is able to compute reliable thermodynamic parameters when free radicals are involved. In the CBS-RAD method, the geometry and zero-point energies are determined considering the quadratic configuration interaction at QCISD/6-31G(d) level, and coupled-cluster theory is used instead of quadratic configuration interaction in single-point computations.
(2) Zhao and Truhlar recommended the M06-2X functional for reactions involving main-group thermochemistry and kinetics [139].
(3) The rate constant, a fundamental kinetic parameter, can be calculated using theoretical methods. For gas-phase reactions, the SCFFAF approach [167] has been successful and is capable of extension to more complicated reactions.
(4) Focal-point analysis is also useful, and in the context of this report, it has been applied successfully to hydrocarbons [156,157].
(5) REs can be determined using the method of Pinnock et al. [195].
(6) Radiative forcing values can be computed with the theoretical methods proposed by Blowers et al. [194].

(7) GWP of gaseous species can be computed with the theoretical methods proposed by Blowers and Hollingshead [203].

This technical report may serve to be useful as novel compounds are introduced and used in industry and, *a priori*, these compounds should be studied in terms of their possible contribution to atmospheric reactions and as potential global warming species. The representative reviews in the themed issue on atmospheric chemistry of *Chemical Society Reviews* and the editorial notes make it clear that there are still many reactions to be understood in the atmosphere [210].

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