Atmospheric Oxidation of Hydrochloroethers (HCEs) initiated by $^{\bullet}OH$, Cl-atoms, and $^{\bullet}NO_3$:A Comprehensive Review

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Abstract:

In this chapter, we explored the atmospheric insight of the oxidation of hydrochloroethers (HCEs) initiated by $^{\bullet}OH$, Cl-atoms, and $^{\bullet}NO_3$ species and explained how they influence the environment. In the modern era, HCEs have consistently attracted researcher, which is broadly employed in laboratories, industries, alkylating agents, and protecting groups. HCEs are being contemplated as the third-generation substitute for CFCs, HFCs, and HCFCs. Their appealing qualities, i.e. high reactivity towards tropospheric oxidants, shorter lifetime in the atmosphere, zero ozone depletion potentials (ODPs), and low global warming potentials (GWPs), may give a solution to the environmental concerns. They have been already utilized in some nations as possible substitutes for chemicals in labs, as well as solvents for fats and oils, cleansers, varnishes, and paints, and in the production of insecticides. However, one must gauge these compounds' atmospheric chemistry and impacts on the ecosystem before their widespread commercial application. This study systematically does a thorough evaluation of the existing literature concerning the kinetic studies on HCEs to show their reactivity towards oxidants and understand the possible degradation of oxidation product radicals formed. Moreover, understanding the findings of atmospheric implications like atmospheric lifetimes, and GWPs.

1. Introduction

The atmosphere consists of a variety of oxygenated organic compounds and has been found in the form of alcohols, ethers, ketones, aldehydes, esters, and so on [1, 2]. These compounds have been released into the troposphere, raising considerable worries about the growing hazards to human health [3]. Each year, large amounts of chemicals are released into the atmosphere from both natural and man-made sources. The atmospheric chemistry of organic oxygenates has piqued a lot of attention in recent years, particularly in relation to their roles in the degradation of indoor air quality, the generation of secondary organic aerosols, and the possible toxicity imposed by them [4-6]. The formation of photochemical smog and tropospheric ozone relies on the processes carried out by the oxygenated compounds. Hydrochloroethers (HCEs) are a well-known example of such anthropogenic organic compounds that are also generated by the oxidation of all hydrocarbons in the atmosphere.

In the modern era, HCEs have received a lot of heed. They have been widely employed in laboratories and industry as components of paints and varnishes, as solvents for fats and oils, cleaning agents for textiles, and so on [7-10]. Moreover, HCEs have been developed as the third-generation substitutes for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) in various applications [11-14]. Since, the ozone layer in the stratosphere is thought to be most vulnerable to CFCs, which are mostly utilized as refrigerants and cleaning agents. Hence, the Montreal Protocol and all of its subsequent amendments forbid the commercial production of these substances [15]. HFCs have little impact on ozone depletion since they don't contain any Cl or Br atoms. However, even though they were once thought to be a good replacement, their considerable C-F bond absorption in the atmospheric window zone (800-1200 cm^{-1}), would cause global warming. Thus, HCEs are marked as a conspicuous alternative refrigerant. An illustration of the timeline of alternative refrigerants is shown in Figure 1.

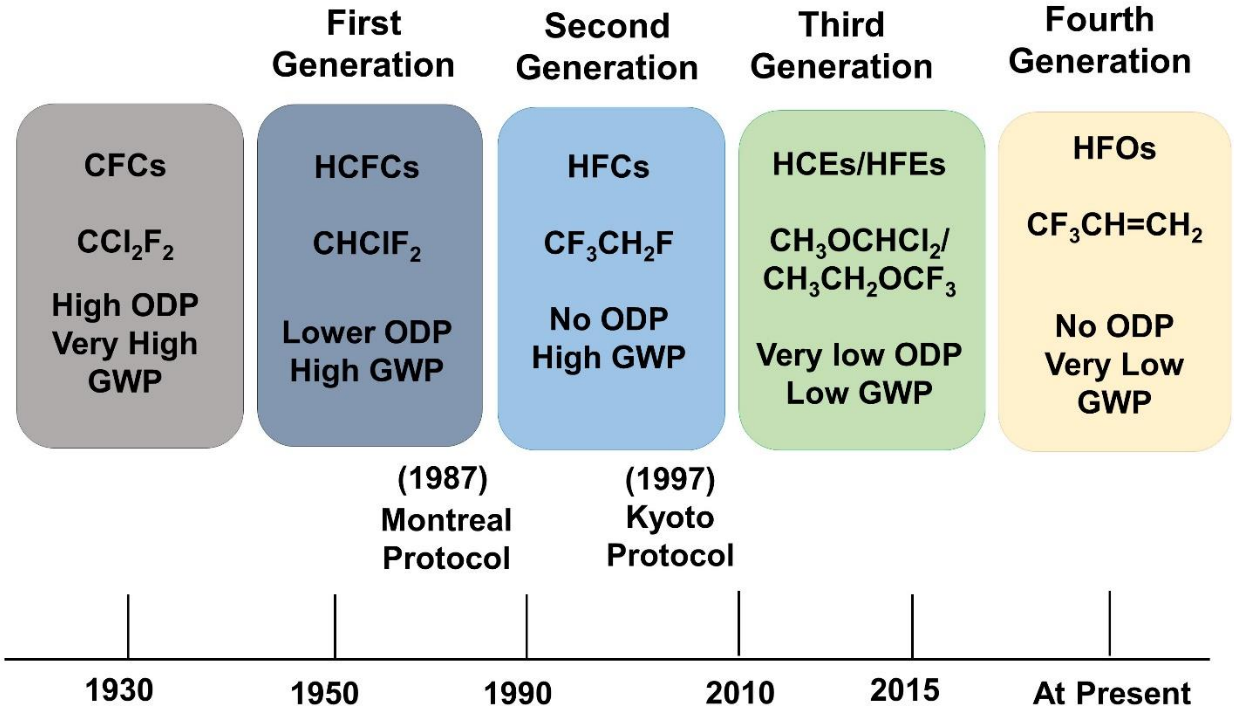
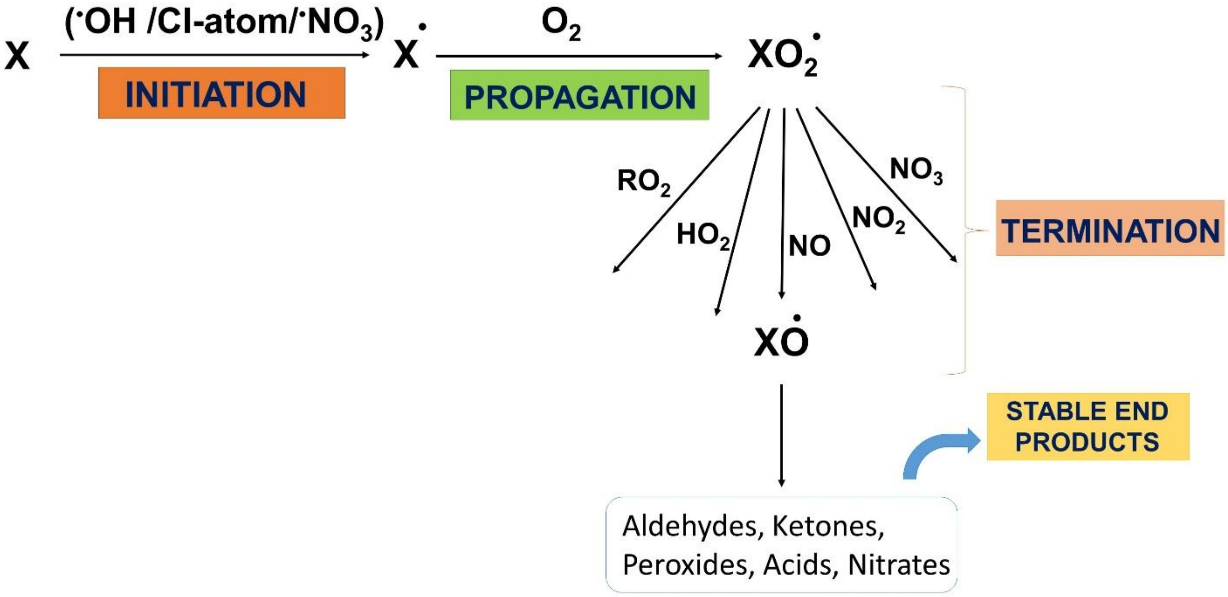


Figure 1: Evolution of alternatives to CFCs over different time horizon [16]

HCEs are degraded in the atmosphere by undergoing photolytic chemical reactions and interaction with atmospheric oxidants. The presence of ether linkage (–O–) in HCEs could cause them to become more reactive in the troposphere [17]. The chemical reactivity of HCEs in the troposphere is initiated by oxidants such as $^{\bullet}OH$ radical (during daylight), Cl-atoms (during daylight in coastal and marine environments), and $^{\bullet}NO_3$ radical (during night time) [18]. For a specific HCE, its potential significance in the atmosphere relies on how it transforms in the atmosphere, what sorts of molecules are produced as a result of those changes, as well as the duration of each degradation product in the atmosphere [3, 19]. Additionally, as HCEs contain Cl atoms, the breakdown products formed from them might release Cl atoms into the atmosphere. This could have a severe influence on the environment by contributing to the depletion of the ozone layer and global warming. Therefore, it is imperative to study the kinetics and mechanistic pathways of degradation of HCEs in order to assess their atmospheric chemistry and understand how these molecules contribute to air pollution mostly in urban and rural areas. In order to evaluate the impacts of HCEs on the environment once they were emitted into the atmosphere, the necessary requirement is to first understand the atmospheric lifetimes of HCEs, as well as atmospheric hazard indices such as the global warming potentials (GWPs). The GWP is a metric that is used to evaluate the contribution of gaseous compounds to the greenhouse effect and is based on its anticipated lifetime in the atmosphere. Thereafter, further grasping the fate of the ensued oxidation products. The probable tropospheric transformation processes of HCEs are shown in Scheme 1 [20].



Scheme 1: A general scheme showing the degradation mechanism of HCEs (say X=HCE) in the troposphere [20]

1.1 List of HCEs and Their Applications

HCEs are used in a variety of sectors including laboratories and industries. Among them, 1,1-Dichlorodimethylether (DCDME) has been employed in the synthesis of commercial insecticides, phenalenyl-fused compounds, and also some of these compounds act as a model complex for anesthetics like enflurane or isoflurane [21, 22]. Another HCE compound, Chloromethyl Ethyl Ether (CMEE, $CH_2ClOCH_2CH_3$) has been utilized in the production of HIV-1 reverse transcriptase inhibitors obtained from TNK-651 [23]. Moreover, employed in the lithiation of lithiomethyl ethyl ether by a DTBB-catalysed process [24]. Bis (2-chloroethyl) ether, also known as BCEE ($ClCH_2CH_2OCH_2CH_2Cl$), is another well-known example of HCE. It is extensively used in agriculture and industry as a cleaning agent for textiles, a component of varnishes and paints, a solvent for fats and oils, and in the creation of pesticides. Another application of it was, as a chemical intermediary in the manufacture of a commercial fungicide [25]. $CH_3CH_2OCH_2CH_2Cl$ (CEEE) is utilized in the separation of protein and saccharides and as sulphur dioxide absorbers in order to prepare ether-functionalized ionic liquids, where it acts as a reagent. Likewise, $CH_3OCH_2CH_2Cl$ (CEME) has been employed in the synthesis of acyclic nucleosides of thieno[2,3-d] pyrimidine derivatives, while CH_3OCH_2Cl (CMME) is employed as an industrial solvent and alkylating medium in order to prepare water repellents, ion exchange resins, and polymers, to manufacture detergent dodecylbenzyl chloride. In some variations of the Blanc chloromethylation, CMME is also utilized as a chloromethylating agent. Due to its role in introducing the methoxymethyl (MOM) protecting group during chemical synthesis, this substance is frequently referred to as MOM chloride [26]. Because of the extensive industrial applications, these compounds will release into the atmosphere during the processes of synthesis, usage, and storage. Therefore, it is crucial to understand the tropospheric oxidation and influence of these compounds in the environment.

2. Literature Review on the oxidation of HCEs

In literature, there have been numerous theoretical and experimental studies on the oxidation of HCEs by $^\bullet OH$, Cl-atoms, and $^\bullet NO_3$. The kinetic investigation of HCE reactions will reveal information about their tropospheric reactivity and help to elucidate how they degrade in the atmosphere. In the following section, we provide an overview of some HCEs that we found in the literature.

2.1. Oxidation of 1,1-Dichlorodimethylether (DCDME)

Firstly, the oxidation reaction of CH_3OCHCl_2 (DCDME) initiated by Cl-atom was studied by Dalmasso *et al*. [27]. They estimated the reaction rate constant using the relative rate technique. An experiment using nitrogen as the bath gas was conducted at 298 ± 2 K and atmospheric pressure. The rate constant for the reaction of a Cl-atom with CH_3OCHCl_2 was determined to be $(1.04 \pm 0.30) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. In another experiment, Dalmasso *et al*. [28] used synthetic air as the bath gas and evaluated the rate constant for the same reaction at 296 ± 2 K and atmospheric pressure. They estimated the rate constant as $(1.05 \pm 0.11) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Thereafter, Mishra *et al*. [29] carried out the oxidation of the same compound with Cl-atom using DFT and couple cluster techniques. Using the canonical transition state theory (CTST) with tunneling correction, they calculated the rate constant as 1.204×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, and this value is in good accord with the experimentally measured ones. Similarly, they also calculated the rate constant of the CH_3OCHCl_2 (DCDME) oxidation process with $^\bullet OH$ using quantum chemical method. They estimated the rate constants using CTST, and reported the rate constant value of 2.03×10^{-13} cm^3 molecule $^{-1}$ s^{-1} at 298 K [30].

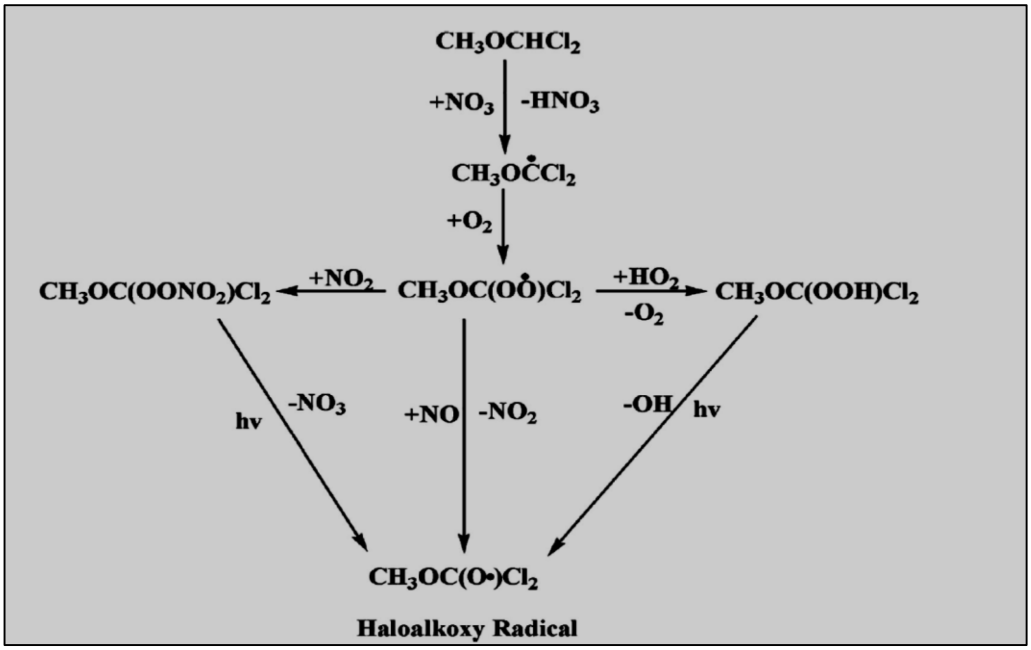
The two main mechanisms that have been taken into account for the oxidation reaction of DCDME by $^{\bullet}OH$, Cl-atom, and $^{\bullet}NO_3$ are given by Eq. 1 and 2 [29, 30] as shown below.

$$CH_3OCHCl_2 + X \rightarrow CH_3OC^{\bullet}Cl_2 + HX \qquad (1)$$

$$CH_3OCHCl_2 + X \rightarrow C^{\bullet}H_2OCHCl_2 + HX \qquad (2)$$

Where X = $^{\bullet}OH$, Cl-atom, and $^{\bullet}NO_3$

Moreover, Mishra *et al*. [30] estimated the branching ratios for the reaction of CH_3OCHCl_2 with $^{\bullet}OH$ and ascertained that the hydrogen abstraction reaction from the $–CHCl_2$ group of CH_3OCHCl_2 is considered to be predominate than $–CH_3$ group, and this is validated with the percentage ratios obtained as 96.0% and 4.0% respectively [27]. The thermodynamic viability is also noted by Mishra *et al*. [29] for the reaction of CH_3OCHCl_2 + Cl-atom. Both reaction channels (Eq. 1 and 2) are found to be exergonic ($\Delta G < 0$) based upon free energy calculations, for which the reaction enthalpies ($\Delta_rH°$) were estimated to be -8.65 and -5.22 kcal mol^{-1}, respectively. This clearly suggests that reaction in Eq. 1 is thermodynamically more preferable than reaction in Eq. 2 [29]. Similarly, Gour *et al*. [31] theoretically explored the oxidation reaction of CH_3OCHCl_2 initiated by $^{\bullet}NO_3$ at the BHandHLYP/6-311++G(d,p) level. The estimated rate constant of this reaction is found to be 8.15×10^{-17}at 298 K. Further, they also explored the fate of alkoxy radical ($CH_3OC^{\bullet}Cl_2$) generated from the aforementioned reaction. The degradation routes of CH_3OCHCl_2 by $^{\bullet}NO_3$ were depicted in scheme 2 [31].



Scheme 2: The degradation mechanism of CH_3OCHCl_2 initiated by $^{\bullet}NO_3$ in the troposphere [31].

2.2. Oxidation of bis (2-chloroethyl) ether (BCEE)

Dalmasso *et al*. [7] carried out an experiment at 298 ±2 K and atmospheric pressure to determine the rate constant of the $ClCH_2CH_2OCH_2CH_2Cl$ (BCEE) reaction with $^{\bullet}OH$ using synthetic air as bath gas. The rate constant was derived using the reference substances n-pentane and n-heptane, and was estimated to be $(7.6 \pm 1.9) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Thereafter, Paul *et al*. [32] conducted a theoretical analysis of the same reaction. They employed the M06-2X method with basis 6-31+G(d,p) set to explore this reaction. The rate constant was computed between 298 and 400 K using the CTST, and at 298 K and 1 atm. The rate constant was determined to be 6.27 $\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. This is quite in agreement with the experimentally determined rate constant value by Dalmasso *et al*. [7].

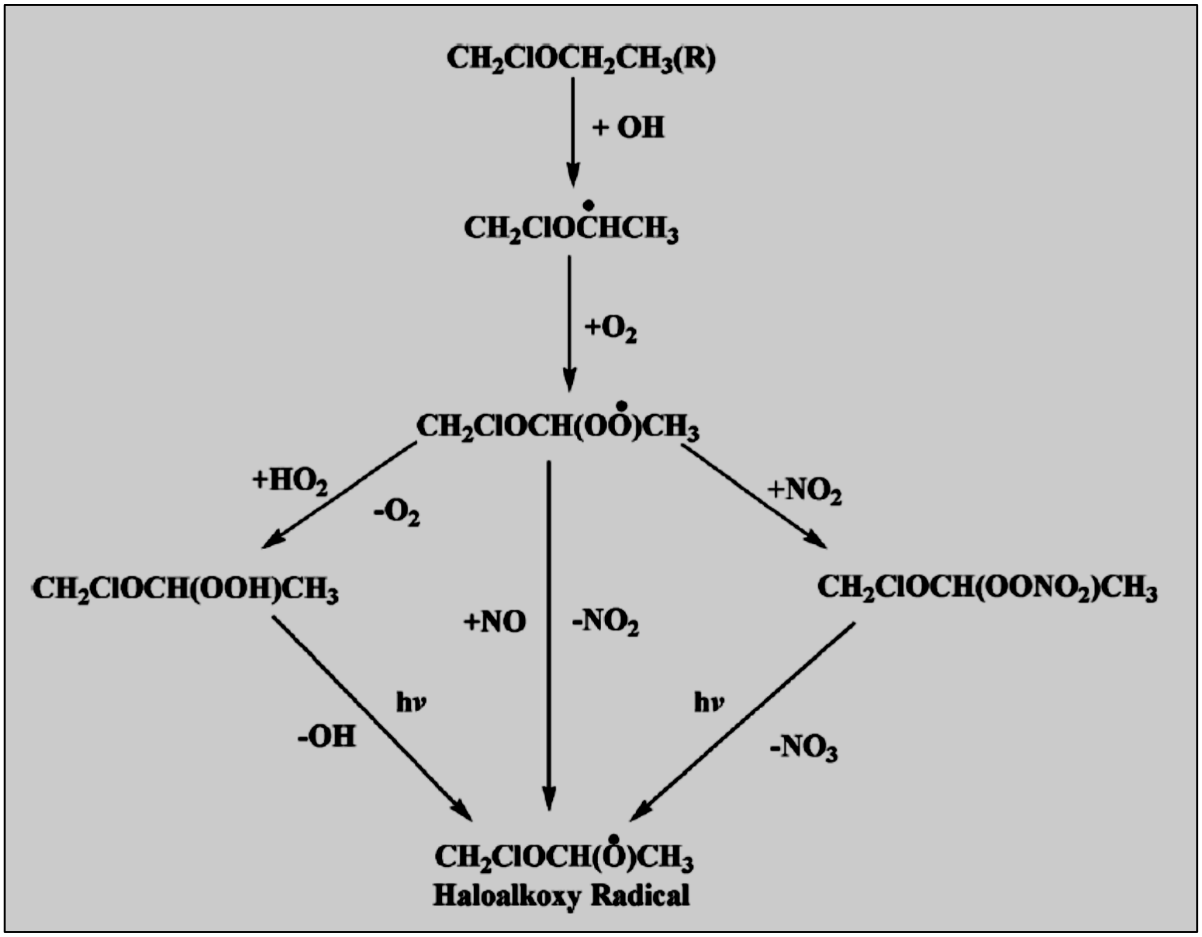
Similarly, Dalmasso *et al.* [33] used the relative rate method to determine the rate constant in relation to those of n-pentane and n-heptane for the Cl-atom induced oxidation of BCEE. The measured value was found to be $(1.0 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}s^{-1}$ at (298 ± 2) K and atmospheric pressure. This result agrees with the theoretically calculated value of 1.33×10^{-10} cm^3 $molecule^{-1}s^{-1}$), studied by Paul *et al*. [32]. Moreover, Paul *et al*. [32] also studied the oxidation of BCEE ($ClCH_2CH_2OCH_2CH_2Cl$) with $^{\bullet}NO_3$. The estimated rate constant was found to be 4.07×10^{-15} cm^3 $molecule^{-1}$ s^{-1}.

2.3. Oxidation of 2-chloroethyl ethyl ether (CEEE)

The oxidation reaction of $CH_3CH_2OCH_2CH_2Cl$ (CEEE) with $^{\bullet}OH$ was studied by Dalmasso *et al.* [7] experimentally utilizing the relative rate technique. They carried out the reaction at (298 ± 2) K and atmospheric pressure using n-pentane and n-heptane as reference compounds, and the rate constant was determined to be $(8.3 \pm 1.9) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The same reaction was investigated theoretically by Ye *et al*. [34] by using an *ab initio* approach and canonical variational transition-state dynamic computations with the small-curvature tunneling correction. The rate constant was estimated to be 6.28×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K, which agreed well with the experimental one. Again, Dalmasso *et al*. [33] studied the Cl-atom initiated oxidation of $CH_3CH_2OCH_2CH_2Cl$ (CEEE). The rate constant at (298 ± 2) K and atmospheric pressure was observed as $(1.7 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Thereafter, theoretically, Ye *et al*. [34] studied the ($CH_3CH_2OCH_2CH_2Cl$ + Cl) reaction and at 298 K rate constant was estimated as 8.09×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. In the same manner, Gour *et al*. [35] carried out quantum chemical computations to determine the rate constant of the $^{\bullet}NO_3$ induced oxidation of $CH_3CH_2OCH_2CH_2Cl$ (CEEE). The rate constants were calculated using the CTST for the temperature range of 250-350 K, and the total rate constant at 298 K and 1 atm pressure was reported as 2.78×10^{-16} cm^3 $molecule^{-1}$ s^{-1}.

2.4. Oxidation of Chloromethyl ethyl ether (CMEE)

To study the oxidation reaction of $CH_2ClOCH_2CH_3$ (CMEE) with $^{\bullet}OH$ and Cl-atom, Dalmasso *et al*. [36] used *ab* initio G3B3 level of theory to calculate the vertical ionization potentials and C-H bond dissociation energies and analyzed the kinetics of the reactions. At room temperature, the observed rate constants were found to be 2.33×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 4.485×10^{-11} cm^3 $molecule^{-1}$ s^{-1} respectively. Thereafter, Paul *et al*. [37] computed the rate constant for $^{\bullet}OH$ initiated oxidation of $CH_2ClOCH_2CH_3$ (CMEE). The rate constants were calculated using the CTST between 250 and 450 K at 1 atm. and at 298 K. The overall rate constant value was estimated as 6.45×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Moreover, in this study, they had provide the detailed mechanism of the formation of $CH_2ClOCH(O^{\bullet})CH_3$ radical by the degradation of $CH_2ClOCH_2CH_3$ (CMEE) initiated by $^{\bullet}OH$ and is shown in scheme 3 [37].



Scheme 3: Formation $CH_2ClOCH(O^{\bullet})CH_3$ radical by the ($CH_2ClOCH_2CH_3$ + $^{\bullet}OH$) degradation reaction [37].

Thereafter, Paul *et al.* [37] also studied the fate of this haloalkoxy radical, $CH_2ClOCH(O^{\bullet})CH_3$ in the atmosphere, that lead to the following mechanism as:-

$$CH_2ClOCH(O^{\bullet})CH_3 \rightarrow CH_2ClO^{\bullet} + CH_3CHO \qquad (4)$$

$$CH_2ClOCH(O^{\bullet})CH_3 \rightarrow CH_2ClOCHO + {}^{\bullet}CH_3 \qquad (5)$$

$$CH_2ClOCH(O^{\bullet})CH_3 \rightarrow CH_2ClOCOCH_3 + {}^{\bullet}H \qquad (6)$$

This study revealed that the C–C bond breaking of the $CH_2ClOCH(O^{\bullet})CH_3$ radical is more dominant and is also validated through thermodynamic calculations with $\Delta_rG°$ value of -7.71 for the reaction (5) – ($CH_2ClOCH(O^{\bullet})CH_3 \rightarrow CH_2ClOCHO + {}^{\bullet}CH_3$). The reaction enthalpy and Gibb's free energy of the reaction channels (4-6) in kcal mol^{-1} are shown in Table 1 [37].

Table 1: Reaction enthalpy and Gibb's Free energy (in kcal mol^{-1}) at M06-2Xand CCSD(T)//M06-2X levels along with 6-311++G(d,p) basis set for the reaction channels (4-6) [37]

Decomposition Reactions	**M06-2X level**		**CCSD(T)//M06-2X level**	
	$\Delta_rH°$	**$\Delta_rG°$**	**$\Delta_rH°$**	**$\Delta_rG°$**
CO Scission **$CH_2ClOCH(O^\bullet)CH_3 \rightarrow CH_2ClO^\bullet + CH_3CHO$**	13.8	1.3	10.3	-2.2
CC Scission **$CH_2ClOCH(O^\bullet)CH_3 \rightarrow CH_2ClOCHO + {}^\bullet CH_3$**	3.0	-7.7	-0.6	-11.3
CH Scission **$CH_2ClOCH(O^\bullet)CH_3 \rightarrow CH_2ClOCOCH_3 + {}^\bullet H$**	5.4	-2.5	3.2	-4.7

No prior investigations on the oxidation reaction of $CH_2ClOCH_2CH_3$ (CMEE) with $^\bullet NO_3$ have been found yet, to the best of our knowledge.

2.5. Oxidation of 2-chloroethyl methyl ether (CEME)

To investigate the kinetics of $CH_3OCH_2CH_2Cl$ (CEME), McLoughlin *et al*. [38] evaluate the rate constants for the reaction of $CH_3OCH_2CH_2Cl$ with $^\bullet OH$ and Cl-atom using a relative rate method. The rate constants value were estimated as $(4.92 \pm 1.09) \times 10^{-12}$, and $(1.44 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} respectively at (300 ± 3) K and total pressure of 1 atmosphere. Similarly, Dalmasso *et al*. [28] used the relative rate technique to examine the same compound with Cl-atom. At (296 ± 2) K and atmospheric pressure, the rate constant value was computed to be $(1.14 \pm 0.10) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Furthermore, for the $^\bullet OH$ initiated reaction with the same compound, Dalmasso *et al*. [7] studied the reaction kinetics and the rate constant value was found to be $(5.2 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at (298 ± 2) K and atmospheric pressure. Thus, from this study, we have observed that the rate constant values are in agreement for all the studies both for the $^\bullet OH$ and Cl-atom initiated oxidation reaction. Thereafter, theoretical studies on the oxidation of this compound was studied by Ye *et al*. [34] for the reaction with $^\bullet OH$ and Cl-atom. Utilizing the *ab* initio approach and canonical variational transition-state dynamic calculations with the small-curvature tunneling correction, they investigated the reaction kinetics. The rate constant at 298 K was measured to be 4.01 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 6.13 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively for the $^{\bullet}OH$ and Cl-atom initiated reaction. Similarly, Gour *et al*. [39] conduct a gas-phase reaction of $CH_3OCH_2CH_2Cl$ with $^{\bullet}NO_3$ employing quantum chemical methods. They computed rate constants using CTST at M06-2X/6-31+G(d,p) level of theory and refining energy even farther at CCSD (T)/6-311++G(d,p) level of theory. The total rate constant computed for the reaction was obtained as 4.88 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 atm pressure. As far as our knowledge, no experimental studies have been found for this compound with $^{\bullet}NO_3$.

2.6. Oxidation of 1-chloromethyl methyl ether (CMME)

The oxidation reaction of CH_3OCH_2Cl (CMME) initiated by $^{\bullet}OH$ and Cl-atom was also investigated by Dalmasso *et al*. [36], and measured the rate constants by relating the room-temperature rate constant values with both the C-H bond dissociation energies and the vertical ionization potentials of CH_3OCH_2Cl, at the G3B3 level of theory. The computed rate constant values for the $^{\bullet}OH$ and Cl-atom initiated reaction were observed as 1.27 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 2.91 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} respectively. The kinetics for the reaction of Cl-atom with CH_3OCH_2Cl was also examined by Jenkin *et al*. [40], and the rate constant was reported as (2.9 ± 0.2) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and agrees well with the reported value given by Dalmasso *et al*. [36]. To the best concern of our study, this compound has not yet been the subject of any investigations on the kinetics of CH_3OCH_2Cl with $^{\bullet}NO_3$.

2.7. Oxidation of 1,1,1-Trichlorodimethyl ether (TCDME)

Dalmasso *et al*. [36] studied the kinetics for this HCE reacting with $^{\bullet}OH$ and Cl-atom. The reaction CH_3OCCl_3 (TCDME) + $^{\bullet}OH$, Cl-atom was investigated using the same method as discussed above for the compound (CMME). The reported rate constants were observed as 2.86 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and 2.86 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} respectively for the $^{\bullet}OH$ and Cl-atom initiated reaction. Further, no studies have been found on the kinetics of CH_3OCCl_3 (TCDME) with $^{\bullet}NO_3$.

2.8. Oxidation of 2,2-Dichloroethylmethylether (DCEME)

The reaction rate investigation of this compound with $^{\bullet}OH$ and Cl-atom was studied by McLoughlin *et al*. [38] with the help of the relative rate method. The rate constant of the oxidation reaction of $CH_3OCH_2CHCl_2$ (DCEME) with $^{\bullet}OH$ was estimated as (2.37 ± 0.50) ×10^{-12} cm^3 $molecule^{-1}$ s^{-1} by using the values of k(OH + pentane) = (3.94 ± 0.98) ×10^{-12} and k(OH + diethyl ether) = (13.6 ± 2.26) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The rate constant for the Cl-atom-initiated reaction with $CH_3OCH_2CHCl_2$ was calculated as (4.4 ± 1.6) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} on the basis of the values of k(Cl + ethane) = (5.84 ± 0.88) × 10^{-11} and k(Cl +diethyl ether) = (25.4 ± 8.05) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. No further information on the kinetic studies of this compound is available for the oxidation reaction with $^{\bullet}NO_3$.

The estimated rate constant values that have been reported for the oxidation reaction of HCEs with $^{\bullet}OH$, Cl-atom, and $^{\bullet}NO_3$ in the literature to date are summarized and listed in Table 2.

Table 2: Rate constants for the oxidation reactions of some HCEs initiated by $^{\bullet}OH$, Cl-atom, and $^{\bullet}NO_3$ (in the temperature range of 296-298K) [27-40]

Sl No.	**HCEs**	**k_{OH}**	**k_{Cl}**	**k_{NO3}**
1	CH_3OCHCl_2 (DCDME)	2.03 × 10^{-13} [30] 0.64× 10^{-12} [36]	(1.04 ± 0.30) × 10^{-12} [27] (1.05 ± 0.11) × 10^{-12} [28] 1.204 × 10^{-12} [29] 0.105 × 10^{-11} [36]	8.15 × 10^{-17} [31]
2	$ClCH_2CH_2OCH_2CH_2Cl$ (BCEE)	(7.6 ± 1.9) ×10^{-12} [7] 6.27× 10^{-12} [35]	(1.0 ± 0.3) × 10^{-10} [33] 1.33 × 10^{-10} [32]	4.07 × 10^{-15} [32]
3	$CH_3CH_2OCH_2CH_2Cl$ (CEEE)	(8.3 ± 1.9) × 10^{-12} [7] 6.28 × 10^{-12} [34]	(1.7 ± 0.5) × 10^{-10} [33] 8.09 ×10^{-11} [34]	2.78 × 10^{-16} [35]
4	$CH_2ClOCH_2CH_3$(CMEE)	2.33 × 10^{-12} [36] 6.45 × 10^{-12} [37]	4.485 × 10^{-11} [36]	—
5	$CH_3OCH_2CH_2Cl$ (CEME)	(4.92 ±1.09)×10^{-12} [38] (5.2 ± 1.2) × 10^{-12} [7] 4.01 × 10^{-12} [34]	(1.44 ± 0.5) × 10^{-10} [38] (1.14 ± 0.10) × 10^{-10} [28] 6.13 × 10^{-11} [35]	4.88 × 10^{-17} [39]
6	CH_3OCH_2Cl (CMME)	1.27 × 10^{-12} [36]	2.91 × 10^{-11} [36] (2.9 ± 0.2) ×10^{-11} [40]	—
7	CH_3OCCl_3(TCDME)	2.86 × 10^{-13} [36]	2.86 × 10^{-12} [36]	—
8	$CH_3OCH_2CHCl_2$ (DCEME)	(2.37±0.50)×10^{-12} [38]	(4.4 ±1.6) × 10^{-11} [38]	—
9	$CH_3OCHClCH_3$(CEME)	10.1× 10^{-12} [36]	24.91× 10^{-11} [36]	—

From these kinetic studies, we can ascertain that HCEs are quite reactive with tropospheric oxidants.

2.8.1 Atmospheric implications

- ***Atmospheric Lifetime:***

The duration of time that a species remains in the atmosphere is referred to as its atmospheric lifetime. Primarily, the atmospheric lifetime of any HCEs may be evaluated by examining its eradication from the atmosphere through its reaction with tropospheric oxidants. Gases with a higher value of atmospheric lifetime impose a greater degree of warming than gases with a lower atmospheric lifetime value. The atmospheric lifetime of a particular molecule may be computed employing the total rate constant of the reactions discussed above via the relation given as [41]

$$\tau_X = (k_{Total} \times [X])^{-1}$$

Where, x = atmospheric oxidants like $^{\bullet}OH$ radical, Cl-atom, and $^{\bullet}NO_3$.

k_{Total}= total rate constant for the reaction of x species with the specific compound

[X] = average atmospheric concentration of the oxidant

The survey of an estimated lifetime of some HCEs found in the literature has shown that their lifetimes are short as of some hours/days. Using the rate constants for the compounds (as provided in Table 2), The estimated atmospheric lifetime values of studied HCEs are provided in Table 3. For example, Dalmasso *et al*. [7] estimated the lifetime for the reaction of $ClCH_2CH_2OCH_2CH_2Cl$ (BCEE) with $^{\bullet}OH$ radical, Cl-atom using the average concentrations of $^{\bullet}OH$ and Cl-atom as [OH] = 2×10^6 radicals cm^{-3} [42], [Cl] = 1×10^3 atoms cm^{-3} [43]. The reported lifetime was found to be 18 hours (0.75 days) and 116 days respectively for reaction with $^{\bullet}OH$ and Cl-atom. Thereafter, Paul *et al*. [32] calculated the lifetime for the same compound with $^{\bullet}OH$ radical, Cl-atom, and $^{\bullet}NO_3$. They have observed lifetimes of 0.9 days (22.1 h), 87 days, and 4.9 days respectively, where average concentrations of oxidants were taken as 2.0×10^6 molecule cm^{-3} [42], 1.0×10^3 molecule cm^{-3} [44], and 5.70×10^8 molecule cm^{-3} [45], and, respectively for $^{\bullet}OH$, Cl-atom, and $^{\bullet}NO_3$. The atmospheric lifetime of $CH_2ClOCH_2CH_3$ (CMEE) was once more computed by Paul *et al.* [37] using the quantum chemical method and taking the concentration of $^{\bullet}OH$ as 1.0×10^6 molecules per cm^3 [46] and rate constant k_{OH} as 6.45×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The estimated lifetime was 1.79 days. This value is found to be slightly less than that reported by Dalmasso *et al*. [36] for the CMEE. Dalmasso *et al*. [36] estimated the lifetime value of CMEE as 5.0 days using the concentration of $^{\bullet}$OH as ([OH] = 1 × 10^6 radicals cm^{-3}) and the total rate constant value as 2.33 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Additionally, they have estimated the lifetime value for Cl-atom initiated reaction. With an average concentration of Cl-atom as ([Cl] = 1 × 10^4 atoms cm^{-3}), the lifetime of CMEE was calculated as 25.8 days using a rate constant of 4.485 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} [36]. For $^{\bullet}NO_3$ initiated reaction with $CH_2ClOCH_2CH_3$ (CMEE), as no kinetic studies are available in the literature, no reported lifetime was found yet. For the compound CH_3OCHCl_2 (DCDME), Dalmasso *et al*. [36] studied the lifetime for $^{\bullet}$OH and Cl-atom. Taking rate constants of 0.64 × 10^{-12} and 0.105 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} respectively for $^{\bullet}$OH and Cl-atom, lifetime was estimated as 18.1 and 1102.3 days, respectively with [OH] =1 × 10^6 radicals cm^{-3}, and [Cl] = 1 × 10^4 atoms cm^{-3}. Since the lifetime for the reaction with Cl-atom of this compound was quite long, it is possible for this compound to degrade through other means, such as transfer into the stratosphere and thereby generating chlorine atoms as a result of photolysis [27]. According to Gour *et al*. [31], who used a rate constant of 8.15 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1} and concentration as $[NO_3]$ =5 × 10^8 molecule cm^{-3}, for the DCDME, the lifetime was estimated as 0.78 years (284.8 days). From these studied HCE compounds, we have observed that lifetimes were found to be quite short (in the order of days), which also implied a minimal contribution to global warming. The short lifetimes of these HCEs imply that they are quite reactive towards tropospheric oxidants. Due to their short atmospheric lives and low global warming potential (GWP), HCEs also prevented the movement of these chemicals into the stratosphere, contributing minimally to the ozone layer's depletion [31]. The following section of studies will provide an outline of the existing literature on the global warming potentials (GWPs) of some HCEs.

Table 3: Atmospheric lifetime of some HCEs with respect to the oxidants viz. $^{\bullet}$OH, Cl-atom, and $^{\bullet}NO_3$

Sl No.	**HCEs**	τ_{OH}	τ_{Cl}	τ_{NO3}
1	CH_3OCHCl_2 (DCDME)	18.1 days [36]	1102.3 days [36]	0.78 years (284.8 days) [31]
2	$ClCH_2CH_2OCH_2CH_2Cl$ (BCEE)	0.9 days [32]	87 days [32]	4.9 days [32]
3	$CH_3CH_2OCH_2CH_2Cl$ (CEEE)	19 hours (0.79 days) [34]	142 days [34]	0.23 years (83.95 days) [35]

4	$CH_2ClOCH_2CH_3$ (CMEE)	1.79 days [37] 5.0 days [36]	25.8 days [36]	_
5	$CH_3OCH_2CH_2Cl$ (CEME)	39 hours(1.625 days) [34]	188 days [34]	1.3 years(474.8 days) [39]
6	CH_3OCH_2Cl (CMME)	9.1 days [36]	39.9 days [36]	_
7	CH_3OCCl_3 (TCDME)	40.5 days [36]	404.7 days [36]	_
8	$CH_3OCH_2CHCl_2$ (DCEME)	_	26.3 days [27]	_
9	$CH_3OCHClCH_3$ (CEME)	1.1 days [36]	4.6 days [36]	_

- ***Global Warming Potentials (GWPs)***

Global Warming Potential can be defined as the measure of the amount of heat trapped by a greenhouse gas in the atmosphere relative to CO_2 [47]. The expression for estimating global warming potential (GWP) given by Hodnebrog *et al*. [48] is given below.

$$\boldsymbol{GWP(H) = \frac{AGWP_i(H)}{AGWP_{CO_2}(H)} = \frac{A\tau(1 - \exp\left(\frac{H}{\tau}\right))}{AGWP_{CO_2}(H)}}$$

Here, A is the instantaneous radiative efficiency (IRE) (unit: $Wm^{-2}ppb^{-1}$), and τ refers to lifetime. $AGWPCO_2$(H) implies the absolute global warming potential for CO_2 (reference compound) for the various time horizons (H), the AGWPi is the absolute global warming potential for a calculated molecule.

The study of GWPs for HCEs is found very scant in the literature for the reaction with tropospheric oxidants. A few of them have been investigated by Gour *et al*. [31], [35], [39], and Dalmasso *et al*. [33]. First, Dalmasso *et al*. [33] estimated GWPs for the studied HCEs viz. $CH_3CH_2OCH_2CH_2Cl$(CEEE) and $ClCH_2CH_2OCH_2CH_2Cl$(BCEE) reacting with Cl-atoms. The radiative efficiency (RE) of these compounds are found to be 0.078 and 0.062 $Wm^{-2}ppbv^{-1}$ respectively. For the 20 and 100-year time periods, GWPs were found to be 0.34, and 0.10 for CEEE; 0.20, and 0.06 for BCEE respectively. Again, Gour *et al*. [35] estimated the GWPs of CEEE for the reaction with $^{\bullet}NO_3$. The GWPs for the time period of 20, 100, and 500 years are 0.13, 0.04, and 0.01, respectively with a RE (A_i) value of 0.024 $Wm^{-2}ppbv^{-1}$. In another study, Ye *et al*. [34], studied the GWPs of $CH_3CH_2OCH_2CH_2Cl$(CEE) for the $^{\bullet}$OH and Cl-atom initiated reaction. For the time horizons of 20, 100, and 500 years, they have found GWPs of 0.34, 0.10, and 0.03, respectively. These values are comparable to those reported by Dalmasso *et al*. [34], which were estimated as 0.34 and 0.10 over time horizons of 20, and 100 years, respectively. In addition, Ye *et al*. [34] calculated the GWPs of $CH_3OCH_2CH_2Cl$(CEME) for the reaction with $^{\bullet}$OH and Cl-atom. The estimated values are 0.69, 0.15, and 0.05, respectively, at 20, 100, and 500 years. [34]. Further, Gour *et al*. [39] determined the GWPs of CEME for the reaction with $^{\bullet}NO_3$ and 20, 100, and 500 years of time period, the estimated values are found to be 0.66, 0.19, and 0.05 respectively. Moreover, for the reaction of CH_3OCHCl_2 (DCDME) with $^{\bullet}NO_3$, Gour *et al*. [31] evaluate the GWPs at 20, 100, and 500 years and its value is found to be 0.49, 0.14, and 0.04 respectively, with RE(A_i) value of 0.12 $Wm^{-2}ppbv^{-1}$. The GWP values obtained from the studied HCEs are listed in Table 4.

Table 4: GWPs of some hydrochloroethers (HCEs) calculated for the specific time horizons

Sl No.	COMPOUNDS	GLOBAL WARMING POTENTIAL (GWP)		
		TH = 20 years	TH = 100 years	TH = 500 years
1.	CH_3OCHCl_2 (DCDME)	0.49 [31]	0.14 [31]	0.04 [31]
2	$ClCH_2CH_2OCH_2CH_2Cl$ (BCEE)	0.20 [33]	0.06 [33]	–
3	$CH_3CH_2OCH_2CH_2Cl$ (CEEE)	0.34 [34] 0.13 [35]	0.10 [34] 0.04 [35]	0.03 [34] 0.01 [35]
4	$CH_3OCH_2CH_2Cl$ (CEME)	0.69 [34] 0.66 [39]	0.15 [34] 0.19 [39]	0.05 [34] 0.05 [39]

Thus, from the overviews of the GWP values of some HCEs, it is observed that they generally have quite low GWP. Additionally, neither the stratospheric ozone nor the radiative forcing of climate change will be significantly impacted by these compounds.

3. CONCLUSION

In concisely, here the primary interest refers to the degradation of hydrochloroethers (HCEs) initiated by $^{\bullet}$OH, Cl-atoms, and $^{\bullet}NO_3$ in the atmosphere. Understanding the kinetics of the reaction of HCEs with tropospheric oxidants requires the calculation of rate constants. Based on the review of the oxidation of HCEs by oxidants, it was observed that rate constants are estimated both experimentally as well as computationally. The rate constant values of the HCEs are found to be quite comparable that are measured both experimentally and computationally. It also validates the fast reactivity of HCEs with the oxidants. Additionally, it has been divulged that studying the kinetics of a reaction is essential to figuring out the atmospheric lifetime and GWPs of compounds. The lifetimes are found to be quite short which leads to low GWP and so that during their release do not produce any long-lived hazardous compounds. Furthermore, understanding the fate of oxidation product radicals in some reported literature would be particularly instructive for comprehending the detailed mechanism and how volatile organic molecules react with oxidants in the atmosphere. Considering the aforementioned studies, HCEs might be preferable to CFCs, HFCs, and HCFCs and thought of as a better alternative.

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