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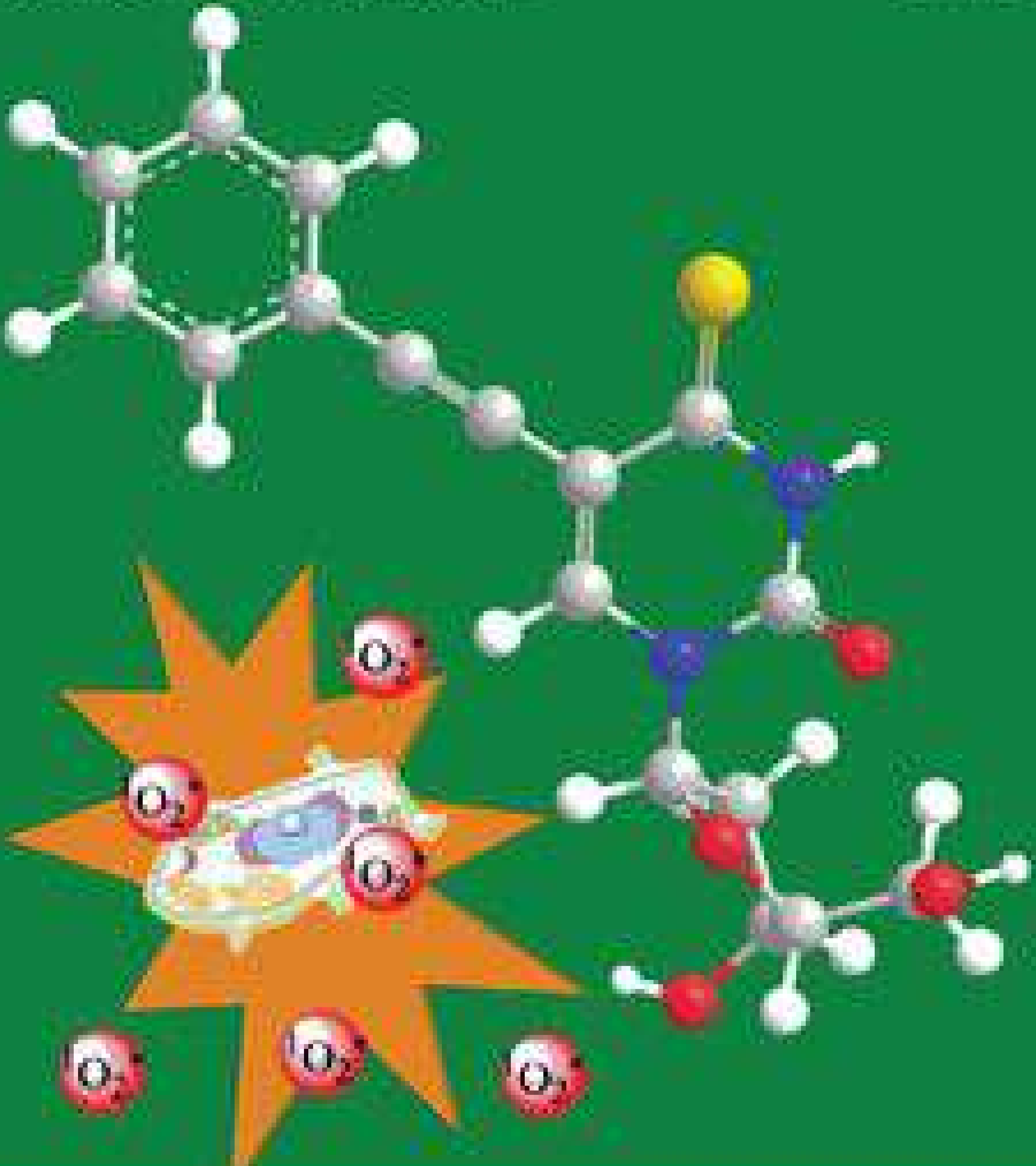

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Experimental and Computational Investigations of the Tropospheric Photooxidation Reactions of 1,1,1,3,3,3-Hexafluoro-2-Methyl-2-Propanol Initiated by OH Radicals and Cl Atoms

Avinash Kumar, Srinivasulu Gonu, S. Vijayakumar, C. B. Ramya, and B. Rajakumar*

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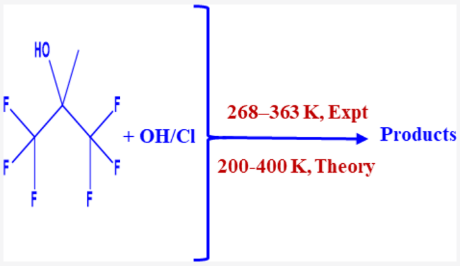

ABSTRACT: The gas-phase kinetics for the reactions of OH radicals and Cl atoms with 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HF2M2P) were measured at temperatures between 268 and 363 K using the relative rate experimental technique. Methane and acetonitrile were used as reference compounds to measure the rate coefficients of the title reactions. For the reactions of HF2M2P with OH radicals and Cl atoms, the rate coefficients were measured to be $(7.07 \pm 1.21) \times 10^{-15}$ and $(2.85 \pm 0.54) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively, at 298 K. The obtained Arrhenius expressions for the reactions of HF2M2P with OH radicals and Cl atoms are $k_{\mathrm{HF2M2P\,+\,OH}}^{\mathrm{Exp}\,-\,(268\,-\,363\ \mathrm{K})} = (7.84 \pm 0.75) \times 10^{-14} \exp[-(717 \pm 59)/T]$ and $k_{\mathrm{HF2M2P\,+\,Cl}}^{\mathrm{Exp}\,-\,(268\,-\,363\ \mathrm{K})} = (3.21 \pm 0.45) \times 10^{-12} \exp[-(1395 \pm 83)/T]$ cm^3 molecule^{-1} s^{-1}. In addition to the experimental measurements, computational kinetic calculations were also performed for the title reactions at the M06-2X/MG3S//M06-2X/6-31 + G(d,p) level of theory using advanced methods such as the canonical variational transition-state theory coupled with small curvature tunneling corrections at temperatures between 200 and 400 K. Theoretical calculations reveal that the H-abstraction from the CH_3 group is a more favorable reaction channel than that from the OH group. Thermochemistry, branching ratios, cumulative atmospheric lifetime, global warming potential, acidification potential, and photochemical ozone creation potential of HF2M2P were calculated in the present investigation.

1. INTRODUCTION

Numerous studies have been carried out on the atmospheric properties of compounds that are considered as possible alternatives to chlorofluorocarbons (CFCs) in order to eliminate them from industrial applications because of their detrimental effects on the ozone layer.[1−4] Partially fluorinated alcohols are considered as a potential alternative to CFCs because of their higher reactivity with the tropospheric oxidants, due to the presence of a hydroxyl (OH) group that shortens their lifetime in the atmosphere.[5] Moreover, due to the absence of a Cl atom in these molecules, their contribution to ozone depletion is expected to be negligible. This class of CFC alternatives also acts as a potential absorber of infrared radiation and thus contributes to global warming due to the presence of both C−O and C−F bonds.[6,7] Thus, prior to their use in a variety of industrial and domestic applications, it is highly necessary to find out the atmospheric impact of such class of compounds. 1,1,1,3,3,3-Hexafluoro-2-methyl-2-propanol (HF2M2P) is used as an activator for the chemical fixation of carbon dioxide to epoxides.[8] It is used as a reagent in the synthesis of highly substituted furfuryl alcohols and amines.[9] It is used as a mobile phase modifier in liquid chromatography−mass spectroscopy (LC−MS) for the analysis of large molecular compounds such as oligonucleotides.[10] The oxidative capacity of the Earth's troposphere is mainly governed by the reactions involving OH radicals.[11] OH radicals initiate chain reactions in both clean and polluted atmospheres.[12] The inherent reactivity and a relatively higher concentration of OH radicals make them crucial in the chemistry of the Earth's troposphere. The Cl atoms are more reactive than OH radicals and even at a lower concentration, they oxidize the volatile organic compounds (VOCs) in the troposphere.[13] Singh et al. estimated that Cl atoms initiate the oxidation processes of 20−40% of nonmethane hydrocarbon (NMHC) in the troposphere and 40−90% of NMHC in the stratosphere.[14] It is proved that the Cl atom reaction plays a major role in the degradation of VOCs in the Arctic region.[15] The photolysis of sea-salt aerosols, production of paper, water purification plants, chemical production, and smelters also contribute to the production of Cl atoms in the troposphere.[16] In addition to these, the abundance of Cl atoms in the marine boundary layers is higher and their reactions with the compounds cannot be ignored. Therefore, kinetic parameters for their reactions with OH radicals and Cl atoms are

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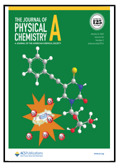

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Wet-Chemical Prepared Bismuth Vanadate Coated On MWCNTS for Supercapacitor Application

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ABSTRACT

This study reports the successful production of bismuth vanadate ($BiVO_4$) using a modified chemical bath deposition method, followed by its decoration onto multi-walled carbon nanotubes (MWCNTs) to enhance supercapacitor performance. X-ray diffraction (XRD) analysis confirmed the formation of the $BiVO_4$ crystalline phase, while scanning electron microscopy (SEM) revealed nanosphere-like $BiVO_4$ structures uniformly distributed over the MWCNTs network. Energy-dispersive spectroscopy (EDS) verified the elemental composition, confirming the presence of Bi, V, O, and C, which indicates successful deposition of $BiVO_4$ onto the carbon nanotube framework. The electrochemical information of the MWCNTs/$BiVO_4$ was assessed in a 1M $NaClO_4$ electrolyte solution by means of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The electrode achieved a determined specific capacitance of 210 F/g at a scan rate of 25 mV/s and 62 F/g at a current value of 0.75 mA/cm^2, indicating favorable charge storage characteristics. Additionally, EIS analysis showed a little charge transfer resistance (Rct) of 6.2 Ω, highlighting efficient electron transport and ion diffusion, which contribute to the enhanced electrochemical performance. The synergy between $BiVO_4$ nanospheres and the conductive MWCNTs network significantly improves charge storage capabilities by facilitating rapid ion transport and increasing the electroactive surface area. These findings position the MWCNTs/$BiVO_4$ composite electrodes as promising candidates for high-performance supercapacitor applications, combining high capacitance, efficient charge transfer, and structural stability.

Keywords: Bismuth vanadate, Energy storage, MWCNTs, Supercapacitor

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Kinetic Investigations on the Gas Phase Reaction of 2,2,2-Trifluoroethylbutyrate with OH Radicals: An Experimental and Theoretical Study

Gonu Srinivasulu, Siripina Vijayakumar, and Balla Rajakumar*[a]

The temperature dependent rate coefficients for the reaction between 2,2,2-trifluoroethylbutyrate (2,2,2-TFEB) with OH radicals were measured as a function of temperature (268-343 K) and pressure (400-760 Torr; N_2 and O_2) using relative rate technique. The temperature dependent rate coefficients for the gas phase reaction of 2,2,2-TFEB + OH were used to deduce the Arrhenius expression: k(268-343 K) = $(2.72 \pm 1.3) \times 10^{-13}$ $\exp\{(530 \pm 72)/T\}$ cm^3 $molecule^{-1}$ s^{-1}. At 298 K, the rate coefficient for the title reaction was obtained to be $(1.58 \pm 0.42) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Extensive computational calculations were also performed as a complement to the present experimental study using canonical variational transition state theory (CVT) with small curvature tunnelling (SCT) correction in combination with the CCSD(T)/CC-PVDZ//M062X/6-31+G(d,p) level of theory. The atmospheric lifetime of the test molecule due to its reaction with OH radical is about 3 days, which is short lived. And therefore, its contribution towards the global warming potentials can be insignificant. The ozone formation potential of the test molecule is calculated to be 0.229 ppm, which is again negligible.

1. Introduction

Chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs) are widely used in refrigerants, blowing, fuel additives, cleaning agents, solvents and medical applications.[1–2] Due to the adverse effects of CFCs and HFCs in the atmosphere, vigorous exercise is being done to find the alternatives to CFCs and HFCs. Hydrofluoroethers (HFEs) are good substituents for CFCs and HFCs.[3–5] HFEs forms corresponding hydrofluorinated esters (fluoroesters, FESs) during atmospheric oxidation with Cl atoms and OH radicals.[6,7] Further oxidation of FESs leads to the formation of trifluoroacetic acid (TFA) or its derivatives.[8] TFA is a ubiquitous component in surface waters and rainwater around the globe.[9,10] Therefore, it is an essential to understand the fate of FESs in the Earth's atmosphere.

In general, HFEs and FESs are removed from the troposphere mainly via their reactions with Cl atoms and OH radicals, in addition to the physical processes such as wet and dry deposition.[11] Therefore, it is required to know the rate coefficients for the reactions of HFEs and FESs with OH radicals and Cl atoms. In connection with this, the kinetics of the oxidation of 2,2,2-trifluoroethylbutyrate (2,2,2-TFEB), a representative compound of FES, initiated by OH radicals were investigated using experimental and computational methods. In this context, the kinetics of the degradation of 2, 2, 2-trifluoroethylbutyrate with Cl atoms was investigated previously using relative rate method using Gas Chromatograph (GC) equipped with Flame Ionization Detector (FID) technique.[12] In addition, the mechanism and different reaction pathways for Cl-initiated oxidation of 2,2,2-TFEB was explored. The fate of the haloalkoxy radical, $CH_3CH_2CH_2C(O)OCHO{\bullet}CF_3$, which is formed as a reaction intermediate was explored in detail using high level computational studies. Five different plausible pathways for the decomposition of haloalkoxy radical which involve in thermal decomposition process, oxidation process, α-ester rearrangement (C–O, C–C, and C–H bond scission) were explored. From computational results, it is concluded that the oxidation pathway is expected to be dominant, whereas α-ester rearrangement and other thermal decomposition pathways do not compete with the oxidation pathway.[12]

Only one study at room temperature for the reaction of 2,2,2-TFEB + OH is reported in the literature till date. Blanco *et al.*[13] have studied the title reaction using relative rate method, only at 298 K. The temperature dependence of the rate coefficients for the title reaction is not explored so far. Therefore, in the present investigation, the temperature dependent rate coefficients for the title reaction were measured using the relative rate technique between the temperatures 268 and 343 K. In addition to the experimental studies, theoretical calculations were also performed for the first time using canonical variational transition state theory (CVT) coupled with hybrid DFT between the temperatures 200 and 400 K. The quantum mechanical tunnelling was incorporated using small curvature tunneling (SCT) method. Dual level calculations were carried out for all the stationary points using CCSD(T)/CC-PVDZ theory to get accurate kinetic parameters. This study provides the estimated branching ratios for different channels. The

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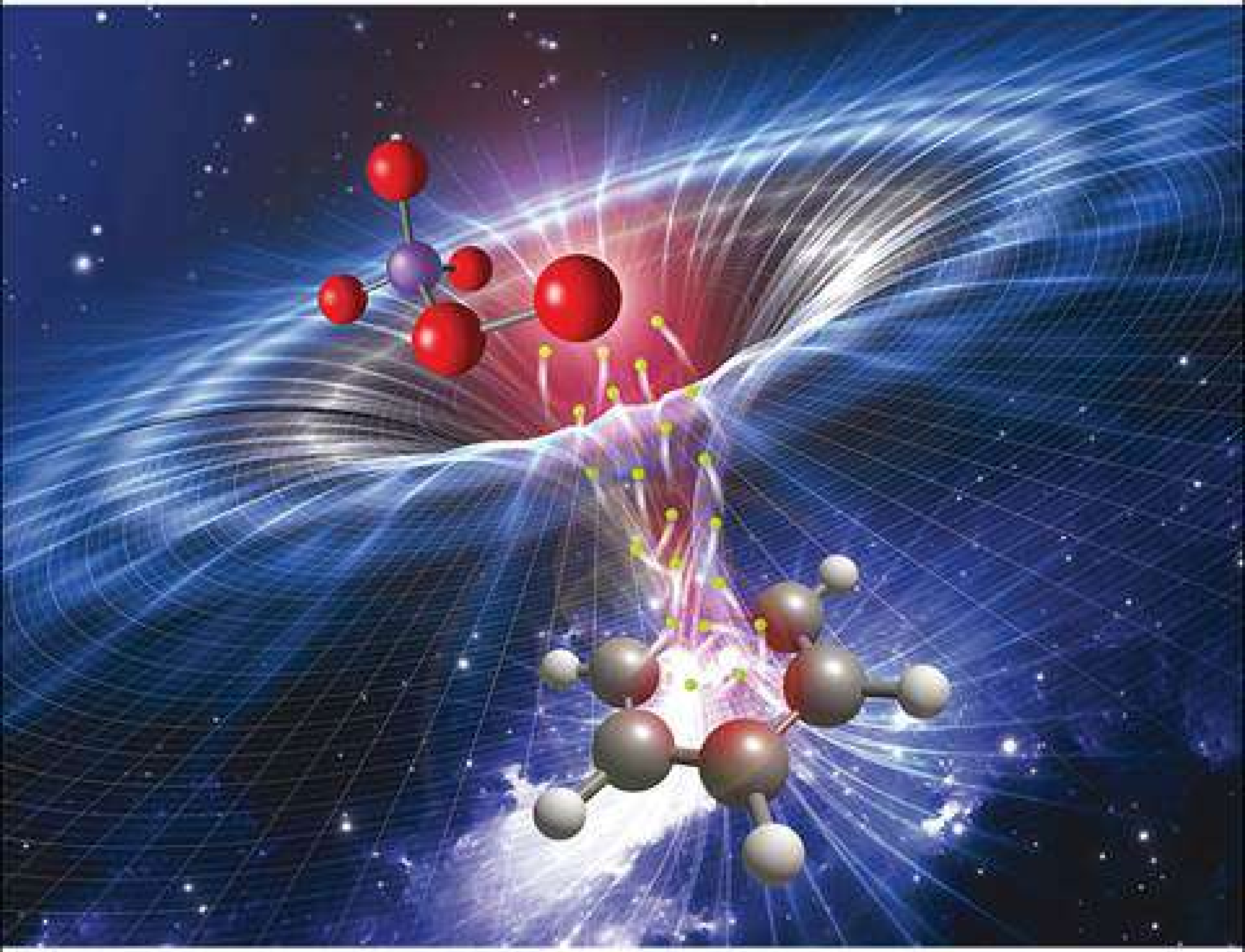

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Products and mechanism of the OH-initiated photo-oxidation of perfluoro ethyl vinyl ether, $C_2F_5OCF{=}CF_2$

A. J. C. Bunkan,[a] G. Srinivasulu,[a] D. Amedro,[a] L. Vereecken,[b] T. J. Wallington[c] and J. N. Crowley*[a]

The OH-initiated photo-oxidation of perfluoro ethyl vinyl ether ($C_2F_5OCF{=}CF_2$, PEVE) in air (298 K, 50 and 750 Torr total pressure) was studied in a photochemical reactor using *in situ* detection of PEVE and its products by Fourier transform IR absorption spectroscopy. The relative rate technique was used to derive the rate coefficient, k_1, for the reaction of PEVE with OH as $k_1 = (2.8 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The photo-oxidation of PEVE in the presence of NO_x at 1 bar results in formation of C_2F_5OCFO, FC(O)C(O)F and CF_2O in molar yields of 0.50 ± 0.07, 0.46 ± 0.07 and 1.50 ± 0.22, respectively. FC(O)C(O)F and CF_2O are formed partially in secondary, most likely heterogeneous processes. At a reduced pressure of 50 Torr, the product distribution is shifted towards formation of FC(O)C(O)F, indicating the important role of collisional quenching of initially formed association complexes, and enabling details of the reaction mechanism to be elucidated. An atmospheric photo-oxidation mechanism for PEVE is presented and the environmental implications of PEVE release and degradation are discussed.

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1 Introduction

The thermal and chemical resistance of fluoropolymers has led to their use in many industrial processes and to their production in large quantities[1,2] and thus to their release to the environment. We recently presented[3] the first detailed kinetic study on the reaction of perfluoro ethyl vinyl ether ($C_2F_5OCF{=}CF_2$, henceforth referred to as PEVE) with OH radicals (R1), determining the rate coefficient, k_1, using absolute and relative-rate techniques. k_1 was found to be independent of pressure but it has a significant negative temperature dependence, indicating that the first step is addition of OH to the C=C double bond. A room temperature value of k_1 close to 3×10^{-12} cm^3 molecule^{-1} s^{-1} implies an atmospheric lifetime of a few days, indicating that PEVE is not an important greenhouse gas. The main environmental concern about fluorinated vinyl ethers is whether their photo-oxidation leads to formation of persistent, fluorinated pollutants in the environment.

The products formed in the atmospheric photo-oxidation of organic trace gases depends on the fate of peroxy-radicals formed in the reaction between the initially generated organic radical fragments and O_2. The chemistry is typically described as either "high NO_x" where the peroxy radicals react with NO to form oxy radicals, which then propagate the radical chain, or "low NO_x" where the dominating fate of the peroxy radical is reaction with HO_2 or other peroxy radicals. Most short lived anthropogenic pollutants are oxidized under high NO_x conditions, but as the two limiting cases have different mechanisms, differences in their product distribution provide valuable information about key reaction steps.

Extending our kinetics study, this work is a detailed examination of the products formed in the OH-initiated atmospheric degradation of PEVE in air, with the aim of deriving a detailed reaction mechanism applicable to atmospheric conditions (both high and low NO_x). We also present a new measurement of the rate coefficient, k_1, for the title reaction.

$$\text{OH} + \text{PEVE} \rightarrow \text{products} \tag{R1}$$

2 Experimental methods

The experimental set-up used to study the OH-initiated photo-oxidation of PEVE has been described in detail previously[4] and only a brief summary of its central components is given here. The reaction volume is a 44 l cylindrical quartz chamber equipped with a White-type multiple reflection mirror system resulting in a 43.7 m optical path length. Infrared spectra of the

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19770	30769	Physica Status Solidi (B): Basic Research	John Wiley & Sons Ltd	3701972	15213951
19771	30770	Physica Status Solidi (C) Current Topics in Solid State Physics	Wiley - V C H Verlag Gmbbh & Co.	18626351	16101642
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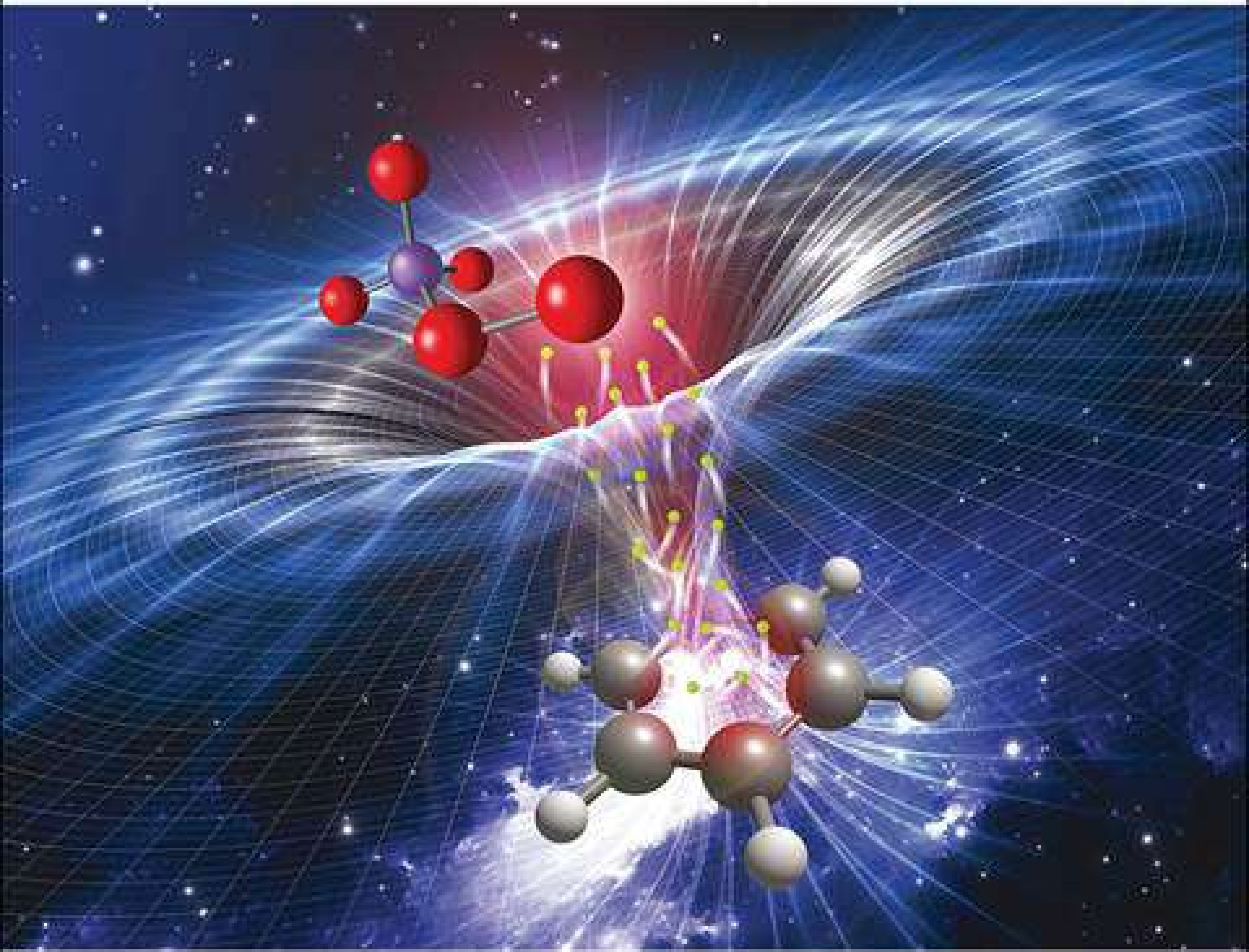

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Absolute and relative-rate measurement of the rate coefficient for reaction of perfluoro ethyl vinyl ether ($C_2F_5OCF{=}CF_2$) with OH

G. Srinivasulu, A. J. C. Bunkan, D. Amedro and J. N. Crowley *

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The rate coefficient (k_1) for the reaction of OH radicals with perfluoro ethyl vinyl ether (PEVE, $C_2F_5OCF{=}CF_2$) has been measured as a function of temperature (T = 207–300 K) using the technique of pulsed laser photolysis with detection of OH by laser-induced fluorescence (PLP-LIF) at pressures of 50 or 100 Torr N_2 bath gas. In addition, the rate coefficient was measured at 298 K and in one atmosphere of air by the relative-rate technique with loss of PEVE and reference reactant monitored *in situ* by IR absorption spectroscopy. The rate coefficient has a negative temperature dependence which can be parameterized as: $k_1(T) = 6.0 \times 10^{-13}\exp[(480 \pm 38/T)]$ cm^3 molecule^{-1} s^{-1} and a room temperature value of k_1 (298 K) = (3.0 ± 0.3) × 10^{-12} cm^3 molecule^{-1} s^{-1}. Highly accurate rate coefficients from the PLP-LIF experiments were achieved by optical on-line measurements of PEVE and by performing the measurements at two different apparatuses. The large rate coefficient and the temperature dependence indicate that the reaction proceeds *via* OH addition to the C=C double bond, the high pressure limit already being reached at 50 Torr N_2. Based on the rate coefficient and average OH levels, the atmospheric lifetime of PEVE was estimated to be a few days.

1 Introduction

Desirable properties such as thermal and chemical resistance have led to the use of fluoropolymers in many industrial processes including the production of plastics, elastomers or membranes[1,2] and to their production in large quantities. The most important commercial fluoropolymers are homopolymers based on only three main monomers; tetrafluoroethylene (TFE), vinyl fluoride and vinylidene fluoride.[3] In addition, smaller amounts of co-polymers with tailored properties are made with co-monomers like hexafluoropropylene and perfluoro vinyl ethers.

Since perfluorinated compounds generally have strong absorption features in the atmospheric infrared window and often have long atmospheric lifetimes, many of them are very potent greenhouse gases.[4–6] To evaluate their impact on climate change, accurate assessment of their atmospheric sinks is essential. From a physical chemical perspective, we note that the reaction kinetics of perfluoro substituted organic trace gases can differ greatly from the non-fluorinated analogues. Study of the OH reaction with a fluorinated ethyl vinyl ether (electrophilic addition of OH to the C=C double bond) allows us to analyse the electronic effects caused by the presence of a fluorinated alkyl group separated from the electron rich double bond by the ether linkage.

To the best of our knowledge, there are no published studies on the atmospheric fate of perfluoro ethyl vinyl ether ($C_2F_5OCF{=}CF_2$, henceforth PEVE) though a few experimental studies on related reactions of perfluoro methyl vinyl ether[7–9] and perfluoro propyl vinyl ether[10] exist. In this work we have studied the kinetics of the reaction of PEVE with OH radicals (R1) using both the technique of pulsed laser photolysis with detection of OH radicals by laser-induced fluorescence as well as relative-rate measurements using FTIR detection of reactants to derive the rate coefficient, k_1.

$$\mathrm{OH + PEVE \rightarrow products} \qquad \text{(R1)}$$

2 Experimental methods

Both absolute and relative-rate methods were used to determine the rate coefficient, k_1, for the title reaction.

2.1 Pulsed laser photolysis, laser-induced fluorescence (PLP-LIF)

Absolute rate coefficients were determined using the pulsed laser photolysis, laser-induced fluorescence technique with two different experimental set-ups (PLP-LIF1 and PLP-LIF2).

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19784	30790	Physical Review Accelerators and Beams	Amer Physical Soc	24699888	24699888
19785	30791	Physical Review Applied	Amer Physical Soc	23317019	23317019
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19787	30793	Physical Review B - Condensed Matter and Materials Physics	American Physical Society	10980121	
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19790	30796	Physical Review D	Amer Physical Soc	24700010	24700029
19791	30797	Physical Review D - Particles, Fields, Gravitation and Cosmology	American Physical Society	15507998	
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19793	30801	Physical Review E - Statistical, Nonlinear, and Soft Matter Physics	American Physical Society	15393755	
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19795	30803	Physical Review Physics Education Research	Amer Physical Soc	24699896	24699896
19796	30804	Physical Review Special Topics - Accelerators and Beams	American Physical Society	10984402	