**Atmospheric Oxidation of Hydrochloroethers (HCEs) initiated by •OH, Cl-atoms, and •NO3 :A Comprehensive Review**

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**Abstract:**

In this chapter, we explored the atmospheric insight of the oxidation of hydrochloroethers (HCEs) initiated by •OH, Cl-atoms, and •NO3 species and explained how they influence the environment. In the modern era, HCEs have consistently attracted researchers and are broadly employed in laboratories, and industries as an alkylating agent, protecting groups, etc. HCEs have been contemplated as the third-generation substitute for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). Their appealing qualities such as high reactivity towards tropospheric oxidants, shorter atmospheric lifetimes, zero ozone depletion potentials (ODPs), and low global warming potentials (GWPs), may give a solution to the environmental concerns. They have already been used in several countries as potential substitutes for chemicals used in laboratories, as well as cleaners, varnishes, paints, and solvents for fats and oils, as well as 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 is made up of a variety of organic compounds that are oxygenated, such as alcohols, ethers, ketones, aldehydes, esters, and others [1, 2]. These substances have been released into the troposphere from both natural and man-made sources, raising severe concerns about the increasing threats to human health [3]. The atmospheric chemistry of these 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 haze and ozone in the atmosphere relies on the processes carried out by the oxygenated compounds. One well-known example of such anthropogenic organic compounds that are also produced by the oxidation of hydrocarbons in the environment is hydrochloroethers (HCEs).

 In the modern era, HCEs have received a lot of heed. HCEs have been extensively applied in laboratories and industry as textile cleaners, solvents for fats and oils, ingredients in paints and varnishes, etc. [7-10]. Moreover, HCEs have been developed as the third-generation substitutes for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) in various uses [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, through Montreal Protocol and subsequent amendments, a global arrangement is made to prevent the depletion of the ozone layer by phasing out the production and consumption of these ozone-depleting substances (ODS) [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 horizons [16]

The degradation of HCEs in the atmosphere are undergoing by photolytic chemical reactions and interaction with atmospheric oxidants. The ether linkage (–O–) present in HCEs could cause them to become more reactive in the troposphere [17]. The chemical oxidation of HCEs is initiated by atmospheric oxidants like •OH, Cl-atoms and •NO3 [18]. It should be noted that •OH radicals react during the daytime, Cl-atoms react during the daytime in coastal and marine environments where Cl-atoms concentration is significant, while •NO3 react during the night. 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 significant harmful effect on the environment by accelerating the ozone layer depletion and increasing the global average temperature of Earth. Thus, it is crucial to investigate the degradation pathways and reaction kinetics of HCE in order to evaluate their atmospheric chemistry and comprehend how these molecules primarily contribute to air pollution in urban and rural environment. In order to comprehend the impacts of HCEs, once they were released into the atmosphere, the necessary requirement is to first understand the atmospheric lifetimes of HCEs, as well as atmospheric hazard indices such as the ozone depletion potentials (ODPs) and global warming potentials (GWPs). This 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 depicted 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. One of these, 1,1-Dichlorodimethylether (DCDME), has been utilized in the production phenalenyl-fused compounds and in the synthesis of pesticides. It has been also utilized as a model compound for anesthetics like enflurane or isoflurane [21, 22]. HCEs such CH2ClOCH2CH3 has been applied in the synthesis of lithiomethyl ethyl ether catalyzed by 4,4’-di-tert-butylbiphenyl (DTBB) and HIV-1 reverse transcriptase inhibitors [23, 24]. Bis (2-chloroethyl) ether, also known as BCEE (ClCH2CH2OCH2CH2Cl), is another well-known example of HCE, which is widely used in industrial and agricultural applications. For example, BCEE has been used as a constituent of varnishes and paints, and insecticides. It has also been used as a cleaning agent for textiles and solvent for fats and oils. The most recent application of it was considered as an intermediate in the manufacturing of a commercial fungicide [25]. Similarly, CH3CH2OCH2CH2Cl (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, CH3OCH2CH2Cl (CEME) has been employed in the synthesis of acyclic nucleosides of thieno[2,3-d] pyrimidine derivatives, while CH3OCH2Cl (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 experimental and theoretical investigations on the oxidation of HCEs by the oxidants present in the atmosphere such as •OH, Cl-atoms, and •NO3. 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, Dalmasso *et al*. [27] investigated the oxidation reaction of CH3OCHCl2 (DCDME) initiated by Cl-atom and estimated the reaction rate constant using the relative rate method. An experiment using nitrogen as the bath gas was conducted at 298 ± 2 K and atmospheric pressure. The rate constant for the reaction of CH3OCHCl2 with Cl-atom was determined to be (1.04 ± 0.30) × 10−12 cm3 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 ± 0.11) × 10−12 cm3 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. They computed the rate constant as 1.204 × 10-12 cm3 molecule-1 s-1 at 298 K using the canonical transition state theory (CTST) with tunneling correction, and this value is in good agreement with the experimentally obtained ones. Similarly, they also determined the rate constant of the CH3OCHCl2 (DCDME) oxidation process with •OH using the quantum chemical method. Using CTST, they calculated the rate constants of DCDME and estimated this value as 2.03 ×10-13 cm3 molecule -1 s-1 at 298 K [30].

The two primary mechanisms that have been taken into consideration for the oxidation reaction of DCDME by atmospheric oxidants are given by reactions (1) and (2) [29, 30], which are illustrated below.

CH3OCHCl2 + X → CH3OC•Cl2 + HX (1)

 CH3OCHCl2 + X ­­­→ C•H2OCHCl2 + HX (2)

 Where X = •OH, Cl-atom, and •NO3

 Additionally, Mishra *et al*. [30] calculated branching ratios, which show the unique contributions made by each reaction channel to the overall rate constant. They have estimated the rate constant of the CH3OCHCl2 reaction with •OH and ascertained that the H-atom abstraction from the –CHCl2 site of CH3OCHCl2 is predominate than –CH3 site. This is validated by the percentage ratios calculations, which are obtained as 96.0% and 4.0% respectively [30]. The thermodynamic viability of the CH3OCHCl2 + Cl-atom reaction is also estimated by Mishra *et al*. [29]. They found that both reaction channels (1 and 2) were exergonic (ΔG < 0) in nature based upon free energy estimations, for which the reaction enthalpies (ΔrH°) were determined as -8.65 and -5.22 kcal mol-1, respectively. It clearly suggests that reaction (1) is thermodynamically preferable to reaction (2) [29]. Similarly, Gour *et al*. [31] using a quantum chemical method explored the oxidation reaction of CH3OCHCl2 initiated by •NO3. The estimated rate constant of the reaction is found to be 8.15 × 10-17 cm3 molecule -1 s-1 at BHandHLYP/6-311++G(d,p) level of theory and at 298 K. Further, they also explored the fate of alkoxy radical (CH3OC•Cl2) generated from the aforementioned reaction. The degradation channels of CH3OCHCl2 by •NO3 were depicted in scheme 2 [31].



**Scheme 2:** The degradation mechanism of CH3OCHCl2 initiated by •NO3 in the troposphere [31].

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

 Dalmasso *et al*. [7] used synthetic air as the bath gas in an experiment to calculate the rate constant of the ClCH2CH2OCH2CH2Cl (BCEE) reaction with •OH at 298 ± 2 K and atmospheric pressure. n-Pentane and n-Heptane were used as reference compounds to calculate the rate constant. They have estimated the rate constant as (7.6 ± 1.9) × 10−12 cm3 molecule−1 s−1. Thereafter, Paul *et al*. [32] conducted a theoretical analysis of the same reaction. To investigate this reaction, they used the M06-2X functional with the 6-31+G(d,p) basis set. Further, the rate constant was calculated using the CTST and within the temperature range of 298-400 K. The rate constant at 298 K and 1 atm. was determined to be 6.27 × 10−12 cm3 molecule−1 s−1. This is in accordance with the experimentally determined rate constant value by Dalmasso *et al*. [7]

 Further, using the relative rate technique, Dalmasso *et al.* [33] calculated the rate constant of the Cl-atom initiated oxidation of BCEE, where they used n-pentane and n-heptane as reference compounds. The estimated rate constant value for this reaction was found to be (1.0 ± 0.3) × 10-10 cm3 molecule-1s-1 at (298 ± 2) K and 1 atm. This result agrees with the theoretically calculated value of 1.33 × 10−10 cm3 molecule-1s-1), studied by Paul *et al*. [32]. Moreover, the oxidation of BCEE with •NO3 was studied by Paul *et al*. [32] and they determined the rate constant value of 4.07 × 10−15 cm3 molecule−1 s−1 at 298 K.

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

 The oxidation reaction of CH3CH2OCH2CH2Cl (CEEE) with •OH was studied experimentally by Dalmasso *et al.* [7] utilizing the relative rate method and n-pentane and n-heptane as reference compounds. They determined the rate constant at (298 ± 2) K and atmospheric pressure and value is (8.3 ± 1.9) × 10-12 cm3 molecule-1 s-1. Further, Ye *et al*. [34] investigated the same reaction using an ab initio technique and estimated the rate constant using canonical variational transition-state dynamic calculations with the small-curvature tunneling correction. The rate constant value at 298 K is found to be 6.28 × 10-12 cm3 molecule-1 s-1, which is in agreement with the experimentally reported rate constant value. Again, Dalmasso *et al*. [33] studied the oxidation of CEEE initiated by Cl-atom and the rate constant value at (298 ± 2) K and atmospheric pressure was found as (1.7 ± 0.5) × 10-10 cm3 molecule-1 s-1. Thereafter, theoretically, Ye *et al*. [34] studied the (CEEE + Cl) reaction at 298 K and the rate constant was calculated as 8.09 × 10-11 cm3 molecule-1 s-1. Similarly, Gour *et al*. [35] investigated the •NO3 induced oxidation of CEEE using quantum chemical calculations. The rate constants were determined using the CTST for the range of temperature between 250-350 K. The estimated overall rate constant at 298 K and 1 atm. is found to be 2.78 × 10-16 cm3 molecule-1 s-1.

***2.4. Oxidation of Chloromethyl ethyl ether (CMEE)***

 In order to study the oxidation reaction of CH2ClOCH2CH3 (CMEE) with •OH and Cl-atom, Dalmasso *et al*. [36] using the *ab* initio theory, computed the vertical ionization potentials and dissociation energies of C-H bond, and the determined the reaction kinetics. At room temperature, the calculated rate constants for •OH and Cl-atom were 2.33 × 10-12 and 4.485 × 10-11 cm3 molecule-1 s-1 respectively. Thereafter, using the quantum chemical method, Paul *et al*. [37] investigated the rate constant of the •OH-initiated oxidation of CMEE. They determined the rate constant using the CTST over the 250-450 K temperature range and 1 atm. The overall rate constant value was estimated as 6.45 × 10-12 cm3 molecule-1 s-1 at 298 K. Moreover, in their study, they provided the degradation mechanism of CH2ClOCH(O•)CH3 radical in detailed, which is produced from CMEE oxidation initiated by •OH and followed by product radical oxidation with O2 and NOx [37]. It is shown in scheme 3.



**Scheme 3:** Formation of CH2ClOCH(O•)CH3 radical by the (CH2ClOCH2CH3 + •OH) degradation reaction [37].

Thereafter, the degradation of this CH2ClOCH(O•)CH3 radical in the atmosphere is also given by

Paul *et al*. [37]. The proposed reaction channels (4-6) are shown below.



From the above reaction channels, it is found from the relative energy calculations that the C–C bond breaking of the CH2ClOCH(O•)CH3 radical (reaction 5) is kinetically more dominant. This is also validated by the thermodynamic calculations with ΔrG° value of -7.71 for the reaction (5) (i.e. CH2ClOCH(O•)CH3 → CH2ClOCHO + •CH3). The change in reaction enthalpy and Gibb's free energy (in kcal mol-1) of the reaction channels (4-6) are shown in Table 1 [37].

**Table 1:** The changeinEnthalpy and Gibb’s Free energy (Unit: kcal mol-1) of the reaction channels (4-6) at M06-2X/6-311++G(d,p) and CCSD(T)//M06-2X/6-311++G(d,p) [37]

No prior investigations on the oxidation reaction of CH2ClOCH2CH3 (CMEE) with •NO3 have been found yet, to the best of our knowledge.

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

 To investigate the reaction kinetics of CH3OCH2CH2Cl (CEME) with atmospheric oxidants, McLoughlin *et al*. [38] using the relative rate method have evaluated the rate constant of •OHand Cl-atom initiated oxidation of the CH3OCH2CH2Cl molecule. They estimated the rate constants value at (300 ±3) K and values were (4.92 ±1.09) × 10-12 , and (1.44 ± 0.5) × 10-10 cm3 molecule-1 s-1 for the oxidation reaction with •OHand Cl-atom, respectively. Further, Dalmasso *et al*. [28] applying the same relative rate technique, calculated the rate constant of CEME reaction with Cl-atom and obtained the rate constant value of (1.14 ± 0.10) × 10-10 cm3 molecule-1 s-1 at (296 ± 2) K. Additionally, Dalmasso *et al*. [7] also investigated the kinetics of the •OH initiated reaction with the same compound and estimated the rate constant value of (5.2 ± 1.2) × 10-12 cm3 molecule-1 s-1 at (298 ± 2) K. From this investigations, it is observed that the rate constant values of the oxidation reaction carried out by •OHand Cl-atom are in agreement with each other. A quantum chemical investigation on the oxidation of this compound with •OH and Cl-atom has been performed by Ye *et al*. [34]. Using the quantum chemical approach and canonical variational transition-state dynamic calculations with the small-curvature tunneling correction, they determined the rate constant of the reactions. At 298 K, the rate constant of the •OH and Cl-atom initiated was determined to be 4.01 × 10−12 cm3 molecule-1 s-1 and 6.13 × 10−11 cm3 molecule-1 s-1, respectively. Recently, Gour *et al*. [39] performed the gas-phase reaction of CH3OCH2CH2Cl with •NO3 using quantum chemical techniques. They computed rate constants using CTST with the refined energy at CCSD(T)/6-311++G(d,p) method. The estimated total rate constant of this reaction is found to be 4.88 × 10-17 cm3 molecule-1 s-1 at 298 K and 1 atm. To the best of our studies, no experimental and theoretical investigation on the •NO3.initiated oxidation of CEME has been found.

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

 The reaction kinetics of CH3OCH2Cl (CMME) initiated by •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 CH3OCH2Cl, at the G3B3 level of theory. The computed rate constant values of the •OH and Cl-atom initiated reaction were 1.27 × 10-12 and 2.91×10-11 cm3 molecule-1 s-1 respectively. Further, reaction rate of the (CH3OCH2Cl + Cl) reaction was examined by Jenkin *et al*. [40], and it was reported as (2.9 **±** 0.2) ×10-11 cm3 molecule-1 s-1, which 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 CH3OCH2Cl with •NO3.

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

 Dalmasso *et al*. [36] studied the kinetics of this HCE for reacting with •OH and Cl-atom. The reaction CH3OCCl3 (TCDME) + •OH/Cl-atom was investigated using the same method as discussed above for the compound CMME. The reported rate constants for the •OH and Cl-atom initiated reaction were 2.86 × 10-13 and 2.86 × 10-12 cm3 molecule-1 s-1 respectively. Moreover, there is not any study in literature on the oxidation reaction of TCDME with •NO3.

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

 The oxidation of the CH3OCH2CHCl2 (DCEME) with •OH and Cl-atom was studied by McLoughlin *et al*. [38] with the help of the relative rate technique. The rate constant of the oxidation reaction of DCEME with •OH was estimated as (2.37 ±0.50) ×10-12 cm3 molecule-1 s-1. The rate constant for the Cl-atom-initiated reaction with DCEME was calculated as (4.4 ±1.6) × 10-11 cm3 molecule-1 *s*-1. No further information on the kinetic studies with the •NO3 of this compound is available in literature.

As discussed above, the estimated rate constant values of the oxidation reactions of various HCEs with •OH, Cl-atom, and •NO3 given in literature to date are listed in Table 2. From these kinetic studies, we can ascertain that HCEs are quite reactive with tropospheric oxidants.

**Table 2:** Computedrate constants values for the oxidation of available HCEs in literature initiated by •OH, Cl-atom, and •NO3 (in the temperature range of 296-298K) [27-40]

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sl No.** | **HCEs** | **kOH** | **kCl** |  **kNO3**  |
| **1** |  CH3OCHCl2 (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** | ClCH2CH2OCH2CH2Cl (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** | CH3CH2OCH2CH2Cl (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** | CH2ClOCH2CH3(CMEE) | 2.33 × 10-12 [36]6.45 × 10-12  [37] | 4.485 × 10-11  [36] | ─ |
| **5** | CH3OCH2CH2Cl (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** | CH3OCH2Cl (CMME) | 1.27 × 10-12  [36] | 2.91 × 10-11  [36](2.9 **±** 0.2) ×10-11 [40] |  ─ |
| **7** | CH3OCCl3(TCDME) | 2.86 × 10-13  [36] | 2.86 × 10-12 [36] |  ─ |
| **8** | CH3OCH2CHCl2 (DCEME) | (2.37±0.50)×10-12 [38] | (4.4 ±1.6) × 10-11 [38] |  ─ |
| **9** | CH3OCHClCH3(CEME) | 10.1× 10-12  [36] | 24.91× 10-11  [36] |  ─ |

* + 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 the removal of it from the atmosphere through the 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]

**τX= (kTotal × [X])-1**

Where, x = atmospheric oxidants like •OH radical, Cl-atom, and •NO3.

 kTotal= total/overall 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 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 HCEs using the above equation are provided in Table 3.

**Table 3:** Atmospheric lifetime values of some HCEs with respect to the oxidants viz. •OH, Cl-atom, and •NO3

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sl No. | HCEs | τOH | τCl | τNO3 |
| 1 | CH3OCHCl2 (DCDME) | 18.1 days [36] | 1102.3 days [36] | 0.78 years (284.8 days) [31] |
| 2 | ClCH2CH2OCH2CH2Cl (BCEE) | 0.9 days [32] | 87 days [32] | 4.9 days [32] |
| 3 | CH3CH2OCH2CH2Cl (CEEE) | 19 hours (0.79 days) [34] | 142 days [34] | 0.23 years (83.95 days) [35] |
| 4 | CH2ClOCH2CH3 (CMEE) | 1.79 days [37]5.0 days [36] |  25.8 days [36] | \_ |
| 5 | CH3OCH2CH2Cl (CEME) | 39 hours(1.625 days) [34] | 188 days [34] | 1.3 years(474.8 days) [39] |
| 6 | CH3OCH2Cl (CMME) | 9.1 days [36] | 39.9 days [36] | \_ |
| 7 | CH3OCCl3 (TCDME) | 40.5 days [36] | 404.7 days [36] | \_ |
| 8 | CH3OCH2CHCl2 (DCEME) | \_ | 26.3 days [27] | \_ |
| 9 | CH3OCHClCH3 (CEME) | 1.1 days [36] | 4.6 days [36] | \_ |

 For example, Dalmasso *et al*. [7] calculated the lifetime of the BCEE reaction with •OH, Cl-atom applying the average concentrations of •OH [=2 × 106 radicals cm-3] and Cl-atom [= 1 × 103 atoms cm-3 [42, 43]. The estimated lifetimes of this compound were found to be 18 hours (0.75 days) and 116 days for •OH and Cl-atom reactions, respectively. Thereafter, Paul *et al*. [32] calculated the lifetime for the same compound with •OH radical, Cl-atom, and •NO3 and they have determined the lifetimes of 0.9 days, 87 days, and 4.9 days respectively, where average concentrations of oxidants [•OH], [Cl] and [•NO3] were taken as 2.0 × 106 molecule cm−3, 1.0 × 103 molecule cm−3, and 5.70 × 108 molecule cm−3, respectively [42, 44-45]. The atmospheric lifetime of CH2ClOCH2CH3 (CMEE)was also computed by Paul *et al.* [37] using the quantum chemical method and taking the •OH concentration of 1.0 × 106 molecules per cm3 [46]. Considering the rate constant kOH (=6.45 × 10-12 cm3 molecule-1 s-1), the estimated lifetime is found to be 1.79 days. Further, Dalmasso *et al*. [36] estimated the lifetime value of CMEE as 5.0 days using the concentration of •OH as ([OH] = 1 × 106 radicals cm-3) and the total rate constant value of 2.33 × 10-12 cm3 molecule-1 s-1. This estimated value is slightly higher than that estimated value given by Paul *et al*. [37]. Additionally, Dalmasso *et al*. [36] have estimated the lifetime value for Cl-atom initiated oxidation of CMEE, using the overall rate constant of 4.485 × 10-11 cm3 molecule-1 s-1 [36] and average concentration of Cl-atom as ([Cl] = 1 × 104 atoms cm-3) and the lifetime of CMEE was found to be 25.8 days. As there is no kinetics study of the •NO3 initiated oxidation of CMEE in the literature, no reported lifetime value was found.

 Similarly, for CH3OCHCl2 (DCDME), Dalmasso *et al*. [36] estimated the lifetime for the •OH and Cl-atom initiated oxidation reaction. Taking overall rate constants of 0.64 × 10-12 and 0.105 × 10-11 cm3 molecule-1 s-1 and average concentration of [OH] =1 × 106 radicals cm-3, and [Cl] = 1 × 104 atoms cm-3, lifetimes were estimated as 18.1 and 1102.3 days, for •OH and Cl-atom respectively. 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]. Further Gour *et al*. [31, taking the overall rate constant of 8.15 × 10-17 cm3 molecule-1 s-1 of (DCDME + •NO3) reaction and average concentration of •NO3 ([NO3] =5 × 108 molecule cm-3), the lifetime of DCDME 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 implies a minimal contribution to global warming. The short lifetimes of these HCEs indicate that they are quite reactive towards tropospheric oxidants. HCEs also inhibited the passage of these chemicals into the stratosphere due to their short atmospheric lifetimes and low global warming potentials (GWPs), which had a minor impact on 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.

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

 Global Warming Potential can be defined as the measure of the quantity of heat trapped by a greenhouse gas in the atmosphere relative to CO2 [47]. The expression for estimating global warming potential (GWP) given by Hodnebrog *et al*. [48] is given below.

Here, A is the instantaneous radiative efficiency (IRE) (unit: Wm-2ppb-1), and refers to lifetime.

 (H) implies the absolute global warming potential for CO2 (reference compound) for the various time horizons (H), the *AGWPi* is the absolute global warming potential for a calculated molecule. The GWP values for different time horizons obtained for HCEs are listed in Table 4.

**Table 4:** theGWPs of some HCEs calculated for the specific time horizons

|  |  |  |
| --- | --- | --- |
| Sl No. | COMPOUNDS | GLOBAL WARMING POTENTIAL (GWP) |
| **TH = 20 years** | **TH = 100 years** | **TH = 500 years** |
| 1. | CH3OCHCl2 (DCDME) | 0.49 [31] | 0.14 [31] | 0.04 [31] |
| 2 | ClCH2CH2OCH2CH2Cl (BCEE) | 0.20 [33] | 0.06 [33] | \_ |
| 3 | CH3CH2OCH2CH2Cl (CEEE) | 0.34 [34]0.13 [35] | 0.10 [34]0.04 [35] | 0.03 [34]0.01 [35] |
| 4 | CH3OCH2CH2Cl (CEME) | 0.69 [34]0.66 [39] | 0.15 [34]0.19 [39] | 0.05 [34]0.05 [39] |

 For the reaction with tropospheric oxidants, the study on the GWPs of HCEs is found very scant in the literature. A few of them have been investigated by Gour *et al*.[31],[35], [39], Dalmasso *et al*. [33] and Ye *et al*. [34]. First, Dalmasso *et al*. [33] calculated the GWPs of CH3CH2OCH2CH2Cl (CEEE) and ClCH2CH2OCH2CH2Cl (BCEE) for the reaction with Cl-atoms. The radiative efficiency (RE) of these compounds are found to be 0.078 and 0.062 Wm-2ppbv-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] computed the GWPs of CEEE for the reaction with •NO3. The GWPs for the time period of 20, 100, and 500 years are 0.13, 0.04, and 0.01, respectively with a RE (Ai) value of 0.024 Wm-2ppbv-1. In another investigation, Ye *et al*. [34], analyzed the GWPs of CH3CH2OCH2CH2Cl (CEEE) oxidation reaction with •OH and Cl-atom. They have found GWPs of 0.34, 0.10, and 0.03 for the time horizons of 20, 100, and 500 years, respectively. These values are comparable to those reported by Dalmasso *et al*. [34]. In addition, Ye *et al*. [34] calculated the GWPs of CH3OCH2CH2Cl (CEME) oxidation with •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 •NO3 and 20, 100, and 500 years of time period, the estimated values are reported as 0.66, 0.19, and 0.05 respectively. Moreover, for the reaction of CH3OCHCl2 (DCDME) with •NO3, 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(Ai) value of 0.12 Wm-2ppbv-1.

 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 •OH, Cl-atoms, and •NO3 initiated degradation of hydrochloroethers (HCEs) in the atmosphere. Understanding the kinetics of the HCEs reactions with tropospheric oxidants requires the determination of rate constants. Based on the review of the oxidation of HCEs by different 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 when it is 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 the 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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