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Atmospheric Chemistry of Alternative Fuels and Alternative Chlorofluorocarbons

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1. Introduction

A central issue of atmospheric chemistry is to understand the impact that anthropogenic substances have on changes in global climate. To achieve this goal, one must understand that there is an intimate connection between the chemistry and physics in the atmosphere that influences these changes. For example, the introduction of chemical species with absorption features in the atmospheric window results in global warming. Issues of chemistry in the atmosphere involve chemical properties of anthropogenic species, in this case, quantum mechanical absorption properties of the specific molecule, and in this particular case, how they affect global warming. However, to fully access the impact of species introduced into the atmosphere requires that there is an understanding of how that species might transform in the atmosphere. New species resulting from the atmospheric degradation of anthropogenic species must also be considered in the assessment of chemical impact. The type of chemistry a molecule participates in and the degree to which it participates are influenced by how long-lived or short-lived these species are in the atmosphere. Removal of anthropogenic species and understanding the unique atmospheric oxidation mechanisms associated with them are central to assessing the atmospheric impact.

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The real drive to understand the impact that the chemistry of anthropogenetic sources has on the chemistry in the environment has been motivated by the concern that our overuse of chlorofluorocarbons (CFCs) has resulted in a higher incidence of skin cancer. This concern sparked in the 1970s led to limitations in the use of these materials, but the environmental concerns languished. The appearance of the ozone hole revitalized the discussion.[1] The chlorofluorocarbon (CFC) example became a classic example of how man-made materials and our widespread use of them can dramatically affect global chemical processes for a very long time. The Montreal Protocol signed in 1987 called for a worldwide reduction of CFCs with their ultimate complete phaseout. Under the Clean Air Act Amendments of 1990, the U.S. Environmental Protection Agency (EPA) proposed regulations that accelerated the domestic phaseout of CFCs. This has also created a need for new materials and viable alternatives as suitable replacements for those CFCs phased-out. Concern over the environmental impact of these replacement materials inspired research into the atmospheric chemistry of them, in particular, the question of whether the atmospheric oxidation chemistry led to byproducts posing perhaps more potential hazard

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than the CFCs or the original replacement material. Thus, the atmospheric degradation chemistry of new materials became an important piece of information critical to the environmental assessment. One of the recent issues our laboratory has been interested in is understanding the connection between the chemical structure of anthropogenic sources and their unique atmospheric oxidation and removal mechanisms. Understanding this relationship is key to better selection and design of atmospherically acceptable materials. We selected the topic of alternative fuels and alternative refrigerants as an opportunity to highlight some special cases in which this relationship provides unique chemical examples.

Many of the atmospheric chemistry concerns of the CFC replacements are also similar to those for alternative fuels. The Clean Air Act mandated reformulated gasoline provisions as a means of improving air quality by air pollution reduction. Alternative fuels show great promise toward achieving these goals. Issues of environmental acceptability of the fuel and combustion byproducts that may be emitted from the tailpipe of vehicles are current concerns. The present review examines the question of atmospheric acceptability of alternative fuels and alternative CFC materials. This is done from the perspective of understanding the atmospheric degradation process of the materials. Recent advances in the search for cleaner fuels and ozone friendly working fuels will be discussed. The review focuses on the chemistry of these materials and the roles that species resulting from the atmospheric degradation play on the formation and destruction of ozone.

2. Some Issues To Consider for the Selection of Atmospherically Acceptable Materials

With regard to whether new materials are environmentally acceptable, a few critical questions should be addressed. One, are the new materials short-lived or long-lived? One goal is to produce materials that have a short residence time in the atmosphere, and this in turn would reduce the degree of chemistry that takes place. Second, does the material once released in the atmosphere destroy ozone in the stratosphere, or does it contribute to ozone formation in the troposphere? These are a few of the key issues that are considered when the environmental acceptability of new alternative CFCs and alternative fuels are evaluated. To help us understand these issues, in this section, some basic terminology and concepts that have evolved in the recent literature are reviewed. This will set the context for the review of the chemistry of alternative fuels and CFCs.

2.1. Atmospheric Lifetime

The atmospheric lifetime of a species influences the type of chemistry the molecule participates in and the degree to which it participates. Short-lived species are dominated by tropospheric processes such as reactions with hydroxyl radical and visible photolysis. Long-lived species may participate to a greater extent in stratospheric processes such as UV photolysis and reactions with $O(^1D)$ and atomic chlorine.

The atmospheric concentration of a gas is generally defined as the ratio of its total atmospheric burden to its integrated global loss rate after the gas is emitted into the atmosphere. The lifetime is defined as the time the global amount of gas takes to decay by $1/e$ or 36.8% of its original concentration. The lifetime must take into account all of the processes that contribute to removal of a gas from the atmosphere, including photochemical losses, heterogeneous removal processes (loss into clouds or rain drops), and permanent uptake by land or ocean.[2,3]

Atmospheric lifetimes for gases of interest range from a few seconds to thousands of years. Lifetimes for the CFCs are quite long, ranging from 50 to 100 years. These chemicals are essentially unreactive in the troposphere but are photolytically dissociated in the stratosphere. The chlorine released in these photolysis reactions participates in catalytic ozone destruction cycles. Thus, a molecule's lifetime as we will see is an important parameter influencing ozone depletion properties of molecules. Lifetimes of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are much shorter than lifetimes for CFCs because of their ability to participate in hydrogen abstraction reactions in the troposphere. The atmospheric lifetime of CF_3I is short because of the incorporation of a weak C−I bond and the resulting photolysis at visible wavelengths. Quick estimates for atmospheric lifetimes of species can be generated from kinetic arguments. Consider a hypothetical species whose dominant loss mechanism comes from photolysis reactions. The expression for the atmospheric lifetime, τ, is

$$\tau = [\text{gas}]/\text{loss rate} \tag{1}$$

The loss is described by a first-order decay for which an expression for the loss rate is given by

$$\text{loss rate} = \mathrm{d}[\text{gas}]/\mathrm{d}t = j[\text{gas}] \tag{2}$$

where j is the photolysis rate constant (units of s^{-1}). The lifetime of the gas is thus $\tau = 1/j$ in the appropriate units of seconds.

As a second example, consider the bimolecular reaction of hydroxyl radical with any hydrogen-containing species whose reactivity in the atmosphere is due solely to reaction with OH. In this reaction the atmospheric concentration of hydroxyl radicals can be considered to be in excess and a pseudo-first-order expression for the loss rate can be used. The resulting atmospheric lifetime[4] is given by τ (seconds) $= 1/k[\text{OH}]$, where k is the bimolecular rate constant in units of cm^3 moelcule^{-1} s $^{-1}$ and [OH] is in units of molecules cm^{-3}.

A common practice for more accurately evaluating atmospheric lifetimes of gases (reacting primarily with OH) is to scale the lifetime of a particular species, x, relative to methyl chloroform such that

$$\tau_x/\tau_{CH_3CCl_3} = k_{CH_3CCl_3}/k_x \tag{3}$$

The methyl chloroform−hydroxyl radical rate expression is $1.8 \times 10^{-12}\ e^{-1500/T}$, which results in a lifetime of ~5.7 years based solely on reaction with OH. The total atmospheric lifetime of methyl chloroform is estimated to be 4.8 years from the work of Prinn et al. based on observations of methyl chloroform and evaluation of its budget.[5−7]

A third approach to lifetime determinations can be made through the use of global atmospheric chemical transport models that represent all of the known dynamic and chemical processes. Different model classifications include zero-dimensional box models, which represent species concentrations as a function of only time; one-dimensional (1D) models simulate species concentrations as a function of altitude; 2D and ultimately 3D models incorporate altitude, latitude, and longitude.

2.2. Ozone Depletion and Formation

Increased understanding of the depletion of stratospheric ozone has led to the need for simple measures for comparing the impact of different compounds on ozone that can be used as scientific guides to developing regulatory guides and public policy.[2] Wuebbles suggested the use of the “ozone depletion potential” (ODP) as a simple scale for quantifying the effects of various compounds upon the ozone layer.[2,8,9] The ODP concept has proven to be a useful index of the effects on ozone from CFCs, halons, and their replacements. The concept of ODPs provides a relative cumulative measure of the expected effects on ozone of the emissions of a gas relative to CFC-112. The ODP of a gas is defined as the change in total ozone per unit mass emission of CFC-11. As a relative measure, ODPs are subject to fewer uncertainties than estimates of the absolute percentage of ozone depletion caused by different gases.[2]

ODPs are currently determined by two different means: calculations from two- and three-dimensional models of the global atmosphere and semiempirical approaches such as that developed by Solomon et al.[9] The numerical models attempt to account for all of the known chemical and physical processes affecting chemical species in the troposphere and stratosphere. Semiempirical methods rely on the postulate that local ozone destruction is determined mainly by the release of chlorine into the stratosphere. The semiempirical treatment for determining ozone depletion potentials as put forth by Solomon et al.[9] relies on two factors: the stratospheric chemistry of the halocarbon and its tropospheric removal.

Tropospheric removal is the primary factor in determining the chlorine loading potential (CLP), which indicates the fraction of surface emission of chlorine delivered to the stratosphere and the time scale over which the compound remains present in the atmosphere. The CLP is defined by

$$\mathrm{CLP} = \tau_x/\tau_{\mathrm{CFC-11}} M_{\mathrm{CFC-11}}/M_x n_x/3 \tag{4}$$

where τ_x and $\tau_{\mathrm{CFC-11}}$ represent the lifetimes of compound x and of CFC-11, M represents the molecular weight of each species, and n_x denotes the number of chlorine atoms in compound x. The CLP is a relative measure of the theoretical maximum effectiveness a molecule has in delivering chlorine to the stratosphere.

The second factor important in stratospheric ozone depletion, the fractional chlorine release, attempts to quantitate the effectiveness a molecule has at releasing chlorine radicals once the molecule reaches the stratosphere, divided by its value at entry into the stratosphere. The fractional chlorine release ($\mathrm{FC}_{\mathrm{release}}$) factor is defined as the difference between the mixing ratio upon entry into the stratosphere and its value at any point within the stratosphere, divided by its value at entry into the stratosphere.

$$\mathrm{FC}_{\mathrm{release}} = \frac{\mu_{\mathrm{entry}} - \mu_{(\theta,z)}}{\mu_{\mathrm{entry}}} \tag{5}$$

If we multiply the above CLP by the fraction of chlorine molecules released (termed $\mathrm{FC}_{\mathrm{release}}$), then we obtain an estimate of how much active chlorine each compound contributes to ozone loss. In regions of rapid chlorine-catalyzed destruction of ozone, the ODP will be proportional to the mixing ratio of active chlorine released by a particular compound to that released by CFC-11.

$$\mathrm{ODP} = \mathrm{FC}_{\mathrm{release}\ x}/\mathrm{FC}_{\mathrm{release\ CFC-11}}\mathrm{CLP} \tag{6}$$

The actual release of chlorine is a function of the chemical properties of the reference species and the resulting degradation chemistry.[9] As an example, as mentioned above, not all forms of chlorine are readily available to interact with ozone. HCl, HOCl, and $\mathrm{ClONO_2}$ do not interact with ozone and are thus inactive forms of chlorine or reservoir species.[10] The analogous treatment for bromine systems includes a 40% enhancement factor to account for the fact that bromine is more efficient than chlorine at destroying ozone and a 22−84% factor representing the fraction of total observed ozone loss that takes place in the polar lower stratosphere.[9]

Just as atmospheric species in the stratosphere have ODPs, species in the troposphere can have ozone formation potentials.[11,12] Generally, tropospheric concentrations of ozone are typically small, on the order of a few tens of parts per billion, as compared to stratospheric concentrations, which reach mixing ratios of 10 parts per million. These small levels of ozone pose a serious health threat for many people. It is important to know if species have ozone formation properties. Thus, a particular species in the atmosphere has associated with it a unique atmospheric oxidation mechanism and thus a unique ability to form tropospheric ozone. The relative ozone-forming potentials of individual volatile organic compounds (VOCs) can differ by more than an order of magnitude from one compound to another. One scale used as a measure of ozone formation is the maximum incremental reactivity (MIR) scale. MIRs for individual hydrocarbons are calculated in 10-h box model simulations and are defined as the maximum sensitivity of the peak ozone concentration $[\mathrm{O_3}]$ to a small increase in the initial conditions and emissions of a certain compound, E.[11,12]

$$\mathrm{MIR} = \mathrm{d}[\mathrm{O_3}]/\mathrm{d}E \quad \text{(max for all hydrocarbon/NO}_x\text{ ratios)} \tag{7}$$

The MIRs are simulated using a certain ratio of hydrocarbon to NO_x. The specific ratio is chosen so that the maximum sensitivity of the hydrocarbon with respect to change in ozone concentration is realized. Hydrocarbon/NO_x ratios are typically low to represent urban environments.

The MIR scale can be used to predict the effect a fuel has on ozone formation by noting each component in the emission and multiplying each individual MIR with the mass fraction in the emission. The summation is thus the net reactivity (NR) (sometimes standard reactivity, SR) for the particular fuel.

$$\mathrm{NR} = \sum_{i=1}^{n} f_i \,\mathrm{MIR}_i \tag{8}$$

The NR of a particular alternative fuel is scaled to the NR of standard gasoline to obtain the reactivity adjustment factor (RAF).[13]

$$\mathrm{RAF} = \frac{\sum_{i=1}^{n} f_i \,\mathrm{MIR}_i}{\sum_{j=1}^{m} f_j \,\mathrm{MIR}_j} \tag{9}$$

The above measurement scenarios thus allow for the estimation of the ozone-forming properties of fuels.[12]

3. Atmospheric Chemistry of Alternative Fuels

At the present time, fuels derived from petroleum supply virtually all of the world's transportation needs. Petroleum products have become popular because of their extremely high energy densities and their ease of handling. The combustion of petroleum-based fuels leads to the formation of particulates (soot), NO_x, SO_x, ozone, and, ultimately, air pollution as described in the preceding section. The National Ambient Air Quality Standard (NAAQS) for ozone allows no more than one exceedance per year (on average over a three-year period) of a daily maximum 1-h average ozone concentration of 0.12 ppm by volume.[11] There is the potential that even with mandated vehicle tailpipe emission regulations several urban areas will remain out of compliance with the NAAQS for ozone well into the next century. In 1990 the Clean Air Act mandated reformulated gasoline programs. The oxygenated fuels program requires the use of fuels containing 2.7% oxygen by weight in the wintertime to reduce CO emissions while requiring that fuels contain 2.0% oxygen in summer to reduce ozone formation.[14,15]

The effects of oxygenated fuels on CO concentrations are small, however. Studies have shown wintertime reductions ranging from 0 to 10%. In addition, evidence indicates that the use of these fuels may lead to increased ambient levels of other air pollutants, specifically aldehydes and peroxyacetyl nitrates.[14,16−19]

The use of alternative fuels has become an issue in air pollution reduction programs. Because vehicles designed to use alternative fuels have not been optimized and tested, there is continuing research conducted to obtain emission data. For alternative fuels to be candidates to replace petroleum-based fuels, it must be demonstrated that their impact on air quality will show characteristics that will improve air quality.[20] Much research is devoted to assessing the economic and environmental impact that would result from the use of an alternative fuel. Currently, the leading contenders include methanol, ethanol, compressed natural gas (CNG), liquid petroleum gas (LPG), and dimethyl ether. Although the chemistry of the fuel itself is an important consideration in these applications, the combustion/emission products are dominant factors affecting ozone formation in the troposphere. Thus, we will highlight efforts to determine combustion products in addition to atmospheric oxidation products for some of the more popular alternative fuels. Then we will discuss how this product analysis helps to address issues concerning the environmental acceptability of the fuel. The possibility of direct emission of fuel during handling is the motivation for considering the atmospheric degradation of the unburnt fuel. This is also examined in this review.

3.1. Methanol

The use of methanol in diesel engines significantly reduces particulate emissions; therefore, the engine can be modified to reduce NO_x emissions without producing excessive particulate emissions. Because methanol has a very low cetane number, it is not well suited for combustion in diesel engines. Methanol has a high octane number and is more suited for use in spark ignition engines. The cetane number is a measure of the autoignition properties of a fuel. The cetane number is formally defined as the percentage by volume of cetane ($C_{15}H_{34}$) in a mixture of liquid methylnaphthalene that gives the same ignition lag as the fuel being tested. This number is useful for describing diesel fuel substitutes because diesel engines utilize compression ignition rather than spark ignition. The octane number is used to measure the antiknock properties of a fuel.[21−24]

Methanol can be produced from coal, natural gas, and biomass burning. Methanol is a very volatile fuel, which has been used in race cars for many years. Automobile engines can be converted to run on methanol as a fuel or as a possible fuel extender either through using it neat or through its use as a blending agent with conventional fuels. M85, for example, is a blend containing 85% methanol to 15% conventional gasoline. When methanol is produced from biomass burning, it results in no net production of CO_2 because the CO_2 released was recently taken from the atmosphere during photosynthesis. Consumption of methanol produced from natural gas results in a net production of CO_2, whereas burning methanol as derived from coal processes results in twice the CO_2 emission as compared to gasoline fueled processes.[25]

The pyrolysis of methanol has been studied by many investigators.[26−32] Norton and Dryer reviewed the relevant literature and suggested a single kinetic mechanism for the pyrolysis of methanol. The modeling results were compared against data from static, flow, and shock tube reactors. Temperatures ranging from 973 to 2000 K and pressures of 0.3−1 atm were covered. The results are summarized as follows:[32]

1. Methanol pyrolysis is governed by a simple straight-chain mechanism.
2. Products include formaldehyde, CO, H_2, and CH_4 along with traces of C_2H_4 and C_2H_6.
3. The initiation step is the conversion of methanol to CH_3 and OH radicals.
4. Methane is produced from CH_3 radical attack on CH_2O, H_2, and CH_3OH.
5. Ethane and ethene are produced from methyl radical recombinations.

The combustion of methanol under pyrolysis conditions as well as with various concentrations of O_2 has recently been investigated by Taylor et al.,[20] who used a fused silica flow reactor coupled to a GC-MS instrument to monitor combustion products as a function of the fuel-to-oxygen ratio and exposure temperature. In the presence of oxygen, analysis of combustion effluent showed methanol to undergo predominantly dehydrogenation to form formaldehyde at temperatures <800 °C. In addition, ethane was formed from the recombination of methyl radicals. Formaldehyde accounted for >75% of the degradation products. At temperatures >800 °C no organic products were observed.

Norton et al.[33] developed a comprehensive mechanism for the combustion of methanol. Methanol oxidation was found to be highly sensitive to the kinetics of the hydroperoxyl, HO_2, radical through a chain-branching reaction sequence involving hydrogen peroxide at low temperatures and a chain-terminating path at high temperatures. The sensitivity persists at high temperatures due to the fast rate of reaction 10 compared to that of reaction 11.

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \qquad (10)$$

$$CH_2OH + M \rightarrow CH_2O + H + M \qquad (11)$$

The branching ratio of reactions 12 and 13 was found to be a more important parameter under the higher temperature conditions.[33]

$$CH_3OH + OH \rightarrow CH_2OH + H_2O \qquad (12)$$

$$CH_3OH + OH \rightarrow CH_3O + H_2O \qquad (13)$$

Under atmospheric conditions, reaction 12 accounts for ~85% of the overall reaction at 298 K (Figure 1). Both CH_3O and CH_2OH react with molecular oxygen to yield formaldehyde and HO_2. The atmospheric lifetime of methanol is on the order of 13 days.[34]

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \qquad (14)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (15)$$

The HO_2 formed in reactions 14 and 15 can react with NO to form NO_2 and ultimately ozone. Both atmospheric oxidation and combustion lead to the production of formaldehyde, which is very effective at producing tropospheric ozone.

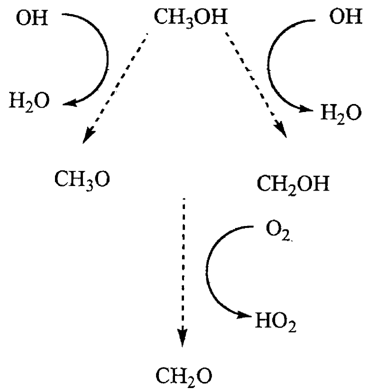

Figure 1. Atmospheric oxidation mechanism for methanol illustrating the ultimate degradation into formaldehyde.

3.2. Ethanol

Ethanol is currently used as a fuel additive and can be produced from a number of renewable resources such as corn, sugar, wood, and grain crops. Ethanol is analogous to methanol in that it can be used in blends with conventional gasoline. E50, for example, contains equal parts of ethanol to gasoline. Ethanol is nontoxic and has a higher energy density than methanol.

The gas phase oxidation of ethanol has been the subject of numerous studies. Experimental data have been presented from diffusion flames,[35−37] static reactors,[38−43] shock tubes,[43−45] and flow reactors.[46,47]

Ethanol decomposes via three mechanistic pathways: dehydrogenation to acetylaldehyde, dehydration to ethene, and decomposition to methane and formaldehyde. These three pathways involve the three isomeric forms of the C_2H_5O radical.[36,39,41]

$$CH_3CH_2OH + X \rightarrow CH_2CH_2OH\ (+M) \rightarrow C_2H_4 + OH \qquad (16)$$

$$CH_3CH_2OH + X \rightarrow CH_3CHOH\ (+M,O_2) \rightarrow CH_3CHO + (H,\ HO_2) \qquad (17)$$

$$CH_3CH_2OH + X \rightarrow CH_3CH_2O\ (+M) \rightarrow CH_3 + CH_2O \qquad (18)$$

where X represents an agent capable of initiating hydrogen abstraction reactions. Fundamental kinetic studies of the reactions of CH_3CH_2OH with OH,[48,49] O,[50−53] H,[54] and CH_3[55,56] radicals have shown that abstraction occurs at all three of the possible reaction sites, yielding all three of the C_2H_5O isomers. The models of Borisov and Bhaskaran[43] included ethanol dehydration via the reaction, as suggested by Aders and Wagner.[54]

$$CH_3CH_2OH + H \rightarrow C_2H_5 + H_2O \qquad (19)$$

The pathway has been discounted on the basis of the evidence that the analogous route in methanol has been shown to be negligible.[35,57] The CH_3CHOH radical is the dominant product at low temperatures,[48,50,54−56] but evidence suggests that at higher temperatures the reaction favors the formation of CH_3CH_2O and CH_2CH_2OH radical.[47,51−53] Static reactor studies conducted between room temperature and 900 K found significantly more acetylaldehyde than ethene, thus suggesting that the formation of the CH_3CHOH radical dominates.[38,40,42] Flow reactor studies done at higher temperatures of 100−1250 K found acetylaldehyde and ethane in roughly equivalent ratios.[46,47] High-temperature diffusion flame studies find ethene to be more abundant by a factor of 3, suggesting the dominance of CH_2CH_2OH radical formation.[36] Initiation reactions with OH and H are responsible for a majority of the fuel decay. Norton et al.[35] modeled the oxidation of ethanol and found that the following branching ratios produced the best match with experimental results at 1100 K.

$$CH_3CH_2OH + (OH/H) \rightarrow C_2H_4OH\ (30\%) + CH_3CHOH\ (50\%) + CH_3CH_2O\ (20\%) + H_2/H_2O$$

These results agreed with the results of Tully and Hess for intermediate temperature conditions.[58,59] Reaction with OH was found to be dominant. Major products formed include acetylaldehyde, ethene, methane, ethane, formaldehyde, and carbon monoxide. Acetylaldehyde is an initial product of the CH_3CHOH forming pathway but is quickly reacted away to products such as CO, CH_4, C_2H_6, and CH_2O.

The dominant source of C_2H_4 is from the C_2H_4OH formation channel and subsequent dissociation to C_2H_4 and OH. The mechanism of ethene formation via decomposition of the CH_2CH_2OH radical was proposed by various investigators[35,37,41,44,47] and verified by Tulley et al.[58,59] Freeman[39] gave evidence for a unimolecular mechanism of C_2H_4 formation from CH_3CH_2OH in static reactor experiments at 800 K.

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \qquad (20)$$

$$CH_3CH_2OH \rightarrow C_2H_5 + OH \qquad (21)$$

$$CH_3CH_2OH \rightarrow CH_3 + CH_2OH \qquad (22)$$

RRKM results for various possible unimolecular chain initiation steps show the rates of these reactions to be an order of magnitude slower than the dominant initiation step, even at higher temperatures of 1100 K. Furthermore, these unimolecular decomposition reactions are expected to be slower under flow reactor conditions than the $CH_3CH_2OH \rightarrow X$ abstraction reactions.

The pyrolysis of ethanol has been investigated in a flow reactor operating at atmospheric pressure over the temperature range 1050−1275 K. The concentration profiles of the major molecular species were obtained by MS analysis. Ethanol pyrolysis is initiated predominantly by the decomposition of ethanol via CC bond cleavage into CH_3 and CH_2OH (reaction 23). To a lesser extent reactions 24 and 25 also participate.

$$C_2H_5OH \rightarrow CH_3 + CH_2OH \qquad (23)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (24)$$

$$C_2H_5OH \rightarrow C_2H_5 + OH \qquad (25)$$

CH_2OH radical formed in reaction 23 decomposes to formaldehyde and H atoms, whereas the methyl radical reacts with ethanol, yielding methane and the C_2H_5O isomers. At higher fuel conversions ethanol consumption is mainly due to hydrogen abstraction reactions involving H and OH. Reactions involving H atoms dominate at high temperatures (1275 K), whereas at lower temperatures (1050 K) OH radical reactions dominate. The dominant products include methane, ethylene, H_2, formaldehyde, and acetaldehyde. Acetylaldehyde is produced via the decomposition of CH_3CHOH into $CH_3CHO + H$.[47,60]

In the atmosphere, the oxidation of ethanol is again mediated by hydroxyl radical (see Figure 2). The rate of this reaction has been determined to be 3.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K. Thus, an atmospheric lifetime on the order of 3−4 days can be derived. At 298 K the branching ratios are as follows.[34,58]

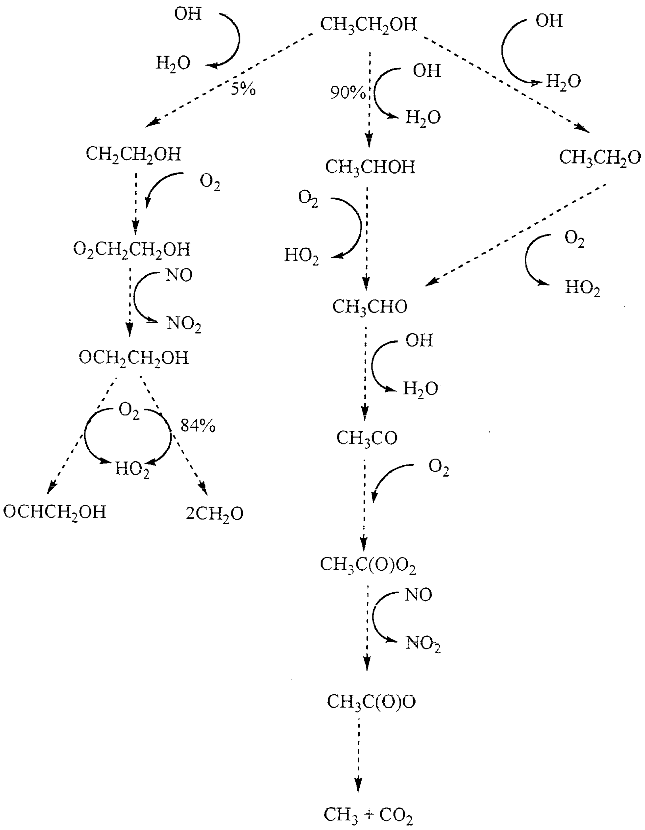

Figure 2. Atmospheric oxidation mechanism for ethanol. Ninety percent of the degradation results in the formation of the CH_3CHOH radical and ultimately acetaldehyde, $CH_3C(O)H$.

$$5\% \quad CH_3CH_2OH + OH \rightarrow CH_2CH_2OH + H_2O \qquad (26)$$

$$90\% \quad CH_3CH_2OH + OH \rightarrow CH_3CHOH + H_2O \qquad (27)$$

$$5\% \quad CH_3CH_2OH + OH \rightarrow CH_3CH_2O + H_2O \qquad (28)$$

The radical intermediates formed in reactions 27 and 28 react with molecular oxygen to form CH_3CHO (acetylaldehyde) and HO_2. The CH_3CHO radical also reacts with tropospheric hydroxyl radical with a reaction rate of 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, thus yielding an atmospheric lifetime of ~20 h.[5,34] Reaction with hydroxyl radical can be described by the following mechanism:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad (29)$$

$$CH_3CO + O_2 \rightarrow CH_3C(O)O_2 \quad (30)$$

$$CH_3C(O)O_2 + NO \rightarrow CH_3CO_2 + NO_2 \quad (31)$$

$$CH_3CO_2 \rightarrow CH_3 + CO_2 \quad (32)$$

The CH_2CH_2OH radical in reaction 26 undergoes the following oxidation mechanism:

$$CH_2CH_2OH + O_2 + M \rightarrow O_2CH_2CH_2OH \quad (33)$$

$$O_2CH_2CH_2OH + NO \rightarrow OCH_2CH_2OH + NO_2 \quad (34)$$

$$OCH_2CH_2OH + O_2 \rightarrow 2CH_2O + HO_2 \quad (35)$$

$$OCH_2CH_2OH + O_2 \rightarrow HOCH_2CHO + HO_2 \quad (36)$$

Reactions 35 and 36 are competitive channels yielding formaldehyde (84%) and $HOCH_2CHO$ (16%). Overall, the dominant products from the atmospheric oxidation of ethanol are formaldehyde (from reaction 35 and oxidation of the methyl radical formed in reaction 32) and CO_2.

3.3. Dimethyl Ether

Dimethyl ether (DME) is a colorless, nearly odorless, gas at room temperature and atmospheric pressure. DME is quite stable and reacts or decomposes only at extreme conditions. Currently, 150,000 metric tons of DME is produced per year. The DME produced is mostly used as a propellant in aerosol cans. In 1986, a patent described a method for burning a fuel composed of 94−99.9% DME in a diesel engine.[21] Early testing of DME as a diesel fuel indicated lowered NO_x emissions, essentially zero particulate matter, and lower noise without loss of efficiency. The low emissions of particulate matter are due to the absence of carbon−carbon bonds in the molecular structure. Emissions of hydrocarbons and carbon monoxide are slightly higher for DME-fueled engines unless an oxidation catalyst is used. Emission tests have demonstrated the potential for meeting California's ULEV standards for medium- and heavy-duty vehicles.[23,24]

DME has a high cetane number and is thus suited to compression ignition applications. The energy density of DME is higher than that of methanol or ethanol but is significantly lower than that of conventional diesel fuel. The use of dimethyl ether would require 1.8 times the volumetric flow of diesel fuel to obtain the same power output. In addition, the cost of production of DME is currently higher than that of conventional diesel fuel. DME is produced from methanol in dehydration plants. Thus, the cost of DME is roughly 2 times the cost of diesel fuel. Alternatively, DME can be produced directly from synthesis gas generated from various feedstocks ranging from natural gas to coal and biomass. The direct process can produce neat DME or blends of DME, water, and methanol. The synthesis of DME from synthesis gas involves the following three steps:

$$H_2O + CO \rightarrow CO_2 + H_2 \quad (37)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (38)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (39)$$

Reactions 37 and 38 represent conventional synthesis of methanol, which is thermodynamically endothermic and requires high pressure to drive the reaction. Reaction 39 is catalytically induced, its incorporation resulting in a strong synergistic effect, which dramatically increases the conversion of the synthesis gas. The combustion and emission properties of DME/methanol/water blends have been found to be similar to those of pure DME; thus, it would not be necessary to completely purify DME produced from the above synthesis. This would also result in a significant cost reduction.[21−29]

Many investigators have studied the fate of dimethyl ether in combustion applications. Studies by Askey et al.[6] and Leifer et al.[62] determined that the thermal decomposition of DME followed first-order kinetics. Benson later proposed that CO bond fission (reaction 40) initiated a chain of thermal degradation reactions.[63,64]

$$CH_3OCH_3 \rightarrow CH_3 + CH_3O \quad (40)$$

The barrier for reaction was estimated at 81.1 kcal mol^{-1}. Product studies found concentrations of CH_2O, C_2H_6, H_2, and CH_4. The formation of C_2H_6, CH_2O, and CH_4 was explained by the following mechanism:

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (41)$$

$$CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_2OCH_3 \quad (42)$$

$$CH_2OCH_3 + (M) \rightarrow CH_3 + CH_2O + (M) \quad (43)$$

The net result of eqs 42 and 43 is the conversion of DME into CH_4 and CH_2O via CO bond cleavage. Evidence was presented by Pottie et al.[65] suggesting CH bond cleavage could compete with CO bond cleavage in mercury-photosensitized decomposition experiments, that is, reaction 44.

$$CH_3OCH_3 \rightarrow CH_2OCH_3 + H \quad (44)$$

Nash et al.[66] identified 1,1 elimination of H_2 (reaction 45) and 1,2 elimination of CH_4 (reaction 46) as competitive channels using ab initio methodology.

$$CH_3OCH_3 \rightarrow CH_3OCH + H_2 \quad (45)$$

$$CH_3OCH_3 \rightarrow CH_4 + CH_2O \quad (46)$$

Thus, the formation of CH_4 and CH_2O can be explained by reactions 42 and 43 via CO bond cleavage or by reaction 46, which proceeds through a four-centered transition state. Reaction 45 is a possible explanation for the detection of hydrogen in previous experimental investigations. A recent study has

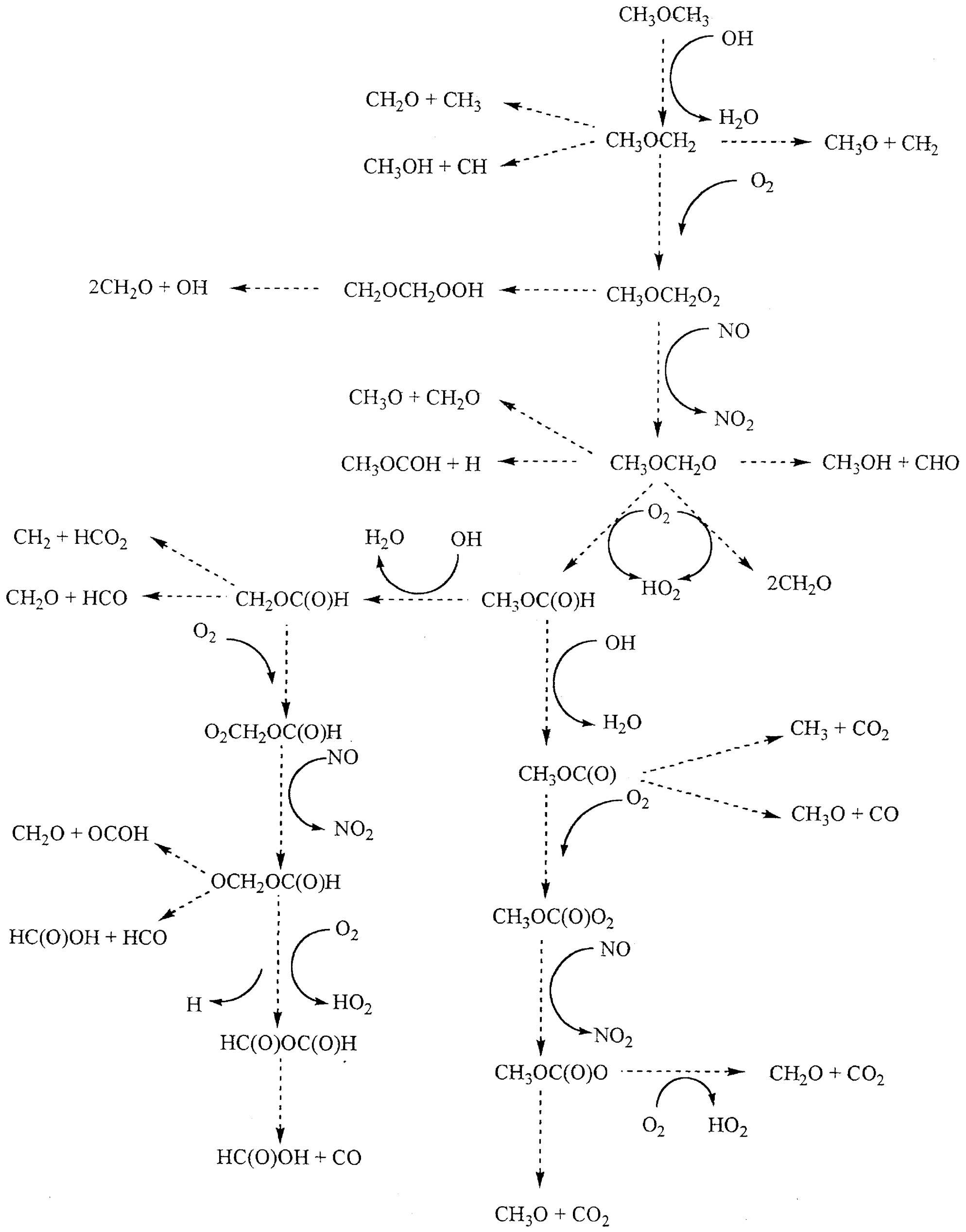

Figure 3. Atmospheric oxidation mechanism for dimethyl ether. The production of methyl formate relative to dimethyl ether loss is found to be 0.90 under atmospheric conditions.

examined the competition of CO cleavage versus hydrogen abstraction by O_2 for typical combustion conditions. This study found that the initiation of DME combustion is via hydrogen abstraction by O_2 to form the CH_3OCH_2 radical. Reactions 42 and 44 yield CH_2OCH_3 radical as a product, yet only one reaction (reaction 43) describes its fate. A thorough investigation into the possible thermal degradation channels of CH_2OCH_3 has yet to be undertaken.

The atmospheric oxidation mechanism of DME is shown in Figure 3 and has been studied by Japar et al.,[62] Jenkin et al.,[67] Wallington et al.,[68] Langer et al.,[69] and Sehested et al.[70,71] The first step involves abstraction of a hydrogen atom from dimethyl ether by tropospheric hydroxyl radical:

$$CH_3OCH_3 + OH \rightarrow CH_3OCH_2 + H_2O \tag{47}$$

The rate of this reaction has been studied by Perry et al.,[72] Trully et al.,[73] and Wallington et al.[74,75] An average activation energy of 0.7 kcal mol^{-1} has been reported. At 298 K, the rate constant for this reaction is 2.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Using experimental rate data and 2D chemical transport models, Good et al.[6] determined an atmospheric lifetime of 5.1 days for dimethyl ether reaction with hydroxyl radical. Atmospheric degradation of DME was predicted to occur solely in the troposphere.

The CH_3OCH_2 formed in reaction 47 participates in one of three channels, as proposed by Sehested et al.[71]

$$CH_2OCH_3 + M \rightarrow CH_3 + CH_2O + M \tag{43}$$

$$CH_2OCH_3 + CH_2OCH_3 \rightarrow \text{products} \tag{48}$$

$$CH_2OCH_3 + O_2 + M \rightarrow O_2CH_2OCH_3 + M \quad (49)$$

$$CH_2OCH_3 + O_2 \rightarrow O_2CH_2OCH_3^* \quad (50)$$

Reaction 43 is the aforementioned CO bond cleavage reaction, reaction 48 is the methoxymethyl radical self-reaction, and reactions 49 and 50 are O_2 addition reactions. Reaction 49 results in the formation of ground state $O_2CH_2OCH_3$ through collisional quenching with a third body, M, whereas reaction 50 results in the formation of excited state OCH_2OCH_3*. Reactions 43 and 48 were studied at low pressures in the absence of O_2. At low temperatures, reaction 43 was found to be the dominant reaction. Concentrations of CH_2OCH_3 versus time were determined by monitoring CH_2OCH_3's absorption at 300 nm. The rate constant for reaction 48 was found to be $k_{48} = 4.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, although no product information was determined. At higher temperatures (>573 K), an increase in the loss rate of CH_2OCH_3 was observed. This increase in loss rate was ascribed to thermal decomposition of methoxy radicals, reaction 43. The rate data were found to fit the expression $k_{43} = 1.6 \times 10^{13} \exp(-12800/T)$ put forth by Louks et al.[76,77]

The reaction of methylmethoxy radical with O_2 (reactions 49 and 50) and the subsequent fate of methoxymethylperoxy radical, $O_2CH_2OCH_3$, has been the subject of numerous studies. Jenkin et al.[67] examined DME degradation pathways in the absence of NO. With this scenario two methoxymethylperoxy radicals, $O_2CH_2OCH_3$, can combine to yield two methoxymethoxy radicals, OCH_2OCH_3 (reaction 51).

$$O_2CH_2OCH_3 + O_2CH_2OCH_3 \rightarrow OCH_2OCH_3 + OCH_2OCH_3 + O_2 \quad (51)$$

$$OCH_2OCH_3 + O_2 \rightarrow HO_2 + CH_3OC(O)H \quad (52)$$

$$O_2CH_2OCH_3^* \rightarrow HO_2CH_2OCH_2 \rightarrow 2CH_2O + OH \quad (53)$$

The two methoxymethoxy radicals can further react with O_2 to yield methyl formate and HO_2, reaction 52. In Jenkin's investigation, the kinetics of reaction 51 were investigated by monitoring the formation and then disappearance of the methoxymethylperoxy radical, $O_2CH_2OCH_3$, by following its absorbance at 230 nm. Chlorine radicals, produced from photolysis of Cl_2, were used to initiate hydrogen abstraction of dimethyl ether in various concentrations of O_2. Jenkin et al.[67] found that the self-reaction (reaction 51) rate constant varied with pressure and that it also depended on the ratio $[O_2]/[Cl]$. This result implied the existence of a secondary chemical reaction. The following observations were made: (i) $O_2CH_2OCH_3$ always displayed second-order kinetics, eliminating the possibility of unimolecular bond cleavage reactions. (ii) As the relative amount of O_2 increased, the rate constant increased; thus, the intermediate may react with O_2 and ultimately lead to further removal of $O_2CH_2OCH_3$. (iii) As the relative amount of Cl_2 increased, the rate constant decreased; thus, the intermediate may react with Cl_2 and ultimately lead to the regeneration of $O_2CH_2OCH_3$.

One possible explanation for these observations is H atom ejection from methoxymethoxy radical, that is, reaction 54.

$$OCH_2OCH_3 + M \rightarrow CH_3OC(O)H + H + M \quad (54)$$

$$HO_2 + O_2CH_2OCH_3 \rightarrow OH + OCH_2OCH_3 + O_2 \quad (55)$$

Thus, at high concentrations of O_2, hydrogen atoms formed in reaction 54 can react with excess oxygen to yield HO_2 radicals. HO_2 radicals may then react with methoxymethylperoxy radicals to yield methoxymethoxy radicals, reaction 55, thus explaining the increased rate of $O_2CH_2OCH_3$ loss at high O_2 concentrations.

At high concentrations of Cl_2, the hydrogen atom emitted in reaction 54 may react with excess chlorine to form hydrochloric acid and additional chlorine radicals. The excess chlorine radical further reacts with DME and ultimately produces additional $O_2CH_2OCH_3$, thus explaining the decrease in rate of $O_2CH_2OCH_3$ loss. A question to be addressed is the possibility of other thermal degradation pathways besides CH bond cleavage in CH_3OCH_2O. CO bond cleavage and other rearrangements may compete.

At low total pressures, significant concentrations of formaldehyde, CH_2O, were detected using FTIR. A possible explanation for this finding is the isomerization of $O_2CH_2OCH_3$ to form CH_2OCH_2OOH via a six-membered transition state. Formaldehyde can then be formed from the decomposition of CH_2OCH_2OOH to form $2CH_2O$ and OH radical, reaction 53.

Sehested et al.[70] investigated further the isomerization reaction of methoxymethylperoxy radicals. Once energetic methoxymethylperoxy radicals are formed from reaction 50, ($O_2CH_2OCH_3$*), one of two reaction paths can be followed: collisional quenching to form ground state $O_2CH_2OCH_3$ or intermolecular rearrangement to form CH_2OCH_2OOH (reaction 53), which decompose to form two formaldehyde molecules and hydroxyl radical. For total pressures above ~10 Torr, collisional quenching and formation of ground state methoxymethylperoxy radicals was found to dominate. Below 10 Torr, the concentration of third bodies is too low for significant collisional quenching. Intermolecular rearragement and formation of formaldehyde was found to dominate. The rate constant for reaction 50, k_{50}, was compared to reaction of chlorine with dimethyl ether radical.

$$CH_3OCH_2 + Cl_2 \rightarrow CH_3OCH_2Cl \quad (56)$$

At the low-pressure limit, Jenkin et al.[67] found k_{49}/k_{56} to be 1.97×10^{-19} cm^3 molecule^{-1}, whereas at the high-pressre limit $k_{49}/k_{56} = 0.108$. At the low-pressure limit, the rate constant for consecutive reactions 50 and 53 was compared to k_{56}. $(k_{50} + k_{53})/k_{56}$ was determined to be 0.063. In addition, a pressure-independent estimate for k_{56} was calculated to be 1.0 $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This value for k_{56} results in the following rate data: $k_{49,\text{low-pressure}} = 2.0 \times 10^{-29}$ cm^6 molecule^{-2} s^{-1}, $k_{49,\text{high-pressure}} = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $(k_{50} + k_{52})_{\text{low-pressure}} = 6.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Thus, under atmospheric conditions where significant concentrations of third bodies exist, formation of ground state methoxymethylperoxy radicals would be expected to dominate.

Sehested et al.[71] revisited this work using the pulse radiolysis technique. In this investigation, the following rate data were obtained: $k_{49,\mathrm{low-pressure}} = 9.4 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}, $k_{49,\mathrm{high-pressure}} = 1.14 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $(k_{50} + k_{53})_{\mathrm{low-pressure}} = 6.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The values in this study are in reasonable agreement with the previous investigation.

Wallington et al.[68] examined reactions of methoxymethylperoxy radicals with peroxy (HO_2) radicals, reactions 57 and 58. Reaction was found to proceed

$$O_2CH_2OCH_3 + HO_2 \rightarrow CH_3OCH_2OOH + O_2 \quad (57)$$

$$O_2CH_2OCH_3 + HO_2 \rightarrow CH_3OCOH + O_2 + H_2O \quad (58)$$

via two channels of almost equal branching ratios. Reaction 57 can proceed from a simple hydrogen transfer reaction, but more likely through a four-centered transition state. The four-centered transition state is preceded by the addition of HO_2 to $O_2CH_2OCH_3$ to form CH_3OCH_2OOOOH, a tetraoxide intermediate. Reaction 58 also proceeds through the tetraoxide intermediate to a six-membered transition state and finally forms methyl formate, water, and oxygen.

All of the previous investigations have studied the degradation of dimethyl ether in the absence of NO. Japar et al.[62] provided studies in the absence of NO. Langer et al.[69] studied the kinetics of reaction 59 using the pulse radiolysis−UV absorption technique. The rate for this reaction is 9.1×10^{-12} cm^3 molecule^{-1} s^{-1}. This rate is >4 times faster than that of the methoxymethylperoxy self-reaction 51 studied by Jenkin et al.[67] Under atmospheric conditions, NO concentrations are much higher than methoxymethylperoxy radical. Therefore, methoxymethylperoxy reaction with NO is expected to dominate over the self-reaction.

$$O_2CH_2OCH_3 + NO \rightarrow NO_2 + OCH_2OCH_3 \quad (59)$$

Japar et al.[62] used $Cl^\bullet$ and $OH^\bullet$ radical initiated hydrogen abstraction to simulate the reaction of DME with tropospheric OH radical in the presence of NO. Reaction products were determined using FTIR spectroscopy. The production of methyl formate accompanied the loss of dimethyl ether quantitatively. The yield of methyl formate relative to DME loss was found to be 0.90. The following reaction mechanism was put forth to rationalize experimental findings.

Cl atoms initiate the hydrogen abstraction reaction, producing methylmethoxy radical, CH_2OCH_3. Addition of O_2 results in the formation of the methoxymethylperoxy radical, $O_2CH_2OCH_3$. The formed alkylperoxy radical relinquishes an oxygen atom to NO, forming NO_2 and the methoxymethoxy radical OCH_2-OCH_3. The final step involves hydrogen abstraction by O_2 to form methyl formate, $CH_3OC(O)H$, and HO_2. O_2 abstraction occurs at the CH bond α to the radical center. The other possibility would be O_2 attack at the β carbon forming OCH_2OCH_2 and ultimately $2CH_2O$. However, no evidence of participation in this degradation channel was found. Hansen et al.[78] have examined the initial steps in the oxidation of methyl formate.

One of the major problems with using dimethyl ether as a diesel fuel is the fact that it is a gas at standard operation conditions and is thus difficult to handle. One proposed solution to this problem is the use of a similar species, dimethoxymethane, $CH_3OCH_2OCH_3$. Dimethoxymethane is a liquid under ambient conditions and would thus be easier to handle. The lack of CC bonds would result in low soot production.

3.4. Natural Gas

Natural gas is composed predominantly of methane, a relatively clean-burning fuel, which gives off one-third the amount of CO_2 (greenhouse gas) per unit energy produced of gasoline. Compressed natural gas (CNG) has become one of the most widely researched fuels proposed to replace petroleum-based fuels in spark ignition applications. Under certain conditions, the use of CNG has been found to reduce regulated emissions compared to conventionally fueled engines. CNG has an octane value of ∼130, which allows an engine to run at a higher compression ratio and to operate more efficiently. CNG has been found to have a lean flammability limit, allowing for lean burn operation, which reduces the production of carbon monoxide and NO_x. Nonmethane organic gas (NMOG) emissions are also lower for CNG-fueled engines than for petroleum-based engines due to the absence of heavier hydrocarbons in the fuel. The reduction in emissions of NMOGs leads to a decrease in the potential to form ozone. The major emissions from CNG-fueled engines[79] include high concentrations of methane itself, formaldehyde, ethane, and traces of C_2H_4, C_3H_8, C_4H_{10}, and C_5H_{12}.

The atmospheric oxidation mechanism for methane is illustrated in Figure 4. Methane reacts relatively slowly, with hydroxyl radicals having a rate constant on the order of 6.3×10^{-15} cm^3 molecule^{-1} s^{-1}. The atmospheric lifetime is estimated to be ∼8−10 years.[2,5] The reaction yields water and a CH_3 radical, which adds O_2 to form the methylperoxy radical.

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad (60)$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (61)$$

The methylperoxy radical formed in reaction 61 can then react with NO, NO_2, and HO_2 radicals.

$$CH_3O_2 + NO \rightarrow CH_3O + NO \quad (62)$$

$$CH_3O_2 + NO_2 + M \rightarrow M + CH_3OONO_2 \quad (63)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \quad (64)$$

All three reactions[5] have similar rate constants of 7.76×10^{-12}, 6.46×10^{-12}, and 5.6×10^{-12} cm^3 molecule^{-1} s^{-1}. The result of reaction 62 is the

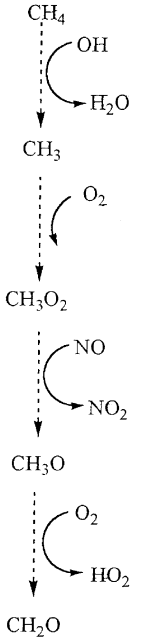

Figure 4. Atmospheric oxidation mechanism for methane.

production of CH_3O radicals, which ultimately react with molecular oxygen to form formaldehyde and HO_2 radicals. The rate of this reaction is relatively slow, having a rate constant of 1.9×10^{-15} cm^3 molecule^{-1} s^{-1}. CH_3OOH reacts with OH with a rate constant of 7.4×10^{-12} cm^3 molecule^{-1} s^{-1}.

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \qquad (65)$$

$$CH_3OOH + OH \rightarrow CH_2OOH + H_2O \rightarrow CH_2O + OH \qquad (66)$$

Reaction 65 is responsible for 70% of the reaction and results in a regeneration of the CH_3O_2 radical. The other 30% results in the formation of formaldehyde and OH. Thus, regardless of which reaction path is taken, the result is the formation of formaldehyde. One disadvantage of methane as an alternative fuel is that its long atmospheric lifetime makes it a greenhouse gas. The global-warming potential (GWP) relative to CO_2 is 62 over a 20-year integration.

3.5. Liquified Petroleum Gas

Liquid petroleum gas (LPG) varies in composition but is predominantly propane (~90−99%) along with isobutane, propene, ethane, and methane in varying concentrations. Major sources of propane in the atmosphere are automobile exhaust, processing and usage of natural gas, and biomass burning.[80]

Allara et al.,[81] Sunderam et al.,[82] Edelson et al.,[82] and Dente et al.[84] have studied the full kinetic mechanism describing the pyrolysis of propane. The mechanism consists of 422 reactions involving 48 species. Tomlin et al.[85] used sensitivity analysis techniques to reduce the mechanism to 122 dominant reactions involving 19 species.

For combustion purposes the decomposition of propane is initiated by thermal decomposition or by reaction with molecular oxygen. The relative importance of these reactions is dependent on the temperature of the system.

$$C_3H_8 \rightarrow C_2H_5 + CH_3 \qquad (67)$$

$$C_3H_8 + O_2 \rightarrow CH_2CH_2CH_3 + HO_2 \qquad (68)$$

$$C_3H_8 + O_2 \rightarrow CH_3CHCH_3 + HO_2 \qquad (69)$$

A dominant reaction in the oxidation of propane is attack of the hydroxyl radical, which can occur either at the terminal methyl group (primary site) or from the CH_2 group (secondary site).

$$CH_3CH_2CH_3 + OH \rightarrow CH_3CHCH_3 + H_2O \qquad (70)$$

$$CH_3CH_2CH_3 + OH \rightarrow CH_3CH_2CH_2 + H_2O \qquad (71)$$

Branching ratio measurements as determined by various investigators[86−89] suggest that reaction occurs at the primary site (reaction 71) 21−30% of the time at room temperature but then increases to 50−60% as temperatures approach 700−800 K.

In the atmosphere, hydroxyl radical initiated decomposition is predominantly initiated at the secondary carbon (Figure 5). Reactions 70 and 71 contribute

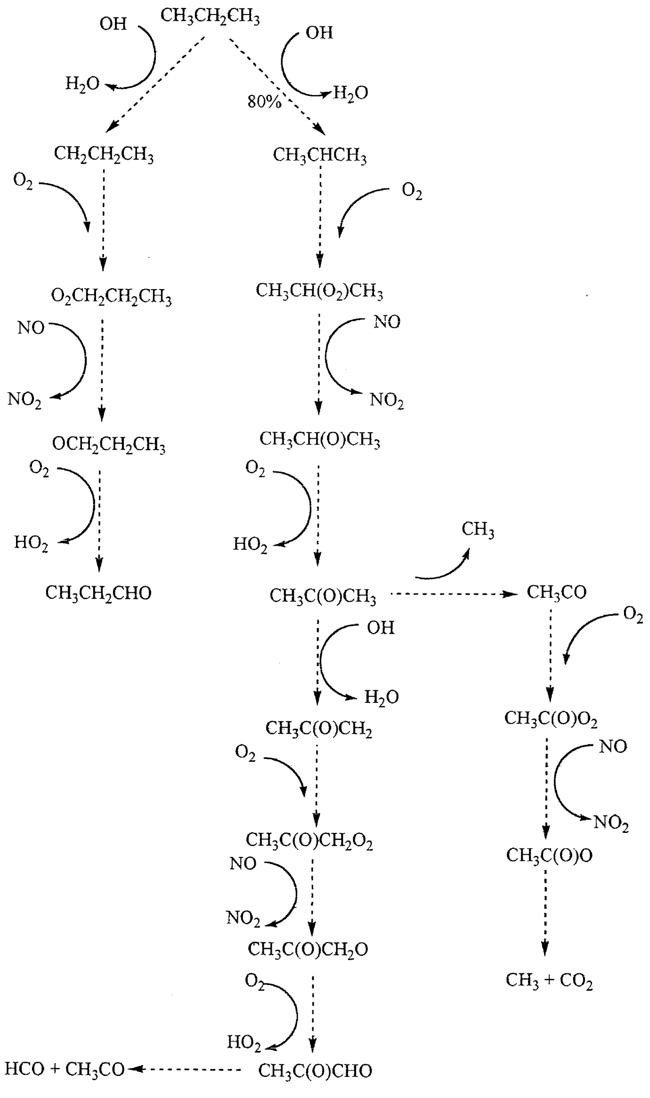

Figure 5. Atmospheric oxidation mechanism for propane. Oxidation primarily results in the formation of acetone.

roughly 80 and 20% of the reaction, respectively. Subsequent reactions with O_2 and NO yield 80% acetone [$CH_3C(O)CH_3$] and 20% propionaldehyde, $CH_3CH_2C(O)H$, as described below.[90] For the formation of acetone in regions of high NO concentrations, the following reactions are relevant:

$$CH_3CHCH_3 + O_2 \rightarrow CH_3CHO_2CH_3 \quad (72)$$

$$CH_3CHO_2CH_3 + NO \rightarrow NO_2 + CH_3CH(O)CH_3 \quad (73)$$

$$CH_3CH(O)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2 \quad (74)$$

Reaction 72 is an oxygen addition step followed by reaction 73, which is the conversion of NO to NO_2 as the alkylperoxy radical is reduced to an alkoxy radical. The $CH_3CH(O)CH_3$ in eq 74 is oxidized to acetone, $CH_3C(O)CH_3$, as mediated by molecular oxygen. In competition with reaction 73 is reaction 75, which forms an alkyl peroxide, ROOH. The alkyl peroxide is subsequently photolyzed in reaction 76. As in reaction 74, the $CH_3CH(O)CH_3$ radical is oxidized to acetone. This set of reactions becomes significant in regions of lower NO_x concentrations.

$$CH_3CHO_2CH_3 + HO_2 \rightarrow CH_3CHO_2HCH_3 + O_2 \quad (75)$$

$$CH_3CHO_2HCH_3 + h\nu \rightarrow CH_3CH(O)CH_3 + OH \quad (76)$$

$$CH_3CH(O)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2 \quad (74)$$

For the formation of propionaldehyde, the following reactions are relevant:

$$CH_3CH_2CH_2 + O_2 \rightarrow CH_3CH_2CH_2O_2 \quad (77)$$

$$CH_3CH_2CH_2O_2 + NO \rightarrow CH_3CH_2CH_2O + NO_2 \quad (78)$$

$$CH_3CH_2CH_2O + O_2 \rightarrow CH_3CH_2CHO \quad (79)$$

The above mechanisms illustrate the conversion of NO to NO_2 and the formation of peroxy radicals, HO_2. Both processes lead to ozone formation in the troposphere.

Acetone, along with formaldehyde, is one of the most important carbonyls in the atmosphere. Recent estimates[91] suggest a loading of ~56 Tg of acetone per year. Acetone in the atmosphere undergoes further oxidation by reacting with hydroxyl radical or photolysis. The lifetime of acetone with respect to OH loss is 66 days, whereas the lifetime with respect to photolysis is 38 days.[34] With respect to photolysis, the following reactions are relevant:

$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3 \quad (80)$$

$$CH_3CO + O_2 \rightarrow CH_3C(O)O_2 \quad (81)$$

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2 \quad (82)$$

$$CH_3C(O)O_2 + NO_2 \rightleftarrows CH_3C(O)O_2NO_2 \quad (83)$$

$$CH_3C(O)O \rightarrow CH_3 + CO_2 \quad (84)$$

Reactions 80 and 84 both produce methyl radicals, which ultimately react with 2 equivalents of molecular oxygen and NO to produce formaldehyde and HO_2 radicals. Additionally, reaction 83 illustrates the formation of PAN.

The reaction of acetone with hydroxyl radical can be illustrated as follows:

$$CH_3C(O)CH_3 + OH \rightarrow CH_3C(O)CH_2 + H_2O \quad (85)$$

$$CH_3C(O)CH_2 + O_2 \rightarrow CH_3C(O)CH_2O_2 \quad (86)$$

$$CH_3C(O)CH_2O_2 + NO \rightarrow CH_3C(O)CH_2O + NO_2 \quad (87)$$

$$CH_3C(O)CH_2O + O_2 \rightarrow CH_3C(O)CHO + HO_2 \quad (88)$$

$$CH_3C(O)CHO + h\nu \rightarrow CH_3C(O) + HCO \quad (89)$$

$$CH_3CO + O_2 \rightarrow CH_3C(O)O_2 \quad (90)$$

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2 \quad (91)$$

$$CH_3C(O)O_2 + NO_2 \rightleftarrows CH_3C(O)O_2NO_2 \quad (92)$$

$$CH_3C(O)O \rightarrow CH_3 + CO_2 \quad (93)$$

The atmospheric significance of acetone is derived from its ability to sequester reactive nitrogen as PAN (reactions 83 and 92) and the fact that it is a source of HO_x radicals (reaction 88) in the upper troposphere.[91−95] In general, the oxidation of propane leads to the formation of HO_2 radicals, PAN, and formaldehyde and to the conversion of NO to NO_2.

3.6. Comparison of Alternative Fuels

The above analysis of the mechanisms of hydrocarbon oxidation aids in the understanding of the observed degradation products and thus the probable byproducts that are released into the atmosphere. However, the speciation observed is highly dependent on operating conditions. Fuel composition, combustion temperature, fuel-to-air ratio, and reactor dynamics are just a few of the variables that affect the combustion properties of the fuel. Higher accuracy emission characteristics can be obtained through exhaust analysis on actual engines and ultimately on alternatively fueled vehicles (AFVs). The following are two examples of many such analyses.

Nils-Olof et al.[96] monitored exhaust characteristics of engines running on alternative fuels at temperatures ranging from −20 to 22°C. The emission of formaldehyde and methanol from an engine running on M85 (85% methanol and 15% gasoline) at different temperatures was investigated. Colder operating conditions result in increased emissions of both methanol and formaldehyde. Figure 6 illustrates exhaust components for the different test fuels. The test fuels are gasoline without a catalyst, gasoline with a catalyst, M85, LPG, CNG, and diesel. At 22 °C, all alternative fuels showed improvement in NO_x and hydrocarbon emissions compared to gasoline- and diesel-fueled engines. CNG is shown to have high emissions of hydrocarbons; however, the hydrocar-

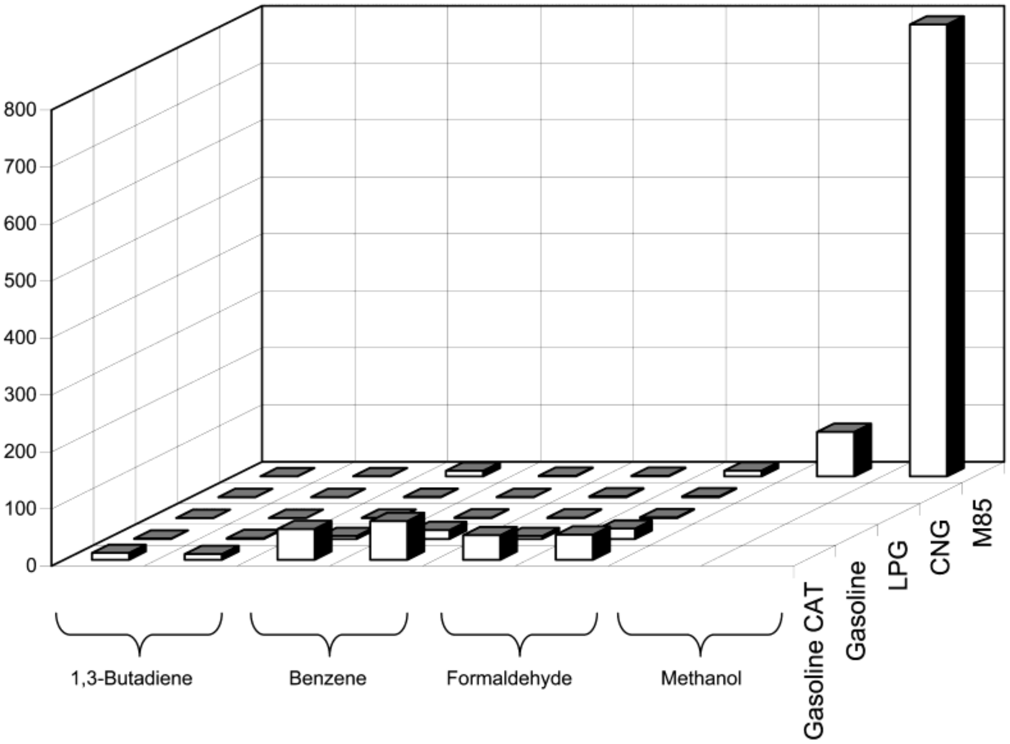

Figure 6. Summary of unregulated gas emissions.[96]

Table 1. Standard Reactivities[a] from the Stoichiometric Oxidation of Methanol, Ethanol, Natural Gas, and LPG as a Function of Exposure Temperature

temp, K	methanol	ethanol	CNG	LPG
600	0.99	4.51	0.10	0.31
650	3.07	4.72	ND[b]	ND
700	2.22	5.22[c]	0.1	1.68
750	0.0[c]	4.75	0.80	2.24
800	0.0	0.0	1.98	6.15[c]
900	0.0	0.0	3.34	0.0
1000	0.0	0.0	0.0[c]	0.0

[a] Reference 20. [b] Not determined. [c] Approximated temperature of 99% fuel conversion.

bons are predominantly unspent methane, which has negligibly small MIR values.[18,34] At the lower temperature, M85 showed substantial emissions of CO and hydrocarbons.[96]

Once the relative yield of combustion products has been discerned, an overall standard reactivity for the fuel can be computed. As described previously, the standard reactivity (SR) is the summation of the individual MIR activity times the production yield. Table 1 lists SR values from the work of Taylor et al.[20] At lower combustion temperatures, natural gas has a lower standard reactivity. At moderate temperatures, methanol is less likely to produce tropospheric ozone, whereas, at the highest temperatures, all SR values are zero due to the fact that all NMOGs have been removed during combustion.[15]

Kelly et al.[97−99] measured evaporative and combustion emissions from a series of flexible fueled vehicles running on regular reformulated gasoline (RFG), M85, E85, and CNG. For engines running on E85, NMHCs, NO_x, and CO emissions were all decreased relative to engines running on regular gasoline by 21, 28, and 18%, respectively. Toxic air emission such as benzene and 1,3-butadiene were decreased by 79 and 80%, respectively, whereas emissions of formaldehyde increased by 29%. In addition, acetylaldehyde emissions from E85 vehicles increased by a factor of 20 over RFG vehicles. Taking the appropriate speciation into consideration, Kelly et al.[97−99] found that changing from RFG to E85 resulted in a 25% reduction in the OFP and a 30% reduction in the SR.

For M85, results showed a decrease in NMHC emissions, a slight increase in NO_x emissions, and little change in CO emissions over RFG-fueled vehicles. Emissions of benzene, 1,3-butadiene, and acetylaldehyde were decreased substantially (69, 88, and 42%, respectively) in M85 vehicles, whereas formaldehyde emissions increased substantially by an order of magnitude. Changing from RFG to M85 resulted in a 36% reduction in the OFP and a 60% reduction in the standard reactivity.[97−99]

For CNG, hydrocarbon emissions and NO_x emissions were reduced by roughly 83 and 31%, respectively. CO emissions decreased slightly from RFG vehicles. As with M85, all toxic emissions decreased substantially except formaldehyde. Formaldehyde emissions increased by a factor of 2. Changing from RFG to CNG resulted in a 74% reduction in the OFP and a 50% reduction in the standard reactivity.[97−99]

All of the alternative fuels show improvements over conventional fuels in terms of ozone and pollution reduction. The major focus is likely to be the efficiency of the alternative fuel system and the resulting emissions of greenhouse gases such as CO_2. Fuels from renewable resources (biomass) would not contribute to global warming. Currently, there is research devoted to determining the potential of natural products such as oils from grapeseed, sunflowers, and soybeans for use as alternative fuels.

4. Atmospheric Chemistry of Alternative CFCs

Currently, the EPA estimates there to be 80,000 centrifugal chillers, 1.6 million retail food refrigeration units, 540,000 transport refrigeration units, and 537 million ft^3 of cold storage warehousing in service in the United States today. The first generation of refrigerants began in the 1830s and lasted through the next 100 years. Working fluids were selected on the basis of performance, with little regard to safety. Screening to improve performance and safety began late in that era. The second generation began in the 1930s with the development of halogenated refrigerants. Refrigerants were synthesized to obtain the desired properties of durability and safety. The third generation began in the 1990s when, in addition to durability and safety, environmental concerns were considered.[100,101] Chlorinated and brominated refrigerants, solvents, foam-blowing agents, aerosol propellants, fire suppressants, and other chemicals are being phased out under a treaty known as the Montreal Protocol on Substances that Deplete the Ozone Layer. This international agreement was introduced in 1987 and has been revised several times (London in 1990, Copenhagen in 1992, and Montreal in 1997).[100] Under the Clean Air Act Amendments of 1990, the EPA proposed regulations that accelerate the domestic phase-out schedules of ozone-depleting substances to meet U.S. obligations for the new international deadlines. CFCs were to be phased out of production by the end of 1995.[102−105] Thus, there is a continued need for new materials to replace banned CFC materials.

4.1. Desired Characteristics of CFC Replacements

Attention is now focused on global warming, with the goal of reducing greenhouse gas emissions. Air conditioners, heat pumps, and refrigeration devices that use refrigerants also use energy. They contribute to global warming both by the release of refrigerants and by emissions of carbon dioxide and other greenhouse gases when powering these devices.[100] As a simple illustration, Epstein et al.[106] considers a conventional coal-producing power plant that produces 0.92 kg of the greenhouse gas CO_2 for every kilowatt hour of electricity produced. A typical high-efficiency (352 kW, COP = 5.9) 100-ton centrifugal chiller operating for 1000 h producing 0.60 kW/ton would indirectly produce 55200 kg of CO_2 per year. This CO_2 can be compared to the global effect produced from the release of a refrigerant into the atmosphere. Epstein assumes that 17.5% of the working fluid (CFC-11) is lost to the atmosphere each year. CFC-11 has a global-warming impact 1300 times that of CO_2. Thus, this leak would be equivalent to the release of ~36400 kg of CO_2.[106] In this scenario, global-warming contributions from both the direct and indirect effect are comparable. The assumption of a 17.5% per year loss rate is rather large, and recent studies have shown that the indirect effect is far greater than the direct effect for many applications, due predominantly to improvements in leak reduction.[100,107,108]

Nevertheless, species with long atmospheric lifetimes and high fluorine contents are targeted as potential greenhouse gases. Perfluorocarbons are already perceived as unacceptable by the technical community, although specific regulatory provisions are still being worked out.[100] A simultaneous movement toward safer (safer with respect to flammability and toxicity concerns) refrigerants is also underway. Hydrocarbons and ammonia are examples of compounds that are promising from an atmospheric point of view, but these compounds are seen by some as unacceptable with regard to flammability and toxicity.

Compounds to be used as alternatives to CFCs must have several characteristics. They should

- have low ozone depletion potentials,
- have thermophysical properties similar to those of existing CFCs,
- have short atmospheric lifetimes,
- be stable, and nonflammable,
- have low global warming potentials,
- not be considered a VOC, and
- be easy and inexpensive to manufacture.

The molecular structure of the refrigerant can be manipulated to obtain desired properties such as flammability, toxicity, and atmospheric lifetime; however, many tradeoffs exist. Incorporating hydrogen within a molecule is beneficial from an environmental point of view because these molecules react more quickly with tropospheric hydroxyl radical in hydrogen abstraction reactions. However, as the number of hydrogen atoms within a molecule increases, the flammability also increases.[100] Refrigerants are considered to be marginally flammable when hydrogen atoms represent half the number of substituents bonded to carbon.[100,108] R-152a (CH_3CHF_2), for example, is more flammable than R143a (CH_3-CF_3), whereas R125 (CHF_2CF_3) and R134a (CH_2-FCF_3) are not flammable under normal operating conditions.[100,109]

Increasing the fluorine content of a molecule tends to decrease the toxicity and the flammability of the molecule. On the other hand, replacing hydrogen with chlorine and then fluorine results in successive increases in the atmospheric lifetime of the species.[100,110−112] CH_4, for example, has a lifetime of ~10−14 years, CCl_4 a lifetime of 42 years, and CF_4 a lifetime of 5×10^4 years. In addition, increases in the amount of fluorine increase the molecule's ability to absorb infrared radiation in the atmospheric window region (800−1400 cm-^{1}). C−H stretches resonate lower in energy at ~700−800 cm^{-1}; C−F stretches resonate in the vicinity of 1100 cm^{-1}, which is within the window region. This increase in the ability to absorb at crucial wavelengths, along with the increase in atmospheric lifetimes, results in an increase in the global-warming properties of heavily fluorinated species.

The number of suitable elements that can be combined at the molecular level is small. The number of potential chemical combinations of these elements drops quickly as individual elements are removed. Most compounds containing chlorine and bromine have been or are being phased out under the Montreal Protocol. Fluorinated compounds are under attack as greenhouse gases. Most chemicals containing nitrogen and sulfur that are suitable refrigerants raise safety concerns. Hydrocarbons tend to be good refrigerants but are highly flammable and are associated with ozone production in the troposphere.[100]

There is currently some opposition to the use of HFCs because of the global-warming concerns. Some environmentalists would like the refrigeration industry to bypass the HFCs entirely and employ natural refrigerants such as hydrocarbons, carbon dioxide, and ammonia. Refrigerator manufacturers in Germany are using isobutane, whereas some in Italy are considering the use of propane for window air conditioners. Proponents of the use of hydrocarbons argue that the small quantities used in household refrigerators would result in a minimal fire hazard. Researchers from Norway have proposed carbon dioxide for automotive air conditioning, whereas ammonia is still used today in large refrigerated warehouse applications.[100,101] However, a key issue from the atmospheric chemistry perspective is the atmospheric photooxidation chemistry of the materials adopted as CFC replacements. There have been several earlier reviews of the chemistry of chlorofluorocarbons and their replacements.[102,113−116]

4.2. CFC Relacements

4.2.1. HCFCs

HCFCs are transitional refrigerants that still contain chlorine and are thus scheduled for phaseout over the next couple of decades because estimates suggest that 2−15% of the chlorine content of HCFCs with intermediate lifetimes (1−22 years) is released in the stratosphere.[102,117] The two most popular HCFCs are HCFC-22 (CHF_2Cl) and HCFC-123 (CF_3CHCl_2). Calm et al.[100] and Sanvordenker[101] argue against the indiscriminant elimination of classes of compounds without regard to offsetting benefits. HCFC-123, for example, has a small ODP (0.02 relative to CFC-11), and thus its use in closed systems is likely to have a negligible impact on stratospheric ozone. In addition, HCFC-123 has a short atmospheric lifetime (~2 years), extremely low GWP (28 relative to CO_2), and a very high thermodynamic efficiency.[100,107,118]

Blends containing mostly HCFC-22, along with the minor components HCFC-124 and HCFC-142b, are replacements for CFC-12. Some blends were designed to provide the same capacity as CFC-12; others were designed to maintain the same discharge temperatures for the sake of reliability. These alternatives require minimum changes in existing systems. The traditional lubricants are acceptable, and service practices need not be modified.

As shown in Table 2 data from Pinnock et al.,[119] HCFC-22 has a fairly substantial radiative forcing value of 0.227 W m^{-2} ppb^{-1}, a lifetime of 13.3 years, and a global-warming potential of 1700 (100 year integration relative to CO_2). For comparison, CFC-12 (the compound HCFC-22 is likely to replace) has a forcing value of 0.28 W m^{-2} ppb^{-1}, a lifetime of 102 years, and a GWP of 7300.[117,118]

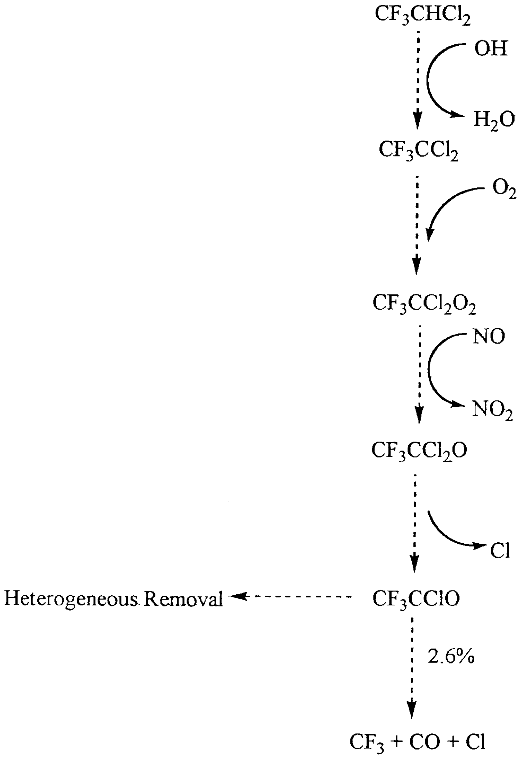

Figure 7. Atmospheric oxidation mechanism for HCFC-123. Atmospheric oxidation leads to the formation of CF_3CClO, which is subsequently removed via heterogeneous processes.

Atmospheric removal of HCFC-22 ($CHClF_2$) is initiated by hydroxyl radical, as described in previous sections. The rate of this reaction has been measured to be 4.7×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, which results in a lifetime of ~13.3 years.[5] Thus, significant quantities of chlorine from HCFC-22 can be delivered to the stratosphere through the following series of reactions:

$$CHClF_2 + OH \rightarrow CClF_2 + H_2O \qquad (94)$$

$$CClF_2 + O_2 \rightarrow CClF_2O_2 \qquad (95)$$

$$CClF_2O_2 + NO \rightarrow CClF_2O + NO_2 \qquad (96)$$

$$CClF_2O \rightarrow CF_2O + Cl \qquad (97)$$

Reaction 97 is a CCl dissociation process that results in the formation of chlorine radicals, which have the potential for interaction with the ozone layer. The ozone depletion potential of HCFC-22 is 0.04 (relative to CFC-11), whereas that for CFC-12 is an order of magnitude higher, 0.9.[119] Clearly, HCFC-22 is an improvement over CFC-12, in terms of both its global-warming and ozone depletion properties.

For HCFC-123 (CF_3CHCl_2), the radiative forcing value is slightly lower at 0.206 W m^{-2} ppb^{-1}. As mentioned, HCFC-123's atmospheric lifetime is very short (1.4 years), resulting in a very low GWP value of 93 relative to CO_2 over a 100 year integration. The consequence of atmospheric oxidation (Figure 7) is the release of two chlorine atoms.

$$CF_3CHCl_2 + OH \rightarrow CF_3CCl_2 + H_2O \qquad (98)$$

$$CF_3CCl_2 + O_2 \rightarrow CF_3CCl_2O_2 \qquad (99)$$

$$CF_3CCl_2O_2 + NO \rightarrow CF_3CCl_2O + NO_2 \qquad (100)$$

Table 2. Properties of Alternative CFCs

species	formula	lifetime,[a] years	radiative[b] forcing, W m^{-2} ppb^{-1}	ODP[c]	GWP, 20 years	GWP, 100 years	GWP, 500 years
CFC-11	$CFCl_3$	50	0.269	1.0	5000	4000	1400
HCFC-22	$CHClF_2$	13.3	0.227	0.04	4300	1700	520
HCFC-123	CF_3CHCl_2	1.4	0.206	0.014	300	93	29
HCFC-124	CH_3CHFCl	5.9	0.224	0.03	1500	480	150
HCFC-141b	CH_3CFCl_2	9.4	0.157	0.10	1800	630	200
HCFC-142b	CH_3CF_2Cl	19.5	0.210		4000	1900	590
HFC-32	CH_2F_2	6.0	0.136	0.0	1800	580	180
HFC-143	CHF_2CH_2F	3.5	0.145	0.0	1000	300	94
HFC-143a	CH_3CF_3	55	0.168	0.0	5000	3800	1400
HFC-134a	CF_3CHF_2	14	0.181	0.0	3400	1300	420
HFC-125	CF_3CHF_2	36	0.251	0.0	4600	2800	920

[a] Dutton, N. J.; Fletcher, I. W.; Whitehead, J. C. *J. Phys. Chem.* **1985**, *89*, 569. [b] References 2 and 6. [c] Reference 2.

$$CF_3CCl_2O \rightarrow CF_3COCl + Cl \qquad (101)$$

$$CF_3COCl \rightarrow CF_3 + CO + Cl \qquad (102)$$

Because of the short atmospheric lifetime of HCFC-123, the resultant chlorine atom is much less likely to penetrate the stratosphere. The ODP of HCFC-123 is 0.014 relative to CFC-11. The photolysis of CF_3COCl (reaction 101) occurs only 2.6% of the time. In addition to these products, CF_3Cl has also been reported in <1% yields. An alternative mechanism for the removal of CF_3COCl is wet deposition.[116,120]

HCFC-124 (CF_3CFClH) has one more fluorine at the expense of a chlorine atom than HCFC-123. Its reaction rate with hydroxyl radical is slower, and thus its atmospheric lifetime is longer, 5.9 years. Despite having one fewer chlorine atom than HCFC-123, the longer lifetime results in a 2-fold increase in the ODP of HCFC-124 over HCFC-123. The additional CF bond resonating in the window region imparts an increase in the radiative forcing of HCFC-124, 0.224 W m^{-2} ppb^{-1}. The longer lifetime and greater climate forcing properties result in a GWP that is almost 5 times that of HCFC-123 (see Table 3).

The atmospheric degradation of HCFC-124 is shown in Figure 8 and is analogous to that of HCFC-123.

$$CF_3CHFCl + OH \rightarrow CF_3CFCl + H_2O \qquad (103)$$

$$CF_3CFCl + O_2 \rightarrow CF_3CFClO_2 \qquad (104)$$

$$CF_3CFClO_2 + NO \rightarrow CF_3CFClO + NO_2 \qquad (105)$$

$$CF_3CFClO \rightarrow CF_3COF + Cl \qquad (106)$$

$$CF_3CClO \rightarrow CF_3 + CO + F \qquad (107)$$

The strong CF bond in CF_3COF makes removal via heterogeneous process even more dominant over removal by photolysis (reaction 107). Photolysis is expected to account for only 0.1% of the removal of CF_3COF.[120]

Table 3. Lifetime with Respect to Heterogeneous Processes[a]

species	$Hk_{hyd}^{1/2}$, M atm^{-1} $s^{-1/2}$	lifetime[a] clouds, days	lifetime oceans, years	degradation products
CF_2O	6	5−10	0.3−2.0	HF, CO
CClFO	2	5−20	0.5−5.0	HF, HCl, CO_2
CHFO		150−1500	80	HF, HCOOH
CF_3COCl	1	5−30	1.0−10.0	HCl, $CF_3C(O)OH$
CF_3COF	4	5−15	0.3−3.0	HF $CF_3C(O)OH$

[a] Reference 120.

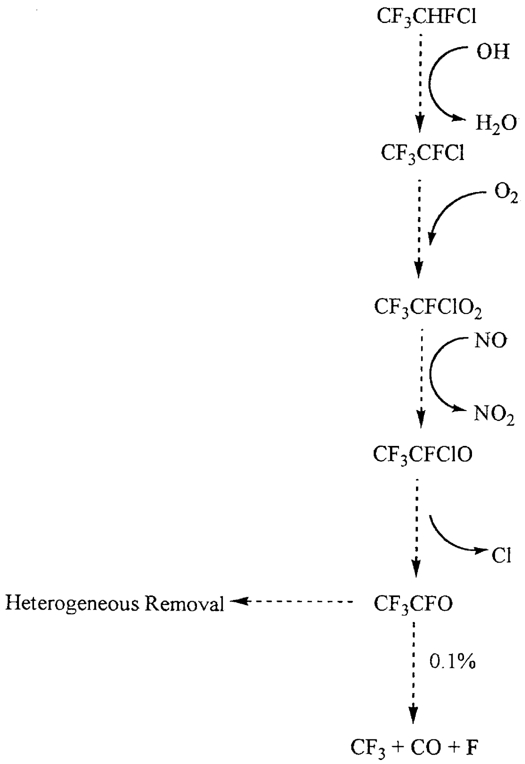

Figure 8. Atmospheric oxidation mechanism for HCFC-124 showing the oxidation to CF_3CFO, which is predominantly removed via heterogeneous processes.

HCFC-141b (CH_3CFCl_2) is primarily an alternative to CFC-11 and, to some extent, a replacement for CFC-113. Its atmospheric concentration has been growing at roughly 63 ± 9% per year and, in 1997, was estimated to have an atmospheric concentration of 5.7 ± 0.6 pptv. The reaction with OH[5] has been measured to be 6.0×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, yielding a lifetime on the order of 9.4 years.[119] HCFC-141b has an ODP that is an order of magnitude less than that of CFC-11 (ODP = 0.1), a radiative forcing value of 0.157 W m^{-2} ppb^{-1}, and a GWP of 630. The atmospheric oxidation (Figure 9) of HCFC-141b has been found to proceed as follows:

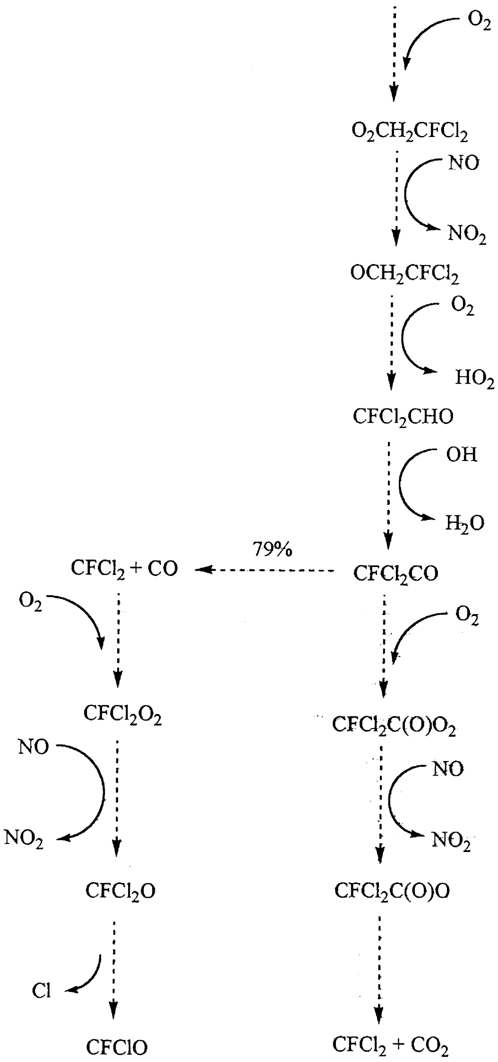

Figure 9. Atmospheric oxidation mechanism for HCFC-141b. CFClO is the main degradation product produced predominantly from CC bond cleavage of the $CFCl_2O$ radical.

$$CH_3CFCl_2 + OH \rightarrow CH_2CFCl_2 + H_2O \quad (108)$$

$$CH_2CFCl_2 + O_2 \rightarrow O_2CH_2CFCl_2 \quad (109)$$

$$O_2CH_2CFCl_2 + NO \rightarrow OCH_2CFCl_2 + NO_2 \quad (110)$$

$$CFCl_2CH_2O + O_2 \rightarrow CFCl_2COH \quad (111)$$

$$CFCl_2COH + OH \rightarrow CFCl_2CO + H_2O \quad (112)$$

$$CFCl_2CO + O_2 \rightarrow CFCl_2C(O)O_2 \quad (113)$$

$$CFCl_2CO \rightarrow CFCl_2 + CO \quad (114)$$

$$CFCl_2C(O)O_2 + NO \rightarrow CFCl_2C(O)O + NO_2 \quad (115)$$

$$CFCl_2C(O)O \rightarrow CFCl_2 + CO_2 \rightarrow CFClO + CO_2 + Cl \quad (116)$$

Reaction 111 is a hydrogen abstraction reaction mediated by molecular oxygen to yield $CFCl_2COH$. This reaction dominates over any photolysis reaction of the $CFCl_2CH_2O$ radical.[116,121] Subsequent reaction of the metastable carbonyl generated in reaction 111 has been shown to be rapid, having a lifetime on the order of 11 days. Reactions 113 and 114 are competitive reactions for the $CFCl_2CO$ radical. Tuazon et al.[121] determined that bond scission (79 ± 7%) to form $CFCl_2$ and CO dominates over O_2 addition (21 ± 5%). Regardless of the particular pathway, the end result is 100% production of CFClO.

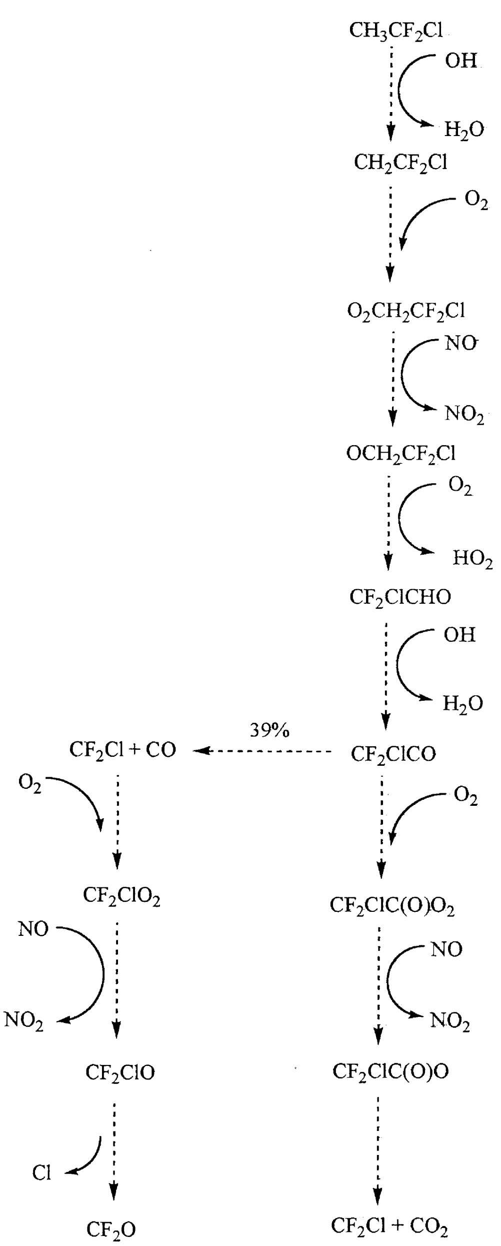

Figure 10. Atmospheric oxidation mechanism for HCFC-142b. The oxidation mechanism is analogous to that of HCFC-141b except that the halogenated derivative of formaldehyde, CF_2O, results from O_2 addition to CF_2ClCO and not CC bond cleavage.

HCFC-142b (CH_3CF_2Cl) is structurally similar to HCFC-114b; however, the relative numbers of chlorine and fluorine atoms have been reversed. For HCFC-142b, the lifetime (119.5 years), radiative forcing (210 W m^{-1} ppb^{-1}), and GWP (1900) are all significantly larger as compared to HCFC-141b. The degradation mechanism is also similar to that of HCFC-141b, yielding CF_2O instead of CFClO (see Figure 10). In this case, 39% of the reaction of CF_2ClCO decays via CC bond scission.[121]

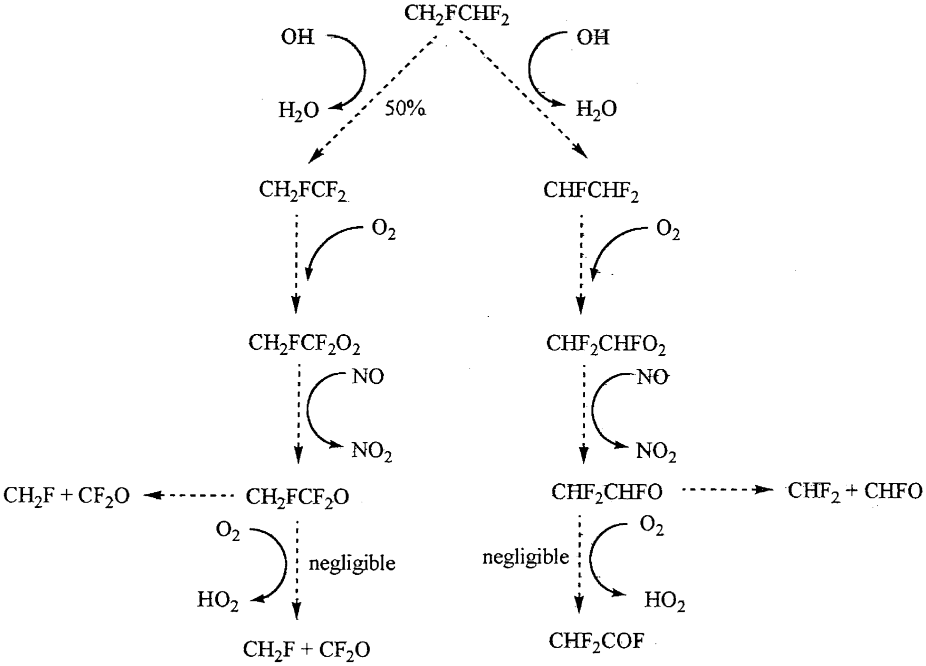

Figure 11. Atmospheric oxidation mechanism for HFC-143. CC bond scission of alkoxy radicals is found to dominate over O_2 addition. Oxidation results in the formation of CF_2O and CHFO.

4.2.2. HFCs

HFCs contain no chlorine and are thus given ozone depletion potentials of essentially zero. In the United States, HFCs are seen as long-term replacements for CFCs and HCFCs. The mobile air conditioning and home refrigerator/freezer industries have converted from CFC-12 directly to HFC-134a without using a transitional HCFC in between. Low-temperature grocery/supermarket applications have begun conversion to blends of HFCs (404A, 507, 407A, and 407B). The home air conditioners that apply HCFC-22 are in the testing stages of conversion to blends of HFCs 407C and 410A. R404A is a blend of HFC-125/HFC-143a/HFC-134a in a 44:52:4 ratio. R507 is a blend of HFC-125/HFC-143a in a 50:50 ratio. HFCs as replacements for HCFC-123 and HCFC-124 are still to be determined.[100,107] The following is a review of some of the more popular HFCs.

The degradation mechanism for HFC-32 (CH_2F_2) is as follows:

$$CH_2F_2 + OH \rightarrow CHF_2 + H_2O \qquad (117)$$

$$CHF_2 + O_2 \rightarrow CHF_2O_2 \qquad (118)$$

$$CHF_2O_2 + NO \rightarrow CHF_2O + NO_2 \qquad (119)$$

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2 \qquad (120)$$

The rate of reaction 117 is 1.0×10^{-14} cm^3 molecule^{-1} s^{-1}, which yields a lifetime of roughly 6.0 years. This lifetime, along with a moderate radiative forcing value of 0.136 W m^{-2} ppb^{-1}, yields a moderate GWP of 580 over a 100 year integration with respect to CO_2. Reaction 119 involves the reduction of the peroxy radical to an alkoxy radical, as mediated by NO. It should be mentioned that, in addition to reactions with NO, the peroxy radical can also react with NO_2 and HO_2 in the atmosphere. The addition of NO_2 to yield a peroxy nitrate ($CHF_2O_2NO_2$ in this example) was discussed in the previous section. These species are thermally unstable and ultimately revert to the peroxy radical. The peroxy radical may also react with HO_2 to yield alkylperoxides, CHF_2-OOH in this illustration. Again, the alkylperoxides are returned to the peroxy radicals via reaction with OH or photolysis.[116,122] Reaction 120 is a hydrogen abstraction reaction to yield HO_2 and the fluorinated derivative of formaldehyde.

HFC-143 (CHF_2CH_2F) is a potential foam-blowing agent. Clyne and Holt,[123] using a discharge resonance fluorescence system, measured the rate of reaction with hydroxyl radical to be $(5.2 \pm 0.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Martin and Paraskevopoulos,[124] using a flash photolysis−UV absorption technique, measured the rate to be $(1.8 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Barry et al.,[125] using a relative rate technique referenced to methyl chloroform, measured the rate to be $(1.61 \pm 0.05) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. On the basis of this rate constant, an atmospheric lifetime on the order of 3.1 years is calculated (IPCC 1994 recommends 3.5 years). The climate forcing properties for HFC-143 are relatively small. Pinnock[119] determined a radiative forcing value of 0.145 W m^{-2} ppb^{-1} and a GWP of 300 relative to CO_2.

Hydroxyl radical initialized attack on HFC-143 can occur at one of two sites, as illustrated in Figure 11.

$$CH_2FCHF_2 + OH \rightarrow CHFCHF_2 + H_2O \quad (121)$$

$$CH_2FCHF_2 + OH \rightarrow CH_2FCF_2 + H_2O \quad (122)$$

Tschuikow-Roux et al.[126] determined a value for the branching ratio k_{121}/k_{122} to be 0.97, thus implying relatively equal participation in both pathways. Barry et al.[125] found yields of CF_2O and CHFO of nearly 100% and rationalized these findings with the following mechanism. The above alkyl radicals each add O_2 to form peroxy radicals and then return half of the used oxygen as two peroxy radicals to form two alkoxy radicals and O_2 ($2RO_2 \rightarrow 2RO + O_2$). Or, under atmospheric conditions, NO would mediate this reaction (125 and 126).

$$CH_2FCF_2 + O_2 \rightarrow CH_2FCF_2O_2 \quad (123)$$

$$CHFCHF_2 + O_2 \rightarrow CHF_2CHFO_2 \quad (124)$$

$$CH_2FCF_2O_2 + NO \rightarrow CH_2FCF_2O + NO_2 \quad (125)$$

$$CHF_2CHFO_2 + NO \rightarrow CHF_2CHFO + NO_2 \quad (126)$$

The alkoxy radicals formed at this point have two possibilities: hydrogen abstraction by molecular oxygen or CC bond scission. Hydrogen abstraction of CHF_2CHFO would form a stable intermediate CHF_2CFO. This species was not detected, and thus CC bond scission was proposed to dominate.[125]

$$CH_2FCF_2O \rightarrow CH_2F + CF_2O \rightarrow CF_2O + CHFO \quad (127)$$

$$CHF_2CHFO \rightarrow CHF_2 + CHFO \rightarrow CHFO + CF_2O \quad (128)$$

HFC-143a (CF_3CH_3) has a surprisingly long lifetime of 55 years. For comparison, the preceding structural isomer, HFC-143 (CHF_2CH_2F), has a lifetime of only 3.5 years. The reason for the long lifetime of HFC-143a lies with the electron-withdrawing nature of the CF_3 functional group. The CF_3 group pulls electron density toward that side of the molecule, resulting in C−H bonds that are shorter, stronger, and more difficult to abstract. In addition to this long atmospheric lifetime, HFC-143a has a moderate forcing value of 0.168 W m^{-2} ppb^{-1}. The GWP is thus relatively high, 3800 with respect to CO_2 over a 100 integration. HFC-143a has one of the highest GWP values in Table 2.

The oxidation of HFC-143a results in the formation of a stable aldehyde intermediate, CF_3CHO, as shown in Figure 12.

$$CF_3CH_3 + OH \rightarrow CF_3CH_2 + H_2O \quad (129)$$

$$CF_3CH_2 + O_2 \rightarrow CF_3CH_2O_2 \quad (130)$$

$$CF_3CH_2O_2 + NO \rightarrow CF_3CH_2O + NO_2 \quad (131)$$

$$CF_3CH_2O + O_2 \rightarrow CF_3\ CHO \quad (132)$$

The lifetime of CF_3CHO with respect to OH loss has been estimated to be ~24 days.[127]

$$CF_3CHO + OH \rightarrow CF_3CO + H_2O \quad (133)$$

$$CF_3CO \rightarrow CF_3 + CO \quad (134)$$

$$CF_3CO + O_2 \rightarrow CF_3C(O)O_2 \quad (135)$$

$$CF_3C(O)O_2 + NO \rightarrow CF_3C(O)O + NO_2 \quad (136)$$

$$CF_3C(O)O \rightarrow CF_3 + CO_2 \quad (137)$$

$$CF_3CHO \rightarrow CF_3H + CO \quad (138)$$

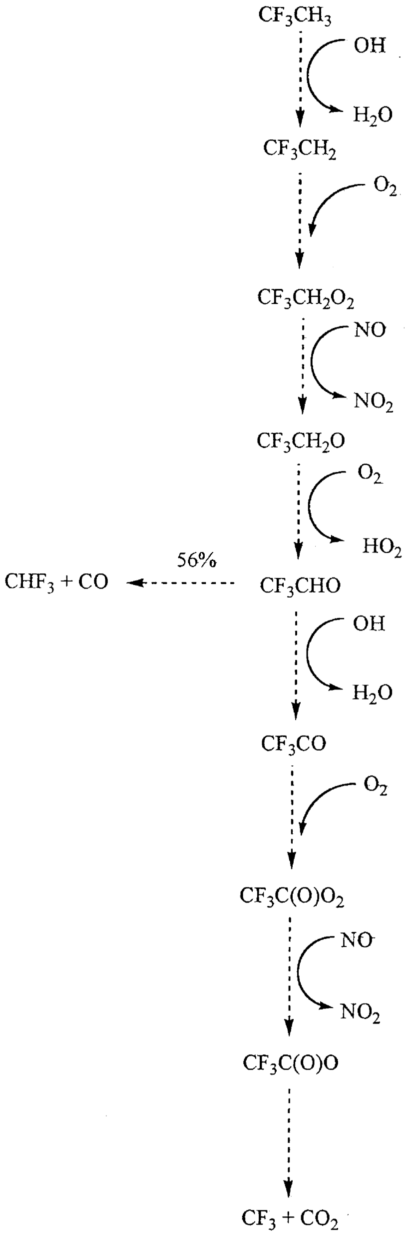

Figure 12. Atmospheric oxidation mechanism for HFC-143a. A significant fraction of the degradation mechanism involves a rearrangement to form CHF_3.

Reactions 134 and 135 are loss processes for the CF_3CO radical. Reaction 134 is endothermic, and thus reaction 135, which is generally very exothermic and proceeds without barrier, dominates. Reaction 138 is a photolytic rearrangement resulting in the formation of carbon monoxide and trifluoromethane. Estimates suggest a 56% yield of trifluoromethane.[116] CHF_3 has a lifetime of >250 years with strong IR-absorbing CF stretches. As a result, CHF_3 is a substantial greenhouse gas. In addition, the atmospheric oxidation of HFC-143a results in the formation of CF_3 and CO_2.

HFC-134a is a substitute for CFC-12 in refrigeration and air conditioning units.[128−130] The current global production is on the order of 10^5 tonnes $year^{-1}$ and is anticipated to double in the next 25 years.[131,132] The concentration of this compound in the troposphere, in the northern hemisphere, has been growing exponentially at >100% per year. In the mid 1990s, the mixing ratio was determined to be 2.0–2.6 pptv. A year later, Engen et al.[133] measured a concentration of 4.1 ± 0.8 pptv. Shirai et al.[134] report that the concentration is increasing by 83 ± 6% per year and, in 1998, was at 5.9 ± 1.2 pptv. HFC-134a is the result of exchanging a hydrogen atom for a fluorine atom in E143a. A fluorine atom opposing the CF_3 functional group negates some of the electron-withdrawing character of the CF_3 group. As a result, the rate constant is faster and the lifetime is much shorter, 14 years. The radiative forcing value continues to increase as the number of fluorine atoms within the molecule increases. HFC-134a has a radiative forcing value of 0.181 W m^{-2} ppb^{-1}. Despite the larger radiative forcing value, the shorter atmospheric lifetime results in a much smaller GWP, only 1300 as compared to HFC-143a's value of 3800.

There is also a marked change in the chemistry of the two species.

$$CF_3CH_2F + OH \rightarrow CF_3CHF + H_2O \quad (139)$$

$$CF_3CHF + O_2 \rightarrow CF_3CHFO_2 \quad (140)$$

$$CF_3CHFO_2 + NO \rightarrow CF_3CHFO + NO \quad (141)$$

$$CF_3CHFO \rightarrow CF_3 + CHFO \quad (142)$$

$$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2 \quad (143)$$

Reaction with hydroxyl radical has been measured to be 4.9 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K.[128,135] This value would lead to a calculated atmospheric lifetime on the order of 6.5 years based on reaction with OH; however, the total lifetime is suggested to be ~14.3 years.[2,119] Reaction with chlorine is equally slow ($k_{298} = 1.4 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-11}).[36] Because the atmospheric concentration of OH is roughly 3 orders of magnitude larger than the concentration of chlorine radicals, reaction with OH is expected to be the primary removal mechanism.

One difference now encountered in the oxidation mechanism is the competition between reactions 142 and 143. For the previous species, reaction with O_2 to yield HO_2 and a carbonyl was the dominant reaction. In this case, however, dissociation competes with the hydrogen abstraction reaction.[116,137,138] Wallington et al.[137] and Tuazon et al.[128] found the yield of CF_3COF to have both a pressure and a temperature dependence, and lower temperatures and pressures result in less fragmentation of the CF_3CFHO radical and thus higher yields of CF_3COF.[128] The CF_3COF yield was then predicted to be 25% at 0 km, 44% at 5 km, 71% at 10 km, and 80% at 15 km. Reaction of E134a is expected to yield mainly CF_3 and CHFO at the surface and CF_3COF at the tropopause. Reaction 141 has been determined to be exothermic by 17 kcal mol^{-1}. Wallington et al.[139] determined that roughly 64% of the resulting CF_3CHFO radicals had sufficient internal energy to undergo unimolecular decomposition. Maricq and Szente[140] measured k_{142} between the temperatures of 200 and 372 K using 230 Torr of N_2 and O_2. They report a rate expression of $k_{142} = 3.7 \times 10^7 \exp^{-2200/T}$. At 298 K, the rate constant is 2.0 × 10^4 s^{-1}. Bednarek et al.[141] measured the same rate constant to be 1.8 × 10^4 s^{-1} at 295 K. Mogelberg et al.[131] measured a lower limit for the rate of this reaction to be an order of magnitude faster at 3.3 × 10^5 s^{-1}. They found that at 1 atm of SF_6 diluent, 79 ± 20% of the CF_3CHFO radicals formed from reaction 141 decompose via CC bond scission. Thus, 21% of the time the oxidation of HFC-134a produces a very stable reservoir species, CF_3COF. Reaction with OH is impossible and photolysis is so slow that now heterogeneous processes dominated the removal of this intermediate.

HFC-125 (CF_3CHF_2) is almost fully fluorinated and, as a result, its rate of reaction with OH is slow. The rate expression is given by 4.9 × 10^{-13} $e^{-1655/T}$, yielding an atmospheric lifetime of ~36 years.[5,117,142] The larger number of C–F bonds yields a large value for the radiative forcing of 0.251 W m^{-2} ppb^{-1}. The result of these two properties is a substantial GWP of 2800. The degradation of HFC-125 is summarized by the following mechanism.[128,138,142,143] In this case, the alkoxy radical's only pathway is dissociation into CF_3 and CF_2O.

$$CF_3CHF_2 + OH \rightarrow CF_3CF_2 + H_2O \quad (144)$$

$$CF_3CF_2 + O_2 \rightarrow CF_3CF_2O_2 \quad (145)$$

$$CF_3CF_2O_2 + NO \rightarrow CF_3CF_2O + NO_2 \quad (146)$$

$$CF_3CF_2O \rightarrow CF_3 + CF_2O \quad (147)$$

Laboratory experiments show the formation of trioxy (i.e., $CF_3O_3CF_3$ and $CF_3O_3C_2F_5$) radicals resulting from secondary reactions involving CF_3O_2 and CF_3O radicals. However, under atmospheric conditions, these radicals have the following fates:

$$CF_3 + O_2 \rightarrow CF_3O_2 \quad (148)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \quad (149)$$

$$CF_3O + NO \rightarrow FNO + CF_2O \quad (150)$$

$$CF_3O + H_2O \rightarrow CF_3OH + OH \quad (151)$$

$$CF_3OH \rightarrow CF_2O + HF \quad (152)$$

The ultimate fate is the production of CF_2O, by either reaction 150 or 152. Reaction 150 is a fluorine abstraction reaction initiated by NO, whereas reaction 152 is a rearrangement followed by dissociation. In addition to reaction 152, CF_3OH can also be incorporated into water droplets and removed via wet deposition. In fact, reaction 152 is predicted to be negligibly slow under atmospheric conditions; thus, heterogeneous removal of CF_3OH is expected to dominate.[144,145]

One of the most stable intermediates formed during the oxidation of the above HFCs is CF_2O. Species such as this, as well as CF_3COF and CF_3COCl, are removed from the atmosphere through heterogeneous processes. These heterogeneous processes include wet deposition via rainout following incorporation into tropospheric clouds or dry deposition to the Earth's surface, predominately to the oceans. The rates of these processes are largely determined by the species' chemistry in aqueous solution and upon the solubility of these compounds in water. More specifically, atmospheric removal rates depend on both solubility as expressed in terms of the Henry's law constant (H in units of M atm^{-1}) and the hydrolysis rate (k_{hyd} in units of s^{-1}). The results from experimental determinations[116,122,146] of these values are listed in Table 3.

For CF_2O, CF_3COF, and CF_3COCl, the lifetime with respect to wet deposition is on the order of days. Thus, the lifetimes of these species are relatively insignificant with respect to the lifetime of the parent molecule. The major product from the hydrolysis of CF_3COF and CF_3COCl is $CF_3C(O)OH$, which is known as trifluoroacetic acid (TFA). TFA has no known sinks aside from rainout, and it is speculated that this species may impact agricultural and aquatic systems.[116,140] Visscher et al.[147] report that TFA may undergo microbial degradation in oxic sediments to produce the potent greenhouse gas CHF_3. TFA has been found to be only weakly phytotoxic; however, harmful levels could be reached over time in surface water systems that are characterized by little or no outflow.[148,149] On the basis of projected emissions of HFC-134a, HCFC-123, and HCFC-124, mass conservation arguments[121] suggest an annually averaged global concentration of 0.16 μg/L of TFA in rainwater by the year 2010. 3D chemical transport modeling results predict global annually averaged concentrations of 0.12 μg/L.

4.2.3. HFEs

Many of the HFCs listed above have fairly significant global warming potentials. Leading CFC replacements such as HFC-125, HFC-134a, and HFC-143a have GWPs not much lower than those of the CFCs they replace. In fact, many of the HCFCs would be better replacements than HFCs from a climate forcing perspective. Couple this to the indirect global-warming effect resulting from differences in the efficiencies of these systems, and the result is a serious issue concerning the use of many HFCs and their impact on climate. For this reason, research is still devoted toward the exploration of novel CFC alternatives, third-generation CFC alternatives.

One such third-generation CFC alternative is the hydrofluorinated ether (HFE) series. These species are analogous to the HFCs with the insertion of an ether linkage. The EPA developed a list of 37 candidate compounds proposed for use as working fluids, 13 of which were fluorinated ethers. The list was narrowed to 11 species, including CH_3OCF_3 and CHF_2OCF_3.[150−152]

Cooper et al.[153] used ab initio and semiempirical methods to estimate the energy of the highest occupied molecular orbital, which is then proportional to the rate of reaction with hydroxyl radical. Using this methodology, lifetimes for fluorinated derivatives of dimethyl ether were found to range from 7.3 days (CH_3OCH_2F) to 85 days (CHF_2OCF_3).

In 1992, Zhang et al.[154] measured the rate of reaction of fluorinated ethers with hydroxyl radical using a flash photolysis resonance fluorescence technique. E143a, E134, E125, E263, and E245 were found to have rate constants of 2.14×10^{-14}, 2.53×10^{-14}, 3.38×10^{-15}, $6.24 \times 10^{-,13}$ and 1.25×10^{-14} cm^3 molecule^{-1} s^{-1}, and lifetimes on the order of 3.0, 2.6, 19, 0.1, and 5.2 years, respectively, were determined.

Table 4. Rate Expressions, Lifetimes, and Radiative Forcing Values for Selected HFEs[a]

species	298 K rate constant, cm^3 molecule^{-1} s^{-1}	lifetime, years	radiative forcing, W m^{-2} ppb^{-1}
$CH_3OCF_2CF_2H$	$(2.04 \pm 0.33) \times 10^{-13}$	0.22	0.3
CH_3OCF_2CClFH	$(1.65 \pm 0.32) \times 10^{-13}$	0.27	0.26
$CH_3CH_2OCF_2CF_2H$	$(4.33 \pm 0.69) \times 10^{-13}$	0.10	0.315
$CF_3CH_2OCF_2CF_2H$	$(9.35 \pm 0.33) \times 10^{-14}$	0.48	0.465
$CH_2{=}CHCH_2OCF_2CF_2H$	$(1.85 \pm 0.41) \times 10^{-13}$	21.3 h	0.350

[a] Heathfield, A. E.; Anastasia, C.; Pagsberg, P.; McCulloch, A. *Atmos. Environ.* **1998**, *32*, 2825.

Garland et al.[155] in 1993 measured the rate of reaction of OH radicals with E134 using pump and probe laser induced fluorescence of OH. A rate expression of $5.4 \times 10^{-13}\ e^{-1560/T}$ was determined. At 298 K, the rate is found to be $(3.0 \pm 0.7) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. For E134, the results of Garland,[155] Huie,[154] and Hsu[156] are in reasonable agreement.

Good et al.,[6] using 2D chemical transport models, determined lifetimes based on the rate data of Hsu et al.[156] of 5.7, 29.0, and 165.0 years, respectively. These results suggest that these ethers have much longer atmospheric lifetimes than previously suspected.

Heathfield et al.[157,158] measured the integrated infrared absorption coefficients of E134 and E125 using FTIR methodology. Using a simple method for estimating the instantaneous radiative forcing given by Pinnock et al.,[119] Heathfield et al.[157] estimated the forcing values of E134 and E135 to be 0.43 and 0.41 W m^{-2} ppb^{-1}. Good et al.,[6] using integrated band strengths as determined from ab initio methodology along with a radiative transfer model, predicted the forcing values for E143a, E134, and E125 to be 0.26, 0.45, and 0.47 W m^{-2} ppb^{-1}, respectively. The addition of the ether linkage was found to have a dramatic effect on the radiative properties. HFC125, for example, has a radiative forcing value of 0.251 W m^{-2} ppb^{-1}, whereas E125 has a radiative forcing value of 0.47 W m^{-2} ppb^{-1}. Analogous trends exist for E143a and E134. GWPs calculated for each of these ethers are shown in Table 5, along with GWP values for analogous HFCs. Each ether is found to have greater global warming properties than the analogous HFC.[6]

E263 ($CF_3CH_2OCH_3$) has been found to have 298 K rate constants of 6.24×10^{-13} and 6.42×10^{-13} cm^3 molecule^{-1} s^{-1}. These rate constants lead to an atmospheric lifetime of ~18 days. E245 ($CF_3CH_2OCHF_2$) has measured rate constants of 1.25×10^{-14} and 1.07×10^{-14} cm^3 molecule^{-1} s^{-1}, yielding a lifetime of ~3 years.[154,158] Kambanis[159] studied the

Table 5. Comparison of Lifetimes and GWPs for Selected HFCs and HFEs[a]

species	formula	lifetime	GWP	GWP	GWP
HFC-125	CHF_2CF_3	32.6	4600	2800	920
E125	CHF_2OCF_3	165.2	11800	1400	9120
HFC-134	CHF_2CHF_2	10.6	2900	1000	310
E134	CHF_2OCHF_2	29.7	9760	5720	1830
HFC134a	CF_3OCH_2F	14.6	3400	1300	420
HFC143a	CH_3OCF_3	48.3	5000	3800	1400
E143a	CH_3OCF_3	5.7	2200	656	202
HFC-143	CHF_2OCH_2F	3.8	1000	300	94

[a] Reference 6.

rate of these ethers with Cl radicals. Reaction with Cl was found to have a small effect on the atmospheric lifetime of these ethers. The radiative properties of these species have yet to be determined.[159]

Heathfield,[157,158] using a pulsed radiolysis resonance fluorescence technique, measured the OH radical rate constants for the following ethers used in solvent applications: $CH_3OCF_2CF_2H$, CH_3OCF_2CClFH, $CF_3CH_2OCF_2CF_2H$, and $CH_2{=}CHCH_2OCF_2CF_2H$. Rate constants and resulting atmospheric lifetimes[157,158] were determined for each ether as shown in Table 4.

In Table 4, it is shown that the C_3-C_5 ethers are faster to react with hydroxyl radical than the C_2 ethers in Table 5. The ethers in Table 4 have significant hydrogen contents of 50, 50, 60, 30, and 60%, respectively. The slowest reaction in Table 4 has the least amount of hydrogen. As mentioned at the beginning of this section, compounds with 50% hydrogen content are considered to be marginally flammable. Thus, these ethers may be unacceptable alternatives based on flammability considerations.

E216 ($CF_3OCF{=}CF_2$) is used in dry-etching applications in the electronics industry. Li et al.[161] measured the reaction rate with hydroxyl radical using a resonance fluorescence discharge flow technique. The 298 K rate constant was measured to be $(3.16 \pm 0.21) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate may appear to be surprisingly fast for a molecule with no hydrogen atoms to abstract. In this case, reaction with hydroxyl radical proceeds via an addition mechanism across the double bond rather than by hydrogen abstraction. The lifetime derived from this rate constant is on the order of 5 days. A radiative forcing value of 0.266 W m^{-1} ppb^{-1} was measured using FTIR spectroscopy. With such a short atmospheric lifetime, the GWP was found to be small, <0.1 relative to CO_2 over all time horizons.[160] The results of Li et al.[161] have been confirmed by Mashino et al.[162]

The fast rate of this reaction is very interesting considering the conundrum developed at the beginning of this section. Large fluorine contents were associated with good thermophysical properties and lower toxicity but longer atmospheric lifetimes and global warming potentials. Large hydrogen contents were associated with short atmospheric lifetimes and low global warming and ozone depletion properties, but had problems with thermophysical properties and flammability. The incorporation of a double bond seems to offer a possible solution to this tradeoff.

5. Summary

The environmental concerns associated with alternative fuels and alternative refrigerants differ. In the case of alternative refrigerants, the dominant environmental issues are the destruction of stratospheric ozone and global warming caused in part by long atmospheric lifetimes. With respect to alternative fuels, the concern is the formation of tropospheric ozone caused by the rapid oxidation of the fuel and its combustion products. In both instances, there are no obvious replacements. Each fuel or refrigerant must also be evaluated on the basis of economics, material compatibility, efficiency, and safety. More recently, issues concerning the atmospheric fate have become equally important in evaluating the long-term use of replacement materials. For this reason, research is devoted to the development and evaluation of alternative anthropogenic substances.

In the case of alternative fuels, the Clean Air Act mandated the use of oxygenated organics such as *tert*-butyl alcohol and methyl *tert*-butyl ether in reformulated gasoline. These oxygenated organics were added to reduce CO emissions while maintaining engine performance. Later came proposals to use oxygenated organics, not just as additives, but as the base fuel. Methanol, ethanol, and dimethyl ether became popular candidates in fuel applications. DME is promising because it contains no carbon−carbon bonds and thus produces much less soot than conventional diesel fuels. DME may have some material compatibility issues due to volatility and because it is a powerful solvent. For this reason, the higher molecular weight species, dimethoxymethane ($CH_3OCH_2OCH_3$), may be considered. Dimethoxymethane, like DME, contains no C−C bonds and may be an improvement over DME in terms of material compatibility.

Even clean-burning fuels, however, produce the greenhouse gas carbon dioxide. Hydrogen, for example, is a very clean fuel source, yet its use would still result in a net production of CO_2 due to the energy (supplied from the burning of fossil fuels) required to produce hydrogen gas from the electrolysis of water. For this reason, much research is devoted to the exploration of alternative fuels derived from natural resources. The use of alternative fuels from natural resources would result in no net production of CO_2 because the CO_2 emitted to the atmosphere was taken from the atmosphere in connection with photosynthesis.

The first step in the development of novel alternative refrigerants involved the incorporation of hydrogen into the molecule so that degradation could take place in the troposphere instead of the stratosphere. These HCFCs still contained chlorine, however, and are thus meant to serve as temporary transitional species. HFCs contain no chlorine and thus have nearly negligible ozone depletion potentials. The concern now is global warming. Many of the HFCs have significant atmospheric lifetimes and are strong absorbers of infrared radiation due to the fact that their CF stretching modes resonate within the window region. Additional global-warming effects are incurred due to the decreased efficiency over which these systems operate. There is an inherent tradeoff between the relative amount of fluorine and hydrogen within a molecule. Large amounts of fluorine are favorable from a thermodynamic perspective but unfavorable due to increased atmospheric lifetime and radiative forcing properties. Large amounts of hydrogen result in short atmospheric lifetimes but raise thermodynamic and flammability concerns.

Fluorinated ethers were proposed for use because of expected shorter atmospheric lifetimes due to the presence of the ether linkage. Thus, larger amounts of fluorine may be used while maintaining a relatively short atmospheric lifetime. Recent kinetic and modeling studies have suggested that this broad generalization may not be valid.

An alternative (or additional) structural change may be the use of carbon−carbon double bonds or carbonyl bonds to the basic HFC framework. The incorporation of a double bond makes the molecule susceptible to fast OH radical addition reactions. The addition of the carbonyl bond brings in a photochemical removal channel. Thus, the need for hydrogen in the molecule is unnecessary. Fully halogenated compounds can be developed while maintaining short atmospheric lifetimes. It is unclear whether such compounds could potentially be useful; however, as the number of possible candidates increases, so too does the probability of finding acceptable alternatives.

6. References

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