Chem. Rev. **2003,** *103,* 4657–4689

The Atmospheric Chemistry of Alkoxy Radicals

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Received March 31, 2003

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1. Introduction

The importance of hydrocarbons in the Earth's troposphere has been recognized since the 1950s, when their contribution (along with that of NO_x, i.e., NO and NO_2) to urban (Los Angeles) "smog" formation was first outlined.[1−3] While air quality in urban areas is still a major issue, it is also now recognized that about 90% of the hydrocarbons emitted to the atmosphere arise from biogenic sources,[4] implying that the impact of hydrocarbon oxidation chemistry extends over much larger regions of the globe. For example, the combination of biogenic hydrocarbon and anthropogenic NO_x emissions in the southeastern USA has led to widespread surface ozone problems in that region.[5−7] It is also now recognized that the impacts of hydrocarbon chemistry are not limited to the Earth's surface, but also reach to the upper troposphere. Here, photolysis of various oxygenated organics (either generated in situ or transported via convection) has been shown to be a major source of OH and HO_2 radicals, thus driving ozone production in a region where this species exerts a particularly strong radiative (i.e., "greenhouse") effect.[8−10] Thus, it is clear that there is a great need to study hydrocarbon chemistry in detail, not only under urban conditions (1 atm pressure, 298 K), but also at the lower temperature and pressure conditions relevant to the free and upper troposphere. As will be shown below in more detail, it is the chemistry of the alkoxy radicals that is inevitably responsible for the determination of the nature of the first-generation end-products of the oxidation of a hydrocarbon, and thus mechanistic determinations usually reduce to a study of these key intermediates.

A general oxidation scheme for a hydrocarbon RH is outlined in Figure 1.[11−15] The initial attack of OH on the parent hydrocarbon leads to the rapid production of peroxy radicals, $RO_2^{\bullet}$. In the case of a complex hydrocarbon, there can be multiple sites for OH attack, and hence a complex mixture of $RO_2^{\bullet}$ radicals can be produced. The peroxy radicals are then converted to the corresponding alkoxy radical, usually via reaction with NO or, to a lesser extent, via self-reaction or reaction with other peroxy radicals (generally $CH_3O_2^{\bullet}$, since this is usually the most abundant organic peroxy radical in the atmosphere):

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \qquad (1)$$

$$RO_2^{\bullet} + CH_3O_2^{\bullet} \rightarrow RO^{\bullet} + CH_3O^{\bullet} + O_2 \qquad (2a)$$

$$\rightarrow \text{nonradical products (carbonyls, alcohols)} \qquad (2b)$$

It is the conversion of NO to NO_2 in reaction 1 that provides the net source of ozone, as subsequent photolysis of the NO_2 is followed by the recombination of the $O(^3P)$ photoproduct with O_2. In the labor-

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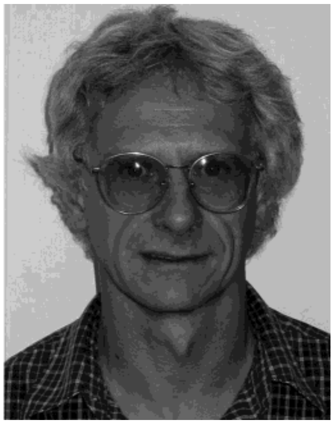
10.1021/cr020527p CCC: $44.00

John J. Orlando was born in Timmins, Ontario, Canada, in 1960. He received both his B.Sc. (1982) and Ph.D. degrees (1987) in chemistry from McMaster University in Hamilton, Canada. He then spent two years as a postdoctoral fellow at the NOAA Aeronomy Laboratory under the supervision of Drs. C. J. Howard and A. R. Ravishankara, working mostly on problems related to the effects of halogens on stratospheric ozone. John has been employed as a scientist in the Atmospheric Chemistry Division of the National Center for Atmospheric Research (NCAR) since 1989, as a member of the laboratory kinetics group. His research at NCAR has focused largely on the determination of the mechanisms of the atmospheric oxidation of carbon-containing species, on halogen chemistry of relevance to the stratosphere, and on the atmospheric chemistry of nitrogen oxide species.



Geoffrey S. Tyndall was born in Mansfield, U.K., in 1955. His undergraduate and graduate studies were conducted at Cambridge University, where he obtained a B.A. in chemistry in 1978, and a Ph.D. in physical chemistry in 1982 (under the supervision of Professor B. A. Thrush). His postdoctoral work was carried out at the Max-Planck-Institut für Chemie in Mainz, West Germany, with Dr. G. K. Moortgat (1983–1986), and at the NOAA Aeronomy Laboratory, with Dr. A. R. Ravishankara (1986–1988). Geoff moved to NCAR in 1988, and has been a scientist in the Atmospheric Chemistry Division ever since. He is currently the leader of the Laboratory Kinetics Group. Geoff's research over the years has focussed on many aspects of atmospheric photochemistry, including the study of the kinetics and spectroscopy of HO_2 and organic peroxy radicals, the study of atmospheric sulfur and nitrogen chemistry, and studies of the atmospheric oxidation mechanisms of anthropogenic and biogenic hydrocarbons.

Timothy Wallington was born in England in 1958. He received his B.A. (1981) and Ph.D. (1983) from Oxford University, where he worked under the supervision of Profs. Richard Wayne and Tony Cox (at A.E.R.E. Harwell). In 1984–1986, he studied air pollution chemistry with Profs. James N. Pitts, Jr., and Roger Atkinson at the Statewide Air Pollution Research Center in Riverside, California. In 1987, he studied OH reaction kinetics at the National Bureau of Standards (now the National Institute of Standards and Technology) in Gaithersburg, Maryland, with Dr. Michael J. Kurylo. In late 1987, he moved to the Scientific Research Laboratory of Ford Motor Company in Dearborn, Michigan. In 1998–1999, he was a Humboldt Fellow at the Universität Wuppertal (Germany), working with Prof. Karl Heinz Becker. In 2003, he completed an MBA at the University of Michigan. He currently leads the Air Quality and Climate Change research group at Ford Motor Company.

atory, these same alkoxy radical source reactions are often employed, though photolysis or pyrolysis of the corresponding alkyl nitrite has also been utilized:

$$\mathrm{RONO} + h\nu, \Delta \rightarrow \mathrm{RO}^{\bullet} + \mathrm{NO} \qquad (3)$$

Once formed in the atmosphere, the alkoxy radicals can potentially undergo a number of competing reaction pathways, including (1) reaction with O_2, which occurs via α-hydrogen abstraction to generate a carbonyl compound and HO_2, (2) unimolecular decomposition, which usually occurs through C−C bond fission to produce a carbonyl compound and an alkyl fragment, and/or (3) unimolecular isomerization (usually via a 1,5-H shift), which generates a hydroxy-substituted alkyl radical. These competing pathways are illustrated for the 2-pentoxy radical in Figure 2. In the case of some halogen- or oxygen-substituted alkoxy radicals, other unimolecular processes are possible, as will be discussed in more detail later. Furthermore, under laboratory settings in particular, reactions of the alkoxy radicals with either NO or NO_2, to form alkyl nitrites or alkyl

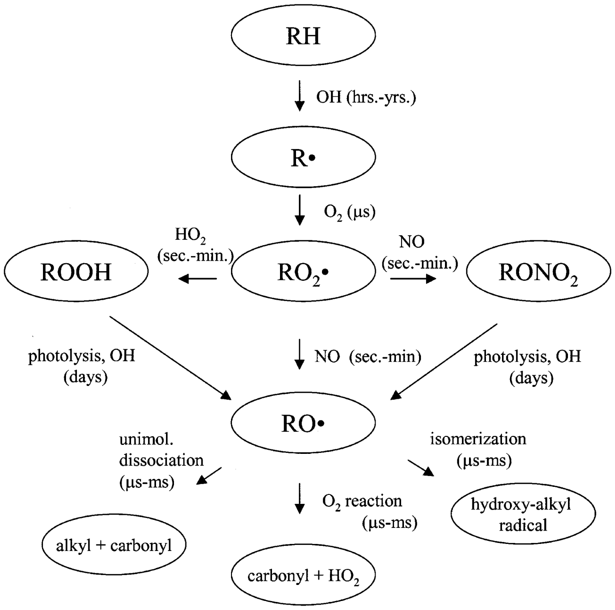


Figure 1. General hydrocarbon oxidation scheme.

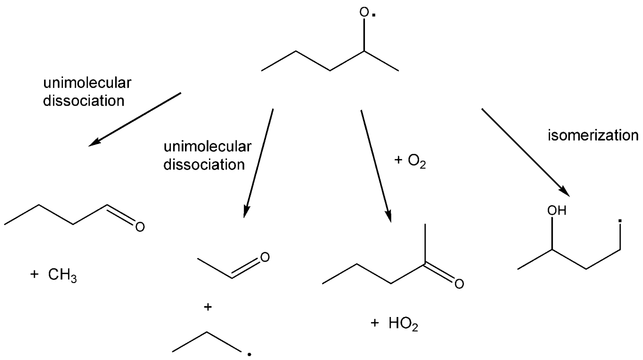


Figure 2. Chemistry of the 2-pentoxy radical, illustrating potential reaction pathways for a typical alkoxy radical.

nitrates, are also encountered:

$$RO^{\bullet} + NO + M \rightarrow RONO + M \qquad (4)$$

$$RO^{\bullet} + NO_2 + M \rightarrow RONO_2 + M \qquad (5)$$

Since reaction with O_2 proceeds with a rate coefficient on the order of 10^{-14} cm^3 $molecule^{-1}$ s^{-1},[11-15] the alkoxy radical lifetime in the lower atmosphere is at most 0.1 ms, and thus other processes must occur on similar time scales to be of atmospheric relevance. An exception is for tertiary alkoxy radicals such as *tert*-butoxy, for which O_2 reaction is not possible, allowing slower unimolecular processes to play a role.

As alluded to earlier, it is the competition between these various potential alkoxy radical reaction pathways that determines the eventual stable products of a particular oxidation scheme, and thus elucidation of the alkoxy radical chemistry is paramount in obtaining a quantitative understanding of the tropospheric impact of a particular hydrocarbon. In general, unimolecular decomposition leads to a more rapid breakdown of the carbon chain, the generation of more reactive short-chain carbonyl compounds, and a larger potential for photochemical ozone formation. On the other hand, reaction with O_2 and unimolecular isomerization leads to a preservation of the carbon chain, the production of less reactive and more highly substituted oxygenated species, and the dampening of the potential for local ozone formation. Furthermore, these more highly substituted species are generally more soluble and less volatile than the shorter-chain species, and are thus more prone to participate in aerosol nucleation and growth processes and aqueous-phase chemistry.

The existence of a wide range of possible reaction channels makes the study of the alkoxy radicals an interesting, yet difficult, challenge. Further complexity arises from the fact that the vast majority of the unimolecular reaction pathways referred to in the preceding paragraphs occur through significant barriers,[11-15] implying large changes in rate with temperature and concomitant changes in product distributions with altitude in the troposphere. These unimolecular processes are typically in the pressure falloff region near atmospheric pressure, making comparisons of environmental chamber data (usually obtained near atmospheric pressure) with direct kinetics studies (often obtained at reduced pressure) difficult; theoretical studies have been particularly useful here in bridging different data sets, and in providing kinetic data over the range of conditions relevant to the atmosphere. Further complications arise from subtleties in the dynamics of the alkoxy radical source reactions. In particular, the reactions of organic peroxy radicals with NO are exothermic and proceed through the formation of activated ROONO complexes, thus imparting internal energy to the nascent alkoxy radical product. As will be discussed in detail below, these chemically activated alkoxy radicals may be more prone to unimolecular reaction than their thermal counterparts.[16-23]

The importance of alkoxy radicals in the atmosphere has prompted the study of their chemistry via a number of different approaches. End-product analyses of hydrocarbon oxidation, which provide information on the relative importance of alkoxy radical reaction pathways, have been complemented by time-resolved kinetics studies involving direct detection of the alkoxy radicals themselves. As alluded to earlier, theoretical methods are now being applied to the determination of alkoxy radical unimolecular rate coefficients. However, a full description of the chemistry of the relevant alkoxy radicals over the full range of atmospheric temperature and pressure conditions has yet to be obtained. Given the complex nature of the systems requiring further study (e.g., monoterpenes, aromatic species), progress in the future will require participation of scientists from a range of disciplines. For example, improved analytical techniques will be required to allow for the direct detection of larger alkoxy radicals in time-resolved studies, and also for the identification and quantification of the complex suite of multifunctional end-products likely to be encountered. The involvement of synthetic organic chemists will also be required to provide standard samples needed for the unique identification and quantification of these multifunctional species.

The following sections will summarize the methods that have been used to study alkoxy radical chemistry, and to present the current state of knowledge regarding the rates and mechanisms of the various reaction pathways. We will then conclude by summarizing some of the remaining uncertainties in the atmospheric chemistry of the alkoxy radicals, and providing some suggestions for future study.

2. Experimental Techniques Employed in the Study of Alkoxy Radical Chemistry

Methods used in the determination of rate coefficients for reactions of alkoxy radicals can, for the most part, be grouped into three categories: (1) pyrolysis or photolysis of static gas mixtures, in which end-product analysis is used to determine relative rates for competing alkoxy radical reactions; (2) time-resolved studies, using pulsed laser photolysis for alkoxy radical generation and pulsed laser-induced fluorescence for detection; and (3) theoretical methods, which have been applied recently to the determination of rate coefficients for unimolecular reactions of alkoxy radicals.

Though not the earliest work on alkoxy radical reactivity, ground-breaking studies were carried out by various groups in the 1970s, in which relative rates for various alkoxy radical reactions were determined.[24−37] Typically, pyrolysis or photolysis of an alkyl nitrite or a dialkyl peroxide was used as the alkoxy radical source, and end-product analyses in the presence of various combinations of O_2 and NO_x were used to determine relative rates. For example, Batt and co-workers[24−29] studied the pyrolysis (at roughly 350−500 K) of alkyl nitrite or dialkyl peroxide precursors, and were able to determine relative rates for alkoxy radical decomposition reactions versus recombination with NO, as illustrated below for the *tert*-butoxy radical:

$$(CH_3)_3CONO + M \rightarrow (CH_3)_3CO^\bullet + NO + M \quad (6)$$

$$(CH_3)_3CO^\bullet + NO + M \rightarrow (CH_3)_3CONO + M \quad (7)$$

$$(CH_3)_3CO^\bullet + M \rightarrow (CH_3)_2CO + {}^\bullet CH_3 + M \quad (8)$$

These studies provided a set of self-consistent Arrhenius parameters for the decomposition of a range of simple, relatively small (five-carbon or less) alkoxy radicals, and provided the foundation for many of the reviews and recommendations[11−15] of tropospheric alkoxy radical chemistry into the 1990s. However, as will become apparent later in this review, recent studies have shown that both the *A*-factors and the activation energies for these alkoxy radical decomposition reactions are significantly lower than the values reported in these earlier works.

Relative rate studies of alkoxy radical rate coefficients under conditions more relevant to the atmosphere have generally been conducted using “smog” or “environmental” chamber methodologies (e.g., refs 38−140). In these studies, static gas mixtures are photolyzed to initiate the oxidation of a particular hydrocarbon (usually via the production of either OH or Cl atoms), and the end-products of the oxidation process are monitored, usually via FT-IR spectroscopy, GC or GC/MS techniques, or chemical-ionization mass spectroscopy. The yields of the various end-products are then used to determine the major reaction pathway(s) available to each of the relevant alkoxy radical(s). In addition, relative rate coefficients can be obtained in cases where competing pathways are occurring in parallel. These most often involve a competition between a unimolecular process and reaction with O_2, as illustrated below for the 2-butoxy radical generated in the oxidation of butane:[42,56,60,69]

$$CH_3CH_2CH(O^\bullet)CH_3 + O_2 \rightarrow \mathbf{CH_3CH_2C({=}O)CH_3} + HO_2 \quad (9)$$

$$CH_3CH_2CH(O^\bullet)CH_3 \rightarrow CH_3CH_2^\bullet + \mathbf{CH_3CHO} \quad (10)$$

$$CH_3CH_2^\bullet + O_2 \rightarrow CH_3CH_2OO^\bullet \quad (11)$$

$$CH_3CH_2OO^\bullet + NO \rightarrow CH_3CH_2O^\bullet + NO_2 \quad (12)$$

$$CH_3CH_2O^\bullet + O_2 \rightarrow \mathbf{CH_3CHO} + HO_2 \quad (13)$$

Thus, relative yields of 2-butanone to acetaldehyde as a function of O_2 partial pressure have been used to establish the rate coefficient ratio k_9/k_{10} that, when coupled with measurements for k_9, can be used to obtain an estimate of k_{10}. As will be detailed later, estimates of unimolecular reaction rate coefficients for a wide range of alkoxy radicals have been obtained in this fashion, including those for a number of oxygen- and halogen-substituted alkoxy radicals.

These environmental chamber types of studies have definite limitations in terms of their ability to provide accurate Arrhenius parameters for alkoxy radical decompositions or isomerizations. Most notably, the lack of a broad, well-established rate coefficient database for reaction of alkoxy radicals with O_2 (see section 3.1 below) limits the accuracy of the retrieved unimolecular rate coefficient data. Note, however, that this is often not a major limitation in terms of understanding the impact of a particular hydrocarbon in the atmosphere, since only the relative rate of the multiple rapid, competing alkoxy radical reactions is required for this purpose. Another limitation stems from the fact that most chamber systems are limited to use at ambient temperature, thus precluding the determination of Arrhenius parameters for the decomposition reactions. One exception is work being carried out by our research groups using a temperature-regulated environmental chamber system, which has been applied to the study of a number of alkoxy radical systems.[16−18,20−23,70−72,79,139,140] Further limitations arise from the inability to detect and quantify complex, multifunctional reaction products by traditional (FT-IR and GC) methods; as mentioned in the Introduction, further developments in our ability to detect these multifunctional species, and the participation of synthetic chemists in preparing quantitative standards, would be helpful in this regard.

Direct studies of alkoxy radical chemistry have predominantly been carried out using pulsed laser photolysis to generate the alkoxy radicals, and pulsed laser-induced fluorescence for their detection. Until very recently, time-resolved rate coefficient data were limited to a handful of studies in the 1980s,[141−149] focusing on the reaction of O_2 or NO_x with only the simplest alkoxy radicals (methoxy, ethoxy, and isopropoxy), and these data have provided the basis for recommendations[11−15] for these and larger alkoxy radicals. There has, however, been a recent resurgence in the study of alkoxy radical reactions via time-resolved LIF techniques.[150−160] This recent work has led to an extension of the database to reactions of larger alkoxy radicals with O_2 and with NO and, perhaps more importantly, has led to the first direct determinations of dissociation processes[150−153,160] for at least a few alkoxy radicals, namely ethoxy, 2-propoxy, *tert*-butoxy, and 2-butoxy. Furthermore, these studies have been conducted over ranges of temperature and pressure, allowing for the construct of full falloff curves for these processes for the first time. In parallel to these LIF studies, Carr and co-workers[161−163] have developed a flash photolysis/mass spectrometer system that they have applied to the time-resolved study of halogenated alkoxy radical reactions. For example, data on the unimolecular dissociation of $CH_2ClO^•$ and its reaction with O_2 and NO have been obtained via time-resolved detection of various products of the chemistry.

Another major recent advancement in the study of alkoxy radical chemistry has been the application of various theoretical methodologies to the determination of the rates of unimolecular reactions of alkoxy radicals.[150−153,164−192] In general, quantum chemical calculations are performed to establish structures, vibrational frequencies, and energies of reactants, products, and transition states, and these data are then used as input for statistical kinetics calculations of the relevant unimolecular processes. While much work[150−153,164−169,175,189] has focused on the study of relatively small alkane-derived alkoxy radicals (e.g., methoxy through the various butoxy and pentoxy isomers), studies of halogen- and oxygen-substituted radicals have also been performed.[170−174,176−192] One of the great advantages of these techniques is their ability to provide data on a whole suite of related radicals via the same method, thus providing self-consistent data sets which have proven useful in the development of structure−reactivity relationships. Also, as is most evident in the work of Dibble and co-workers[179,181,182] and Peeters and co-workers,[177,178] the theoretical treatments are able to assess the likelihood of the occurrence of complicated unimolecular reactions (e.g., isomerization reactions in the oxidation of terpenes), reactions that are difficult to isolate and identify in chamber experiments.

3. Chemistry of the Alkoxy Radicals

3.1. Reaction with O_2

As alluded to earlier, direct measurements of the rate coefficients for reaction of O_2 with alkoxy radicals are rather sparse. In fact, with only two exceptions (the reactions of $CFCl_2CH_2O^•$ and $CH_2ClO^•$ with O_2), data are limited to a subset of the alkoxy radicals derived from the C1−C5 alkanes. While measurements made to date on non-halogenated radicals indicate rate coefficients within a factor of 2 of 1×10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K for all but the methoxy radical, some (but not all)[160] recent data[154,155] suggest that subtleties may exist in the temperature dependence for these reactions, with reactions of smaller radicals possessing positive temperature dependencies and larger radicals showing negative temperature dependencies. In this section, these direct measurements of alkoxy radical reactions with O_2 are summarized and evaluated and used to derive recommended Arrhenius expressions where appropriate. In addition, a number of older, indirect studies are presented and re-evaluated where possible.

3.1.1. $CH_3O^•$ + O_2

The reaction of methoxy radicals with O_2 has been the subject of absolute rate,[141−143,145,146] relative rate,[30−37] and computational[193−195] studies. Product studies conducted by Zellner[196] indicate that the reaction proceeds via an abstraction mechanism to give HCHO and an HO_2 radical in a yield of 0.85 ± 0.15 at 298 K, consistent with the generally accepted mechanism. The absolute studies were all conducted using the laser flash photolysis−laser-induced fluorescence (LFP−LIF) technique, with $CH_3O^•$ radicals generated by photolysis of either CH_3ONO or CH_3OH. In the first absolute rate study of this reaction, no reaction was observed, and an upper limit of $k_{CH_3O+O_2} < 2 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature was reported.[141] In subsequent absolute rate studies, reaction was observed, and the results shown by the filled symbols in Figure 3 were reported. No effect of total pressure on the rate of the reaction has been reported.[143,145,146] As shown in Figure 3, in the three absolute rate studies in which reaction was observed, the results are in good agreement. As noted previously,[146] the results obtained at temperatures greater than 800 K indicate an unusually pronounced curvature in the Arrhenius plot. While the computational study by Setokuchi and Sato[195] indicates that such curvature may be attributable to tunneling effects, the magnitude of the curvature observed in the experimental data is substantially greater than that predicted from the computational study. Further work is needed at high temperatures to better define the kinetics of the reaction. No recommendation can be made for $T >$ 610 K. A linear least-squares fit to the absolute rate combined data set for temperatures in the range 298−610 K gives $k_{CH_3O+O_2} = (7.82^{+4.68}_{-2.93}) \times 10^{-14}$ $\exp[-(1150 \pm 190)/T]$ cm^3 $molecule^{-1}$ s^{-1}. Quoted uncertainties are 2 standard deviations from the regression analysis. At 298 K this expression yields $k_{CH_3O+O_2} = 1.6 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}.

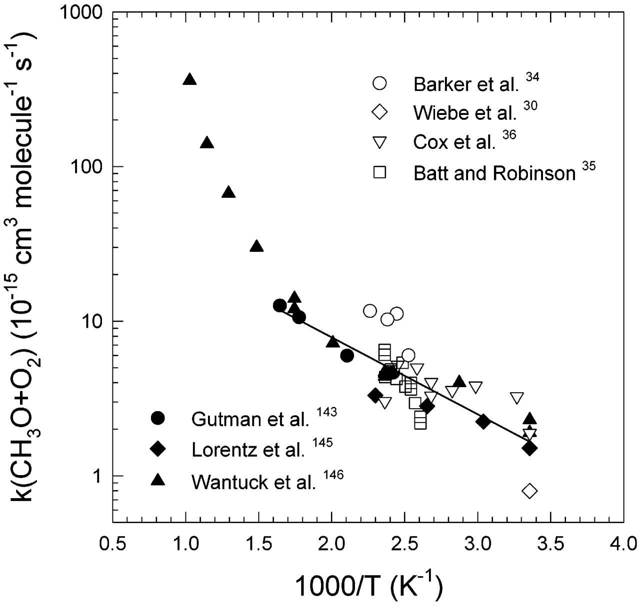


Figure 3. Rate coefficient data for reaction of CH_3O radicals with O_2, plotted in Arrhenius form.

There have been a large number of rather indirect relative rate studies of the kinetics of the $CH_3O^•$ + O_2 reaction. Most studies have used the photolysis of CH_3ONO or the pyrolysis of CH_3OOCH_3 or CH_3ONO in mixtures containing O_2 and at least one other competitor for $CH_3O^•$ radicals (usually NO or NO_2). The chemistry occurring in such systems is complex, and the data analysis is far from straightforward.

Most of the competitive rate studies were conducted in the 1970s. At that time there was limited information concerning the mechanism and kinetics of the reference reactions (particularly the reactions of $CH_3O^\bullet$ with NO and NO_2). In an attempt to update the relative rate data, we have reanalyzed representative data using the latest understanding of the kinetics and mechanisms of the reference reactions as recommended by the IUPAC committee.[197] Details are given below. The results are shown by the open symbols in Figure 3. Although there is considerable scatter in the relative rate data, it can be seen from Figure 3 that there is general agreement between the relative and absolute results.

Wiebe et al.[30] used the photolysis of $CH_3ONO/NO/O_2/N_2$ mixtures in N_2 diluent with added NO and O_2 and measured the reactivity of $CH_3O^\bullet$ toward O_2 relative to reaction with NO. They reported $k_{13}/(k_{14a} + k_{14b}) = 4.7 \times 10^{-5}$ and $k_{14b}/(k_{14a} + k_{14b}) = 0.145$, from which we can derive $k_{13}/k_{14a} = 5.5 \times 10^{-5}$ at 298 K in 106−148 Torr total pressure with N_2 diluent. It is now established that the rate of k_{14a} increases from 1.3×10^{-11} to 1.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} in 106−148 Torr N_2 diluent. Taking an average value of $k_{14a} = 1.45 \times 10^{-11}$ with $k_{13}/k_{14a} = 5.5 \times 10^{-5}$ gives $k_{13} = 7.98 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$$CH_3O^\bullet + O_2 \rightarrow HCHO + HO_2 \quad (13)$$

$$CH_3O^\bullet + NO + M \rightarrow CH_3ONO + M \quad (14a)$$

$$CH_3O^\bullet + NO \rightarrow HCHO + HNO \quad (14b)$$

Barker et al.[34] measured the change in total pressure on pyrolysis of the peroxide CH_3OOCH_3 in the presence of varying amounts of NO_2 and O_2 in 700 Torr total pressure at 396−442 K and derived values for the rate constant ratio k_{13}/k_{15a}.

$$CH_3O^\bullet + NO_2 + M \rightarrow CH_3ONO_2 + M \quad (15a)$$

$$CH_3O^\bullet + NO_2 \rightarrow HCHO + HNO_2 \quad (15b)$$

In their data analysis, Barker et al.[34] assumed $k_{14b}/k_{14a} = 0.18$ and $k_{15b}/k_{15a} = 0.30$. The current understanding suggests that, at pressures >10 Torr, the H-abstraction pathways (eqs 14b and 15b) play only a minor role.[197] Reanalysis of the data presented by Barker et al.[34] using $k_{0(15a)} = 9.0 \times 10^{-29}(T/300)^{-4.5}$ cm^6 $molecule^{-2}$ s^{-1}, $k_{\infty(15a)} = 1.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and $F_c = 0.44$, assuming[197] that $k_{15b}/k_{15a} = k_{14b}/k_{14a} \approx 0$, gives the data shown in Figure 3.

In the most recent of the relative rate approaches, Cox et al.[36] photolyzed CH_3ONO in the presence of NO_2 and O_2 in 1 atm of N_2 diluent and derived values of the rate constant ratio k_{13}/k_{15a}. Experiments at 298 K gave $k_{13}/k_{15a} = (1.25 \pm 0.37) \times 10^{-4}$, which can be combined with $k_{15a} = 1.5 \times 10^{-11}$ (ref 197) to give $k_{13} = (1.88 \pm 0.56) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. As shown in Figure 3, this result is in good agreement with the absolute rate data and the present recommendation. While, as noted by Cox et al.,[36] their data at higher temperature are less well defined than those at 298 K, the results are nevertheless reasonably consistent with the absolute rate data. As shown in Figure 3, the results from the body of relative rate experiments, although rather scattered and subject to significant uncertainties associated with the complex chemical systems employed, are consistent with the results from the more direct absolute rate studies.

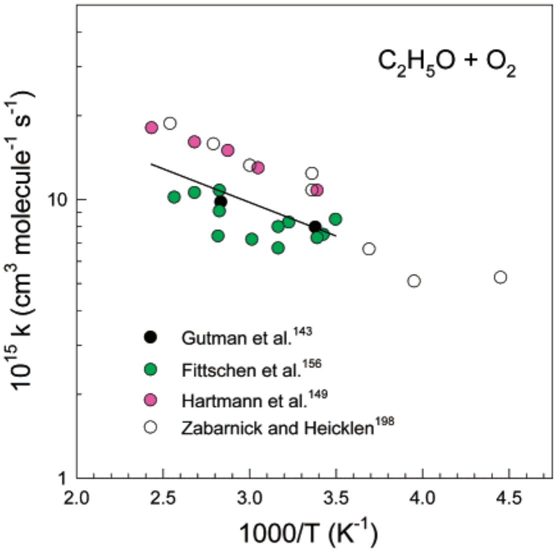


Figure 4. Rate coefficient data for reaction of CH_3CH_2O radicals with O_2, plotted in Arrhenius form.

On the basis of computational results, it has been suggested that reaction of $CH_3O^\bullet$ radicals with O_2 proceeds via the formation of a short-lived trioxide species, $CH_3OOO^\bullet$.[193] However, recent computational work indicates that reaction occurs via a $CH_3O\cdots O_2$ complex which is held together by a noncovalent $O\cdot\cdot\cdot O$ bonding interaction.[194,195] At 298 K, the bulk of the reaction (~90%) proceeds via tunneling of the hydrogen atom through the 2.8 kcal mol^{-1} barrier for hydrogen atom transfer.[194] There are no available data for $k_{CH_3O+O_2}$ at subambient temperature, and, as noted above, the reported data at temperatures greater than 700 K appear to be anomalous. Further work is needed to better define the kinetics of the reaction of methoxy radicals at $T > 700$ K and $T < 300$ K.

3.1.2. $C_2H_5O\bullet + O_2$

There have been absolute rate,[143,149,156] relative rate,[198] and computational[195] studies of the reaction of ethoxy radicals with O_2. All three absolute rate studies used the same experimental method: laser flash photolysis of C_2H_5ONO as a source of $C_2H_5O^\bullet$ radicals, with the decay of $C_2H_5O^\bullet$ in the presence of O_2 monitored by LIF. As shown in Figure 4, all three studies show a small but discernible increase in reaction rate with increasing temperature. For reasons which are unclear, the results from Hartmann et al.[149] lie approximately 30−50% higher than those of Gutman et al.[143] and Fittschen et al.[156] This difference may reflect the presence of systematic error in one or more of the studies, or it may simply reflect the level of difficulty and consequent uncertainty inherent in such measurements. There is no compelling reason to prefer any of the studies, and we recommend a value of $k_{C_2H_5O+O_2} = (5.13^{+9.70}_{-3.32}) \times 10^{-14} \exp[-(550 \pm 350)/T]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 280−420 K, derived from a least-squares fit to the combined absolute rate data set shown in Figure 4. At 298 K, this expression gives $k_{C_2H_5O+O_2} = 8.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Zabarnick and Heicklen[198] measured $k_{C_2H_5O+O_2}$ relative to $k_{C_2H_5O+NO}$ by photolyzing C_2H_5ONO in the presence of O_2 and measuring the effect of O_2 concentration on the yield of CH_3CHO. These results, scaled to the most recent recommendation[197] for the association reaction $k_{C_2H_5O+NO}$, are plotted in Figure 4. The results from the relative rate study are consistent with those derived from the direct studies.

Hartmann et al.[149] measured the yield of HO_2 radicals in the reaction by converting HO_2 radicals into OH radicals by reaction with NO and measuring the OH yield by LIF. Hartmann et al.[149] reported a yield of HO_2 radicals of $0.89^{+0.22}_{-0.12}$, demonstrating that, within the experimental uncertainties, the reaction proceeds essentially 100% via H atom abstraction:

$$C_2H_5O^{\bullet} + O_2 \rightarrow CH_3CHO + HO_2 \qquad (16)$$

Setokuchi and Sato[195] have reported the results of a computational study of the kinetics and mechanism of reaction 16. As with other reactions of O_2 with alkoxy radicals, it was found that reaction 16 proceeds via the formation of a weakly bound complex. Unlike any other reaction of its type studied thus far, it was reported that both ground-state A″ ethoxy radicals and the low-lying electronically excited A′ ethoxy radicals participate in the overall reaction.

Further work is needed both to narrow the uncertainties evident from the data spread in Figure 4 and to extend the temperature range to the atmospherically relevant temperature range (200−300 K).

3.1.3. $1\text{-}C_3H_7O^{\bullet}$, $2\text{-}C_3H_7O^{\bullet}$, $1\text{-}C_4H_9O^{\bullet}$, $2\text{-}C_4H_9O^{\bullet}$, $3\text{-}C_5H_{11}O^{\bullet} + O_2$

Absolute rate studies of $1\text{-}C_3H_7O^{\bullet}$,[156,157] $2\text{-}C_3H_7O^{\bullet}$,[144,154,157] $1\text{-}C_4H_9O^{\bullet}$,[158] $2\text{-}C_4H_9O^{\bullet}$,[154,155,159,160] $1\text{-}C_5H_{11}O^{\bullet}$,[158] and $3\text{-}C_5H_{11}O^{\bullet}$ [154,199] have been conducted using the LFP−LIF technique with alkoxy radicals, $RO^{\bullet}$, generated either by photolysis of the alkyl nitrite, RONO, or by photolysis of the alkyl bromide, RBr, in O_2 diluent in the presence of NO. No effect of total pressure on the kinetics of these reactions has been observed (e.g., over the range 50−150 Torr at 243 K for $3\text{-}C_5H_{11}O^{\bullet} + O_2$). The results are plotted in Figure 5. As seen from inspection of the data indicated by triangles ($1\text{-}C_3H_7O^{\bullet}$) and circles ($2\text{-}C_3H_7O^{\bullet}$) in Figure 5, there is good agreement in the rate data reported for reaction of $1\text{-}C_3H_7O^{\bullet}$ and $2\text{-}C_3H_7O^{\bullet}$ radicals with O_2. From Figure 5, it is clear that $1\text{-}C_3H_7O^{\bullet}$ radicals are almost twice as reactive as $2\text{-}C_3H_7O^{\bullet}$ radicals toward O_2 at all temperatures for which data are available. Zabarnick and Heicklen[200] measured $k_{1-C_3H_7O+O_2}$ relative to $k_{1-C_3H_7O+NO}$ by photolyzing C_3H_7ONO in the presence of O_2 and measuring the effect of O_2 concentration on the yield of C_2H_5CHO in 150 Torr N_2 diluent at 247−361 K. Zabarnick and Heicklen[200] used $k_{C_3H_7O+NO} = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} to derive values of $k_{1-C_3H_7O+O_2}$ which increase from 9.7×10^{-15} to 2.8×10^{-14} cm^3 molecule^{-1} s^{-1} as the temperature is increased from 247 to 361 K. Comparison with the data given in Figure 5 reveals that the relative rate data are within a factor of 2 of those of Balla et al.,[144] Mund et al.,[157] Fittschen et al.,[156] and Deng et al.[154] Given the complexities and assumptions inherent in the relative rate study, this should be considered to be reasonable agreement. Linear least-squares analysis of the data of Mund et al.[157] and Fittschen et al.[156] (see Figure 5) gives our recommendation of $k_{1-C_3H_7O+O_2} = (2.38^{+1.03}_{-0.72} \times 10^{-14}) \exp[-(230 \pm 100)/T]$ cm^3 molecule^{-1} s^{-1} at 220−400 K. At 296 K, this expression gives $k_{1-C_3H_7O+O_2} = 1.09 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Linear least-squares analysis of the data of Balla et al.,[144] Mund et al.,[157] Fittschen et al.,[156] and Deng et al.[154] (see Figure 5) gives our recommendation of $k_{2-C_3H_7O+O_2} = (1.95^{+0.52}_{-0.40} \times 10^{-14}) \exp[-(310 \pm 70)/T]$ cm^3 molecule^{-1} s^{-1} at 200−400 K. At 296 K, this expression gives $k_{2-C_3H_7O+O_2} = 6.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

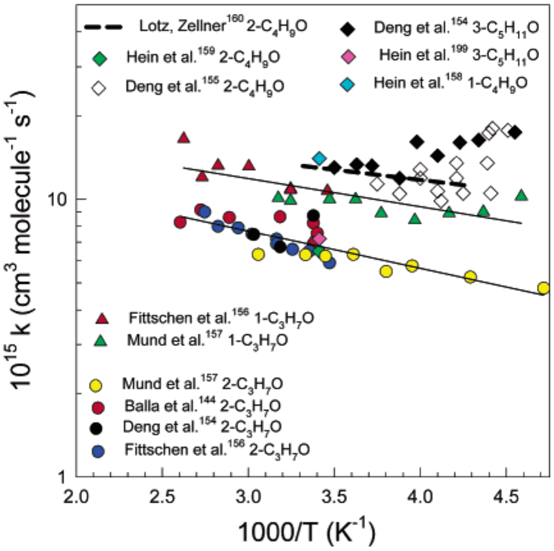


Figure 5. Rate coefficient data for reaction of large alkoxy radicals with O_2, plotted in Arrhenius form.

The reaction of $1\text{-}C_4H_9O^{\bullet}$ radicals with O_2 has been studied using absolute[158] and relative rate[201] methods. The rate constant reported at 293 K, $k_{1-C_4H_9O+O_2} = (1.4 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, by Hein et al.[158] is shown by the blue diamond in Figure 5. Morabito and Heicklen[201] measured $k_{1-C_4H_9O+O_2}$ relative to $k_{1-C_4H_9O+NO}$ by photolyzing $1\text{-}C_4H_9ONO$ in the presence of O_2 and measuring the effect of O_2 concentration on the yield of C_3H_5CHO. These results, scaled to a value of $k_{C_4H_9O+NO} = 4.4 \times 10^{-11}$, give values of $k_{1-C_4H_9O+O_2}$ which increase from 8.7×10^{-15} to 3.7×10^{-14} cm^3 molecule^{-1} s^{-1} as temperature increases from 265 to 393 K. At 296 K, Morabito and Heicklen[201] report $k_{1-C_4H_9O+O_2} = (1.3 \pm 0.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, in agreement with the data of Hein et al.[158]

Various studies of the reactions of $2\text{-}C_4H_9O^{\bullet}$ and $3\text{-}C_5H_{11}O^{\bullet}$ with O_2 have now been conducted (see Figure 5).[154,155,159,160,199] Both Deng et al.[155] ($2\text{-}C_4H_9O^{\bullet}$ and $3\text{-}C_5H_{11}O^{\bullet}$) and Lotz and Zellner[160] ($2\text{-}C_4H_9O^{\bullet}$) derived their kinetic data from a direct measurement of the loss of the alkoxy radical in the presence of O_2. In the studies by Hein et al.,[159,199] the kinetic data were derived in a more indirect fashion, by monitoring the rate of formation of OH radicals and NO_2 formed following reaction of the alkoxy radicals with O_2. Results from an earlier study by Deng et al.[154] are not considered here, as they are superseded by a second study[155] which the authors believed to be less prone to systematic errors. For the reaction of 2-$C_4H_9O^{\bullet}$ with O_2, there is general agreement between the results of Deng et al.[155] and Lotz and Zellner[160] in terms of the rough magnitude of the rate coefficient. However, the data of Deng et al.[155] for reaction of both 2-$C_4H_9O^{\bullet}$ and 3-$C_5H_{11}O^{\bullet}$ with O_2 show small negative temperature dependencies, which contrast with the well-established positive temperature dependencies of the reactions of smaller alkoxy radicals with O_2, and with the data of Lotz and Zellner[160] on the 2-$C_4H_9O^{\bullet}$ reaction. For both the 2-$C_4H_9O^{\bullet}$ and 3-$C_5H_{11}O^{\bullet}$ reactions, the results of Hein et al.[159,199] at 293 K (green and pink diamonds in Figure 5) are ~30−50% lower than those implied by the data of Lotz and Zellner[160] or by extrapolation of the data reported at subambient temperatures by Deng et al.[155]

Zabarnick and Heicklen[202] studied the kinetics of the reaction of $(CH_3)_2CHCH_2O^{\bullet}$ radicals with O_2 relative to their reaction with NO in 150 Torr N_2 diluent at 265−393 K. Scaling the results to $k_{(CH_3)_2CHCH_2O+NO} = 4.4 \times 10^{-11}$ gave values of $k_{(CH_3)_2CHCH_2O+O_2}$ which increase from 1.4×10^{-14} to 4.4×10^{-14} cm^3 $molecule^{-1}$ s^{-1} as the temperature is increased from 265 to 393 K. The chemistry occurring in the system employed by Zabarnick and Heicklen[202] is complex, the data analysis is far from straightforward, and the results should be treated with caution.

Given the limited data available and some of the discrepancies presented above, no recommendation for the kinetics of reaction of butoxy or pentoxy radicals with O_2 is given at the present time. Further work is needed to establish the rates of reaction of large (>C_3) alkoxy radicals at temperatures representative of the atmosphere.

3.1.4. $CH_2ClO^{\bullet}$, $CFCl_2CH_2O^{\bullet}$ + O_2

Wu and Carr have used flash photolysis−time-resolved mass spectrometry to study the kinetics of the reactions of $CH_2ClO^{\bullet}$ [161,162] and $CFCl_2CH_2O^{\bullet}$ [163] radicals with O_2. The first reported measurement[161] of $k_{CH_2ClO+O_2}$ is consistent with, but less precise than, the subsequent study by Wu and Carr and is hence not considered here. There was no discernible effect of total pressure of N_2 diluent over the range studied (5−35 Torr for $CH_2ClO^{\bullet}$, 10−35 Torr for $CFCl_2CH_2O^{\bullet}$). As shown in Figure 6, both reactions show a positive temperature dependence. The lines through the data in Figure 6 are linear least-squares fits which give $k_{CH_2ClO+O_2} = (2.06^{+2.76}_{-1.18}) \times 10^{-12} \exp[-(940 \pm 240)/T]$ and $k_{CFCl_2CH_2O+O_2} = (2.53^{+1.81}_{-1.06}) \times 10^{-15} \exp[-(960 \pm 160)/T]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature ranges 265−306 and 251−341 K, respectively. These expressions give $k_{CH_2ClO+O_2} = 8.6 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{CFCl_2CH_2O+O_2} = 9.9 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K.

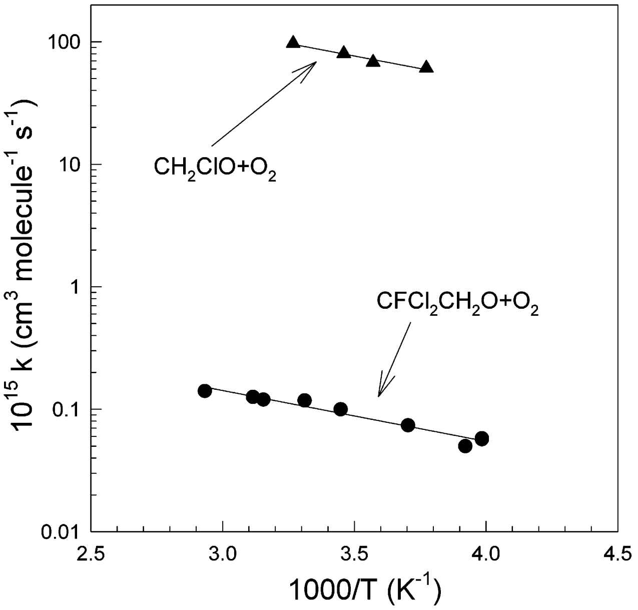


Figure 6. Rate coefficient data for reaction of halogenated alkoxy radicals with O_2, plotted in Arrhenius form.

As part of their study of the reaction with O_2, Wu and Carr[162] also measured the kinetics of HCl elimination from $CH_2ClO^{\bullet}$ radicals. The rate of HCl elimination increased linearly with total pressure over the range 5−35 Torr N_2 diluent at 289 K, and a rate constant of $(1.4 \pm 0.4) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} was derived at the low-pressure limit. This value can be combined with the measured value of $k_{CH_2ClO+O_2} = (8.0 \pm 0.8) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 289 K[162] to give the rate constant ratio $k_{elim}/k_{CH_2ClO+O_2} = 0.0175 \pm 0.0053$. This result is consistent with the rate constant ratio derived at the low-pressure limit by Kaiser and Wallington[108] of $k_{elim}/k_{CH_2ClO+O_2} = 0.023$ at 296 K.

The 1000-fold difference in reactivity between $CH_2ClO^{\bullet}$ and $CFCl_2CH_2O^{\bullet}$ radicals, the low *A*-factor for the reaction of $CFCl_2CH_2O^{\bullet}$ radicals with O_2, and the fact that $CH_2ClO^{\bullet}$ and $CFCl_2CH_2O^{\bullet}$ radicals have reactivities which are very different from any of the unsubstituted alkoxy radicals are very striking. As discussed above, the mechanism of the reaction of alkoxy radicals with O_2 is complex, with a significant fraction of reaction believed to occur via hydrogen atom tunneling in the weakly bound $RO\cdots O_2$ complex. Computational studies of the reactions of $CH_2ClO^{\bullet}$ and $CFCl_2CH_2O^{\bullet}$ radicals with O_2 are needed to provide a fundamental understanding of their mechanism.

3.1.5. Comparison with Previous Recommendations

Our recommendation of $k_{CH_3O+O_2} = (7.82^{+4.68}_{-2.93}) \times 10^{-14} \exp[-(1150 \pm 190)/T]$ cm^3 $molecule^{-1}$ s^{-1} at 298−610 K is essentially identical to the IUPAC[197] recommendation ($k_{CH_3O+O_2} = 7.2 \times 10^{-14} \exp(-1080/T)$ cm^3 $molecule^{-1}$ s^{-1} for $T = 290-610$ K), which is to be expected given that they are based upon essentially the same data set. The small difference in the expressions probably reflects slight differences in the intepretation of the data of Lorenz et al.[145] which are provided in graphical rather than tabular form.

Our recommendation of $k_{C_2H_5O+O_2} = (5.13^{+9.70}_{-3.32}) \times 10^{-14} \exp[-(550 \pm 350)/T]]$ at 280−420 K can be compared to the IUPAC recommendation[197] of $k_{C_2H_5O+O_2} = 6.0 \times 10^{-14} \exp(-550/T)$ cm^3 molecule^{-1} s^{-1} for $T = 290-420$ K. The exponential factors are the same in both recommendations, and hence there is a constant difference (17%) between the expressions given by the ratio of the pre-exponential factors. The difference between the two expressions is explained by the inclusion of the recently published Fittschen et al.[156] data in the current recommendation.

Our recommendations of $k_{1-C_3H_7O+O_2} = (2.38^{+1.03}_{-0.72} \times 10^{-14}) \exp[-(230 \pm 100)/T]$ at 220−400 K and $k_{2-C_3H_7O+O_2} = (1.95^{+0.52}_{-0.40} \times 10^{-14}) \exp[-(310 \pm 70)/T]$ at 200−400 K can be compared to the IUPAC recommendations[197] of $k_{1-C_3H_7O+O_2} = 1.4 \times 10^{-14} \exp(-110/T)$ for 220−310 K and $k_{2-C_3H_7O+O_2} = 1.4 \times 10^{-14} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} for 210−390 K. At $T = 220$ and 310 K, the IUPAC expression gives values of $k_{1-C_3H_7O+O_2}$ which differ by +1% and −13% from those derived from the expression recommended here. At $T = 210$, 300, and 390 K, the IUPAC expression gives values of $k_{2-C_3H_7O+O_2}$ which differ by +16%, <1%, and −7% from those derived from the expression recommended here. These small differences reflect the inclusion in the present evaluation of data reported recently by Fittschen et al.[156] and Deng et al.[154,155]

On the basis of the IUPAC recommendations[197] for $C_2H_5O^\bullet$ and 2-$C_3H_7O^\bullet$, Atkinson[14,15] has recommended that primary ($RCH_2O^\bullet$) and secondary ($R_2CHO^\bullet$) alkoxy radicals formed from the alkanes react with O_2 with kinetics described by $k_{RCH_2O+O_2} = k_{C_2H_5O+O_2} = 6.0 \times 10^{-14} \exp(-550/T)$, and $k_{R_2CHO+O_2} = k_{2-C_3H_7O+O_2} = 1.5 \times 10^{-14} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1}. The results of recent studies of the reactions of 1-$C_3H_7O^\bullet$, 1-$C_4H_9O^\bullet$, 2-$C_4H_9O^\bullet$, and 3-$C_5H_{11}O^\bullet$ with O_2 by Mund et al.,[157] Fittschen et al.,[156] Hein et al.,[158,159] Lotz and Zellner,[160] and Deng et al.[154,155] shown in Figure 5 indicate that the reactivity of $RCH_2O^\bullet$ radicals is significantly greater than that of $C_2H_5O^\bullet$ and the reactivity of $R_2CHO^\bullet$ radicals is significantly greater than that of 2-$C_3H_7O^\bullet$. Further work is needed to better understand the reactivity of large (>C3) alkoxy radicals with O_2.

Finally, it is worthwhile to note the dearth of absolute rate data concerning the reactions of oxygenated and halogenated alkoxy radicals with O_2. Of particular note in this regard are the results of Wu and Carr,[161−163] which give a strong indication that halogenated alkoxy radical reactions with O_2 may be governed by rate coefficients that are different from those applicable to nonsubstituted alkoxy radicals and highly dependent on radical structure, thus making even semiquantitative prediction difficult and limiting our ability to interpret end-product data. Given the atmospheric importance of such compounds, it is particularly troublesome that we have very little information concerning these reactions.

3.2. Dissociation Reactions

In the study of the atmospheric chemistry of alkoxy radicals, the most common unimolecular reaction encountered is a simple C−C bond scission, a process which results in the formation of a carbonyl compound and an alkyl radical. A typical example, for the 2-pentoxy radical, has been illustrated previously in Figure 2. In the case of halogenated alkoxy radicals, cleavage of a C−X bond (X = Cl, Br, or I) may also be encountered. In most cases, these decomposition reactions are slightly endothermic (by about 6 kcal/mol for the 2-pentoxy case) and possess barriers that exceed the endothermicity by roughly 3−10 kcal/mol. As will be detailed later in this section, the endothermicity and the barriers to decomposition are coupled, and generally decrease with increasing substitution at the α-carbon. In the discussion that follows, the available data regarding the rates of unimolecular dissociation for unsubstituted alkoxy radicals (i.e., those obtained from the oxidation of the alkanes), β-hydroxyalkoxy radicals, and other oxygen- and halogen-substituted radicals are presented in detail.

3.2.1. Unsubstituted Alkoxy Radicals

Arrhenius parameters for the unimolecular dissociation of the alkane-derived alkoxy radicals have been reviewed on many occasions;[11−15,25,39] the most recent recommendations are given by Atkinson.[14] Data used in the evaluations stem largely from work of Batt and co-workers,[24−29] whose data on unimolecular dissociation arise from relative rate studies obtained versus reaction with NO, as well as various chamber experiments.[41,42,56,57,59,203] In his analysis, Atkinson[14] assumes that the A-factors for the decomposition processes can be estimated from the following relationship:

$$A = (2 \times 10^{14})d \quad (\mathrm{s}^{-1}) \qquad \text{(A)}$$

where d represents the degeneracy of the dissociation reaction. This recommendation was based on the data available at the time, though the limited temperature range over which many of these processes had been studied precluded an accurate assessment. Activation energies, E_a, were then adjusted to match the dissociation rate constant at the midpoint of the temperature range employed in the various experimental studies. The most recent recommendations[14] obtained from this approach are summarized in Table 1. What follows is largely a discussion of work carried out since that review; in general, these newer studies (which involve both experimental[71,150−153] and theoretical[153,164−168] approaches) point to both lower A-factors and lower activation energies for these dissociation reactions, though often with similar rate coefficients near 298 K.

One indication of lower A-factors comes from theoretical studies done by Méreau et al.[164] Their calculations, carried out using both DFT and BAC-MP4 levels of theory, imply A-factors at the high-pressure limit that are about a factor of 2 lower than those derived from previous studies. Similar conclusions can be drawn from the theoretical studies done by Somnitz and Zellner[166,167] and by Fittschen et al.[153] which point to A-factors at the high-pressure limit that are perhaps a factor of 3−5 lower than those derived from equation (A). Recent direct studies of the dissociation rates for ethoxy,[151] 2-propoxy,[152] and

Table 1. Summary of Available Data on Unimolecular Dissociation Reactions of Nonsubstituted (Alkane-Derived) Alkoxy Radicals

dissociation reaction	ΔH_{rxn} (kcal/mol)	E_a (kcal/mol)	approximate rate (s^{-1})[a]	recommended E_a (kcal/mol)	major atmospheric reaction(s)
$C_2H_5O^\bullet \rightarrow$	13.1[14,164,168,197]	20.2[14]	0.3[14]	18.2	reaction with O_2
$^\bullet CH_3 + CH_2O$		17.9[167]	1.5[167]		
		18.1[164]	3.4[164]		
		18.7[151,153]	6.0[151]		
		18.1[153]			
$CH_3CH_2CH_2O^\bullet \rightarrow$	12.8[164,168,197]	15.2[167]	340[167]	15.7	reaction with O_2
$CH_3CH_2^\bullet + CH_2O$		15.7[164]	250[164]		
		16.2[153]			
$CH_3CH(O^\bullet)CH_3 \rightarrow$	7.8[14,164,168,197]	17.6[14]	15[14]	15.5	reaction with O_2
$^\bullet CH_3 + CH_3CHO$		15.2[167]	350[167]		
		16.4[164]	140[164]		
		15.1[152,153]	600[152]		
		15.9[153]			
$CH_3CH_2CH_2CH_2O^\bullet \rightarrow$	12.3[164,168]	15.1[153]	580[14]	15.8	reaction with O_2,
$CH_3CH_2CH_2^\bullet + CH_2O$	13.1[197]	15.7[167]	40[167]		isomerization
		16.2[164]	140[164]		
$CH_3CH_2CH(O^\bullet)CH_3 \rightarrow$	5.9[14,164,168,197]	14.3[14]	2.3×10^4[14]	12.6	reaction with O_2,
$CH_3CH_2^\bullet + CH_3CHO$		11.3[69]			unimolecular dissociation
		12.4[167]	2.7×10^4[167]		
		12.7[164]	3.5×10^4[164]		
		12.7[153]	2.5×10^4[42,56]		
$CH_3CH_2CH(O^\bullet)CH_3 \rightarrow$	7.0[14,164,168,197]	16.6[14]		17	reaction with O_2,
$CH_3^\bullet + CH_3CH_2CHO$		15.6[167]	46[167]		unimolecular dissociation
		17.1[164]	32[164]		
		17.9[153]			
$(CH_3)_3C(O^\bullet) \rightarrow$	4.7[14,164]	16.2[14]		14.3	unimolecular dissociation
$CH_3^\bullet + (CH_3)_2CO$		14.8[164]	3000[164]		
		14.5[153]			
		13.6[150]	1500[150]		
		14.0[160]	3000[160]		
$(CH_3)_2CHCH_2O^\bullet \rightarrow$	11.5[164]	12.4[164]	5.7×10^4[153]	12.4	reaction with O_2,
$(CH_3)_2CH^\bullet + CH_2O$		12.3[153]			unimolecular dissociation
$CH_3CH_2CH_2CH_2CH_2O^\bullet \rightarrow$	8.7[168]	15.6[167]	2.6[167]	15.1	isomerization
$CH_3(CH_2)_2CH_2^\bullet + CH_2O$		14.7[153]			
$CH_3CH_2CH_2CH(O^\bullet)CH_3 \rightarrow$	6.0[168]	14.1[14]	1.7×10^4[14]	13.3	isomerization,
$CH_3CH_2CH_2^\bullet + CH_3CHO$	6.7[164]	13.1[167]	1×10^4[167]		reaction with O_2,
	6.8[14]	13.1[164]	2.2×10^4[164]		unimolecular dissociation
		13.8[59]	9×10^3[59]		
		13.3[153]			
$CH_3CH_2CH_2CH(O^\bullet)CH_3 \rightarrow$	9.0[164]	15.7[167]	50[167]	16.8	isomerization,
$CH_3^\bullet + CH_3CH_2CH_2CHO$		16.9[164]	47[164]		reaction with O_2,
		18[153]			unimolecular dissociation
$CH_3CH_2CH(O^\bullet)CH_2CH_3 \rightarrow$	7.0[168]		1.6×10^4[14]	13	reaction with O_2,
$CH_3CH_2^\bullet + CH_3CH_2CHO$	7.7[14,164]	12.8[167]	3.3×10^4[167]		unimolecular dissociation
		13.3[164]	3.4×10^4[164]		
			2.6×10^4[41]		
$CH_3CH_2C(O^\bullet)(CH_3)_2 \rightarrow$	4.3[14]	13.9[14]		10.5	unimolecular dissociation
$CH_3CH_2^\bullet + (CH_3)_2CO$	4.3[164]	10.5[164]	9.4×10^5[164]		
$CH_3CH_2C(O^\bullet)(CH_3)_2 \rightarrow$	4.6[14,164]	18.3[14]		13.9	unimolecular dissociation
$CH_3^\bullet + CH_3C(O)C_2H_5$		13.9[164]	1.1×10^4[164]		
$(CH_3)_3CCH_2O^\bullet \rightarrow$	11.5[14,164]		7×10^5[14]	9.6	unimolecular dissociation
$C(CH_3)_3^\bullet + CH_2O$	10[this work]	9.6[164]	3×10^6[164]		
		9.4[153]	2×10^6[203]		
cyclopentoxy →	−1.2[51]	<10[71]	$>1 \times 10^7$[71]		unimolecular dissociation
$^\bullet CH_2CH_2CH_2CH_2CHO$					
cyclohexoxy →	6.3[51]	11.5[71]	5×10^4[71]	11.5	reaction with O_2,
$^\bullet CH_2CH_2CH_2CH_2CH_2CHO$					unimolecular dissociation

[a] Applies to conditions of the lower troposphere (298 K, 1 atm air). Recommended activation energies and rate coefficients are based on assumed *A*-factors of 10^{14} s^{-1}.

tert-butoxy[150,153,160] also provide evidence for the validity of lower *A*-factors. Fits of the experimental data to Troe falloff functions have led to the retrieval of *A*-factors at the high-pressure limit in the range (1−10) × 10^{13} s^{-1}, even for the triply degenerate *tert*-butoxy radical decomposition. A further complication[164] in the determination of appropriate *A*-factors results from the fact that these dissociation reactions are, in general, not at their high-pressure limit at atmospheric pressure. Thus, effective *A*-factors at 760 Torr may be considerably lower than those applicable at infinite pressure.

In concert with this general indication of the validity of lower *A*-factors for the unimolecular dissociation reactions of alkoxy radicals is the finding that some of these reactions are characterized by lower activation energies than previously believed. For example, the direct determinations of the activation energies for ethoxy,[151] 2-propoxy,[152] and *tert*-butoxy[150,153,160] radicals fall roughly 2−3 kcal/mol below the previous data. The theoretical studies done by Méreau et al.[164] and by Somnitz and Zellner[166,167] also point to activation barriers that are about 2 kcal/mol lower than previously believed. Again, because of the nature of pressure falloff as a function of temperature, effective activation barriers at 760 Torr are generally lower than those obtained at infinite pressure, though these differences are usually only on the order of 0.5 kcal/mol or so.

These recent data, obtained via both experimental and theoretical means, are summarized in Table 1, and a lowering in the accepted barriers for many of these processes (e.g., ethoxy, 2-propoxy, 2-butoxy, *tert*-butoxy) compared to older data is clearly evident. Also provided in Table 1 is our recommended activation barrier for the various dissociation processes, which is based on an assumed high-pressure limiting A-factor of 10^{14} s^{-1}, and an average of the more recent activation energy data. While these recent works would seem to provide a more reliable database for the alkoxy radical dissociations and make the derivation of structure−reactivity relationships more accurate (see below), it should also be pointed out that these refinements have led to only modest changes in our understanding of the atmospheric fate of many of these species. In general, the decrease in the A-factor and in the activation energy offset each other, and thus retrieved rate coefficients near 298 K do not change drastically in most cases. Furthermore, dissociation reactions for fairly small (two- and three-carbon) radicals are too slow to be of any importance in the atmosphere, and thus the finding of faster dissociation rate coefficients in the case of these radicals does not alter our understanding of their atmospheric behavior. The largest impact to atmospheric modeling may be for the 2-methyl-1-propoxy radical[164] (for which unimolecular dissocation is now expected to dominate over reaction with O_2) and for species such as 2-butoxy[153,164,167] and cyclohexoxy,[71] where the lower activation energies implied by the more recent studies indicate that dissociation reactions may persist to lower temperature (and thus higher tropospheric altitude) than previously believed.

Concurrent with the development of a database for the Arrhenius parameters that describe these unimolecular dissociation reactions has been the quest for simple structure−reactivity type relationships that can be used to predict rate coefficients for unstudied radicals (including unsubstituted, as well as halogenated and oxygenated species). Early studies[26,204] on unsubstituted alkoxy radicals used a simple equation to relate the activation energies and reaction enthalpy,

$$E_a = a + b\Delta H_{rxn} \tag{B}$$

which was independent of the nature of the alkyl leaving group. Choo and Benson,[205] however, showed that the intercept, a, of such plots was related to the nature of the alkyl leaving group, and in fact could be correlated with the leaving-group ionization potentials (IP). This approach has been adopted and updated by Atkinson in his various reviews,[11−15] and the following expression,

$$E_a = (2.4(\mathrm{IP}) - 8.1) + 0.36\Delta H_{rxn} \tag{C}$$

has been reported.[14] The slope of 0.36 was established using data for methyl radical as the leaving group and assumed to be independent of the leaving group involved. We have used this same approach, using the updated values highlighted in Table 1 and the relevant data from Tables 2 and 3 (i.e., data for $C_2H_5{-}O{-}CH(O^\bullet){-}CH_3$, $CH_3CHClO^\bullet$, and $CH_3CHFO^\bullet$), and obtained the following results:

$$E_a = (2.4(\mathrm{IP}) - 11.8) + 0.58\Delta H_{rxn} \tag{D}$$

Exclusion of the three extra data points from Tables 2 and 3 ($C_2H_5{-}O{-}CH(O^\bullet){-}CH_3$, $CH_3CHClO^\bullet$, and $CH_3CHFO^\bullet$) does not change the fit to any significant extent (slope and intercept change by 5−10%). Plots of our recommended E_a vs ΔH_{rxn} for reactions corresponding to various leaving groups are plotted as the solid black lines in Figure 7. Shown for comparison as the solid red line is the relationship recommended by Atkinson[14] in 1997, based on the data available at that time. Our new fit clearly reflects the recent findings of lower activation energies for a number of dissociation reactions involving methyl group elimination (e.g., ethoxy, 2-propoxy, *tert*-butoxy, and 2-methyl-2-butoxy; see Table 1). It should also be pointed out that Aschmann and Atkinson,[39] based on the inclusion of a datapoint for decomposition of the $CH_3CH(O^\bullet)OC(CH_3)_3$ radical, also proposed a steeper slope to the activation energy/enthalpy relationship for methyl leaving groups, shown as the dotted red line in Figure 7. Although the slope matches up quite well with our newer fit, most of the lower activation energy data were still not available at the time of the Aschmann and Atkinson[39] work, as is reflected in the higher intercept in their fit. Méreau et al.[164] have also derived a revised version of the $\Delta H_{rxn}/E_a$ relationship using their theoretically derived data. Their fit, shown as the green line in Figure 7, does reflect the lowering of the activation energies since the time of the Atkinson and Aschmann[39] and Atkinson[14] analyses. However, because they have not included the low ΔH_{rxn} data points (from halogenated and ether-derived alkoxy radicals), a lower slope and a higher intercept are obtained in their fit.

Other approaches have also been employed to describe structure−reactivity relationships for the alkoxy radical dissociation reactions. For example, Méreau et al.[164] derived a correlation of the E_a vs ΔH_{rxn} in terms of the different “classes” of unsubstituted alkoxy radicals (where “class” refers to primary, secondary, or tertiary substitution at the alkoxy radical carbon), rather than in terms of the leaving group ionization potential. The following formula was reported for ΔH_r and E_a data derived from their DFT calculations:

$$E_a = (10.95 - 5.34n_H) + 1.2\Delta H_r \tag{E}$$

Table 2. Summary of Available Data Regarding the Chemistry of Oxygen-Substituted Alkoxy Radicals

dissociation process (or radical considered)	ΔH_{rxn} (kcal/mol)	E_a (kcal/mol)	approximate rate at 298 K, 1 atm (s^{-1})	major atmospheric reaction(s)
$HOCH_2-CH_2O^\bullet \rightarrow {}^\bullet CH_2OH + CH_2O$	(8)[a]	10.5[17,19]	1.3×10^5 [17]	unimolecular dissociation, reaction with O_2
$CH_3CH(OH)-CH_2O^\bullet \rightarrow CH_3C^\bullet HOH + CH_2O$		7[18]	5×10^7 [18]	unimolecular dissociation
$CH_3CH(O^\bullet)-CH_2OH \rightarrow {}^\bullet CH_2OH + CH_3CHO$		7[18]	5×10^7 [18]	unimolecular dissociation
$CH_3CH_2CH(OH)-CH_2O^\bullet \rightarrow CH_3CH_2C^\bullet HOH + CH_2O$		9.7		unimolecular dissociation
$CH_3C(=O)CH_2O^\bullet \rightarrow CH_3C^\bullet O + CH_2O$	(0)	6.5[22]	2.7×10^7 [22]	unimolecular dissociation
$CH_3C(=O)CH(O^\bullet)CH_3 \rightarrow CH_3CHO + CH_3C^\bullet O$	(−2)	(<7)	($>1 \times 10^7$)	unimolecular dissociation
$CH_3-O-CH_2O^\bullet \rightarrow CH_3OCHO + H$	4[109] 3[186]	14[109] 10[186]	5×10^3 [109]	reaction with O_2, unimolecular dissociation
$CH_3CH_2OCH_2O^\bullet$				reaction with O_2
$C(CH_3)_3-O-CH_2O^\bullet$				reaction with O_2
$CH_3(CH_2)_3-O-CH_2O^\bullet$				reaction with O_2
$C_2H_5-O-CH(O^\bullet)-CH_3 \rightarrow C_2H_5OCHO + CH_3^\bullet$	0[67]	11[67]	5×10^5 [67]	unimolecular dissociation
$C(CH_3)_3-O-CH(O^\bullet)-CH_3 \rightarrow C(CH_3)_3OCHO + CH_3^\bullet$			2×10^5 [39,78,110]	unimolecular dissociation
$(CH_3)_2C(O^\bullet)OCH_3 \rightarrow CH_3C(O)OCH_3 + CH_3^\bullet$			1×10^6 [39,45,106,113]	unimolecular dissociation
$(CH_3)_2C(O^\bullet)OCH_2CH_3 \rightarrow C_2H_5OC(O)CH_3 + CH_3^\bullet$			1×10^6 [39,78,110]	unimolecular dissociation
$CH_3CH_2CH_2CH(O^\bullet)OCH_3 \rightarrow HC(O)OCH_3 + CH_3CH_2CH_2^\bullet$			4×10^7 [39]	unimolecular dissociation
$CH_3CH_2C(O^\bullet)(CH_3)OCH_3 \rightarrow C_2H_5^\bullet + CH_3C(O)OCH_3$			3×10^6 [39,124]	unimolecular dissociation
$CH_3OCH_2CH_2O^\bullet \rightarrow CH_3OCH_2^\bullet + CH_2O$	5[182]	8[182]		unimolecular dissociation
$CH_3OC(CH_3)_2CH_2O^\bullet \rightarrow CH_3OC^\bullet(CH_3)_2 + CH_2O$			1×10^7 [39,45,106,113]	unimolecular dissociation
$CH_3CH_2OC(CH_3)_2CH_2O^\bullet \rightarrow C_2H_5OC^\bullet(CH_3)_2 + CH_2O$			2×10^7 [39,78,110]	unimolecular dissociation
$CH_3OCH_2CH_2CH(O^\bullet)CH_3 \rightarrow CH_3OCH_2CH_2^\bullet + CH_3CHO$			2×10^4 [39]	reaction with O_2, unimolecular dissociation
$CH_3C(O)OCH_2O^\bullet \rightarrow CH_3COOH + H^\bullet CO$	−5[182]	8[182]	7×10^4 [93]	α-ester rearrangement,[182,93] reaction with O_2
$HC(O)OCH_2O^\bullet \rightarrow HCOOH + H^\bullet CO$	−7.7[186]	13[186]	1×10^4 [80]	reaction with O_2, α-ester rearrangement [80]
$CH_3CH_2C(O)OCH_2O^\bullet \rightarrow C_2H_5COOH + HC^\bullet O$				α-ester rearrangement, reaction with $O_2$97
$CH_3C(O)OCH(O^\bullet)CH_3 \rightarrow CH_3COOH + CH_3C^\bullet O$		6.5[185]	7×10^7 [185]	α-ester rearrangement

[a] Values in parentheses are estimates from this work.

where $n_H = 0$ for a tertiary alkoxy radical, 1 for a secondary radical, and 2 for a primary radical. These workers also combined this expression with their version of equation (C) discussed in the preceding paragraph, to derive a relationship for the activation energy of the alkoxy radical dissociation reaction that does not rely on a knowledge of the often uncertain energetics of the dissociation process, but instead depends only on the degree of substitution of the radical and the well-characterized leaving-group ionization potentials:

$$E_a = 2.5(IP) + 2.1n_H - 10.4 \quad (F)$$

Somnitz and Zellner[168] considered a subset of alkoxy radicals, essentially those derived from straight-chain C1−C5 hydrocarbons. They showed that these radicals could be put into three groups, distinguished by the number of carbons in the alkyl leaving group and the number of carbons in the carbonyl product, and that each group could be characterized by a single activation energy. The three groups considered were (1) radicals with one carbon in each fragment (i.e., the ethoxy radical), with E_a = 17.3 kcal/mol; (2) radicals with one carbon in one fragment and at least two in the other fragment (e.g., $CH_3CH(O^\bullet)CH_3$, $CH_3CH_2CH_2O^\bullet$), E_a = 14.8 kcal/mol; and (3) radicals with at least two carbons in each fragment (e.g., 2-butoxy, 3-pentoxy), E_a = 12.0 kcal/mol. This approach would seem to have limited applicability, however, since it applies only to the linear radicals considered; branched species such as *tert*-butoxy and isobutoxy radicals cannot be fit into this framework.

Finally, Vereecken and Peeters[206] have recently reported a structure−reactivity relationship akin to that developed by Atkinson and co-workers for the prediction of OH rate coefficients.[207] In this approach, decomposition of the ethoxy radical is taken as the standard reaction, with an adopted activation barrier

Table 3. Summary of the Available Data Regarding the Chemistry of Halogenated Alkoxy Radicals

radical	dominant reaction pathway(s)[a]	products	reaction enthalpy (kcal/mol)	activation energy (kcal/mol)	approximate rate (s^{-1})[a]	refs
$CH_2FO^\bullet$	rxn. with O_2	$HCOF + HO_2$				49, 103
$CHF_2O^\bullet$	rxn. with O_2	$CF_2O + HO_2$				170
$CH_2ClO^\bullet$	rxn. with O_2	$HCOCl + HO_2$	−10.5			20, 58, 63, 79
	decomp.	$HCO + HCl$				
$CHCl_2O^\bullet$	decomp.	$HCOCl + Cl$	−10.5	2.2		58, 63, 170, 213
$CF_2ClO^\bullet$	decomp.	$CF_2O + Cl$				214
$CFCl_2O^\bullet$	decomp.	$CFClO + Cl$		<11		211
$CCl_3O^\bullet$	decomp.	$CCl_2O + Cl$	−16.8	1.3		211, 226
$CHFClO^\bullet$	decomp.	$HCOF + Cl$	−11.5	1.5		49, 174
$CH_2BrO^\bullet$	decomp.	$CH_2O + Br$	(−6)	<7	$>1 \times 10^7$	65, 70
$CHBr_2O^\bullet$	decomp.	$HCOBr + Br$	(−18)	<7	$>4 \times 10^6$	72
$CBr_3O^\bullet$	decomp.	$CBr_2O + Br$	−21.5	0		187, 188
$CH_2IO^\bullet$	decomp.	$CH_2O + I$				122
$CHBrClO^\bullet$	decomp.	$HCOCl + Br$				102
$CBr_2ClO^\bullet$	decomp.	$COClBr + Br$				21
$CCl_2BrO^\bullet$	decomp.	$COCl_2 + Br$				21
		$COClBr + Cl$				
$CH_3CHClO^\bullet$	decomp.	$CH_3CO + HCl$	−12.3	7.4		23, 105, 212
$ClCH_2CH_2O^\bullet$	rxn. with O_2	$ClCH_2CHO + HO_2$				17, 66, 82
$ClCH_2CHClO^\bullet$	decomp.	$ClCH_2CO + HCl$				95
	rxn. with O_2	$ClCH_2COCl + HO_2$				
$CCl_3CCl_2O^\bullet$	decomp.	$CCl_3 + CCl_2O$				81, 101
		$CCl_3COCl + Cl$				
$CCl_3CH_2O^\bullet$	rxn. with O_2	$CCl_3CHO + HO_2$				76
	decomp.	$CCl_3 + CH_2O$ minor	(6)	14	2×10^3	
$CH_3CHBrO^\bullet$	decomp.	$CH_3CHO + Br$				23
$CF_3CHClO^\bullet$	decomp.	$CF_3CO + HCl$				100
		$CF_3 + HCOCl$				
		$CF_3CHO + Cl$				
	rxn. with O_2	$CF_3COCl + HO_2$				
$CF_3CH(O^\bullet)CF_3$	rxn. with O_2	$CF_3C(O)CF_3 + HO_2$				99
$CH_3CF_2CH_2O^\bullet$	rxn. with O_2	$CH_3CF_2CHO + HO_2$				98
$CF_3CH_2CF_2O^\bullet$	decomp.	$CF_3CH_2 + COF_2$				134
$CH_2FCHFO^\bullet$	decomp.	$CH_2F + HCOF$	−1.8	8.3		94, 171
$CFCl_2CH_2O^\bullet$	rxn. with O_2	$CFCl_2CHO + HO_2$				46
$CF_2ClCH_2O^\bullet$	rxn. with O_2	$CF_2ClCHO + HO_2$				46
$CF_3CH_2O^\bullet$	rxn. with O_2	$CF_3CHO + HO_2$				169
$CF_3CF_2O^\bullet$	decomp.	$CF_3 + COF_2$	−9	8	5×10^6	104, 169, 129
$CF_3CHFO^\bullet$	decomp.	$CF_3 + HCOF$				16, 129, 131
	rxn. with O_2	$CF_3COF + HO_2$				
$CF_3CCl_2O^\bullet$	decomp.	$CF_3COCl + Cl$				49, 130
$CF_3CFClO^\bullet$	decomp.	$CF_3COF + Cl$		<15	$>1 \times 10^3$	49, 129, 227
$CCl_3CHClO^\bullet$	decomp.	$CCl_3 + HCOCl$				132
		$CCl_3CO + HCl$				
$CH_3CHFO^\bullet$	decomp.	$CH_3 + HCOF$	0	12		171
	rxn. with O_2	$CH_3COF + HO_2$				
$CH_3CF_2O^\bullet$	decomp.	$CH_3 + COF_2$				49
$CF_3CF_2CCl_2O^\bullet$	decomp.	$CF_3CF_2COCl + Cl$				46
$CF_2ClCF_2CFClO^\bullet$	decomp.	$CF_2ClCF_2COF + Cl$				46

[a] Applies to conditions of the lower troposphere (298 K, 1 atm air).

of 17.5 kcal/mol, and a set of substituent factors are derived for substitution at either the α- or β-carbon. Thus,

$$E_a = 17.5 - 2.1N_\alpha(\text{alk}) - 3.1N_\beta(\text{alk}) - 8.0N_{\alpha,\beta}(\text{OH}) - 8.0N_\beta(\text{O=}) - 12.0N_\alpha(\text{O=}) \quad \text{(G)}$$

where E_a is derived in units of kilocalories per mole and, for example, N_α(alk) refers to the number of alkyl substituents present at the α-carbon.

It should be pointed out that, in general, structure–reactivity relationships of the sort just described do not provide rate coefficient data of an accuracy sufficient to replace the need for direct experimental study. For one thing, as pointed out by various authors, values of ΔH_r for alkoxy radical decompositions are uncertain by about 1 kcal/mol; thus, an uncertainty of about a factor of 5 is expected in the prediction of the rate coefficients using equations (C)–(E), for example.[164,167,168] Elimination of the need for the use of ΔH_r in the calculations (e.g., equations (F) and (G) above) may provide more accurate predictive capabilities, but uncertainties are still expected to be significant. The various relationships that have been proposed do, however, have utility. For example, the simple fact that reasonably tight relationships exist provides confidence in the validity of the entire data set and provides insight into the mechanism of the reactions. Furthermore, the relationships can be used to derive reasonably accurate activation barriers and rate parameters for unstudied species, and to test the reliability of new data as they become

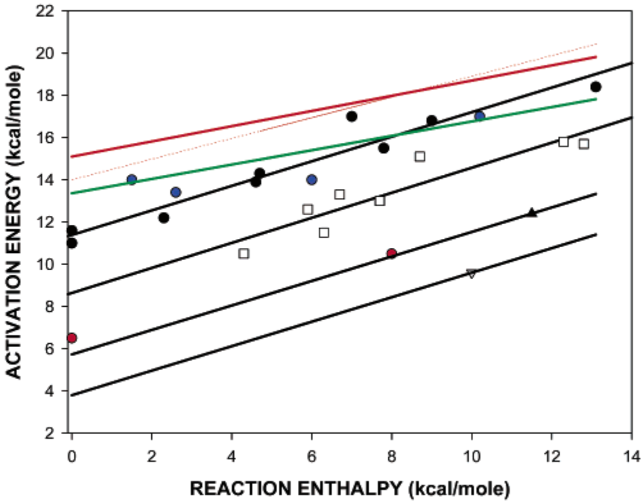


Figure 7. Plots of activation energy versus reaction enthalpy for alkoxy radical dissociation processes, coded according to the nature of the leaving groups. Black circles, methyl radicals; open squares, primary alkyl radicals; solid triangle, secondary alkyl radical; open inverted triangle, tertiary alkyl radical; blue circles, chloroalkyl radicals; red circles, hydroxyalkyl radicals. Solid black lines are given by $E_a = (2.4(\mathrm{IP}) - 11.8) + 0.58{*}\Delta H_{\mathrm{rxn}}$, obtained from fits of the methyl and primary alkyl leaving group data (see text for details). Solid and dotted red lines, previous recommendations[14,39] for methyl leaving group. Solid green line, methyl leaving group.[164]

available. As an example, the 3-methyl-2-butoxy radical has not, to our knowledge, been the subject of recent study. However, on the basis of an estimated $\Delta H_r = 0$ kcal/mol for its decomposition to acetaldehyde and isopropoxy radical, and on the basis of the nature of the leaving group, a 298 K rate coefficient for decomposition of 10^7 s^{-1} can be estimated from the various relationships defined above.

3.2.2. β-Hydroxyalkoxy Radicals

The β-hydroxyalkoxy species are an important class of radicals, generated in the OH-initiated oxidation of alkenes, as shown below for the generic alkene RCH═CHR:

$$\mathrm{OH + RCH{=}CHR \rightarrow R{-}CH(OH){-}C^{\bullet}HR} \quad (17)$$

$$\mathrm{RCH(OH)C^{\bullet}HR + O_2 \rightarrow RCH(OH)CHRO_2^{\bullet}} \quad (18)$$

$$\mathrm{RCH(OH)CHRO_2^{\bullet} + NO \rightarrow RCH(OH)CHRO^{\bullet} + NO_2} \quad (19)$$

As discussed in the article by Atkinson[14] and summarized in Table 2, decomposition reactions for this class of alkoxy radicals are rapid, considerably more so than for the corresponding non-hydroxylated radical, a fact that can be understood in terms of the lower ionization potential of the RC•HOH-type leaving group and a lowering of the reaction enthalpy upon hydroxylation:

$$\mathrm{RCH(OH){-}CHRO^{\bullet} \rightarrow RC^{\bullet}H(OH) + CHR{=}O} \quad (20)$$

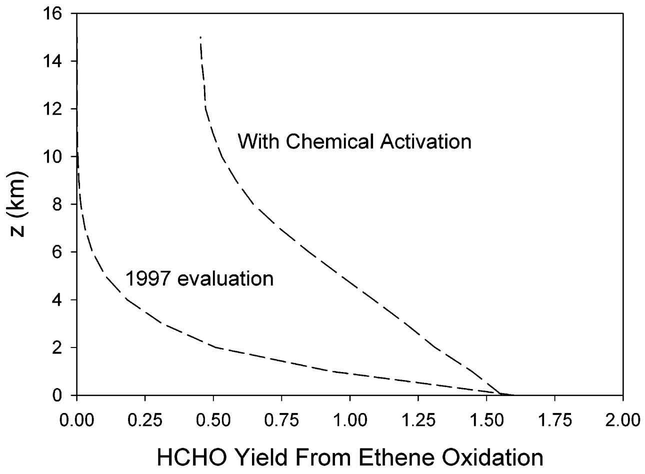


Figure 8. Molar formaldehyde yield from OH-initiated oxidation of ethene as a function of altitude. Yields were calculated with and without[14] allowance for chemical activation of the $\mathrm{HOCH_2CH_2O^{\bullet}}$ radical.

Work on ethene oxidation[17,19,61,62,114] has shown that unimolecular decomposition and reaction with O_2 are competing fates of the 2-hydroxy-1-ethoxy radical under conditions of relevance to the lower troposphere:

$$\mathrm{HOCH_2CH_2O^{\bullet} + O_2 \rightarrow HOCH_2CHO + HO_2} \quad (21)$$

$$\mathrm{HOCH_2CH_2O^{\bullet} \rightarrow {}^{\bullet}CH_2OH + CH_2O} \quad (22)$$

with the barrier to the decomposition process reported to be ~10 kcal/mol.[17,19] As will be discussed in more detail later, the 2-hydroxy-1-ethoxy and other β-hydroxyalkoxy radicals are prone to chemical activation; that is, their formation in the exothermic reaction of the corresponding β-hydroxyperoxy radical with NO imparts internal energy to the nascent alkoxy fragment that allows for a "prompt" dissociation to occur a fraction of the time. Thus, in the case of 2-hydroxy-1-ethoxy, for example, the relative importance of dissociation does decrease at the lower temperatures of the upper troposphere, but not as rapidly as would be expected from a purely thermal process (see Figure 8).

In the case of larger β-hydroxyalkoxy radicals, unimolecular dissociation is even more rapid than is the case for 2-hydroxy-1-ethoxy. Various studies have shown that dissociation is the major, if not sole, atmospheric fate of the β-hydroxyalkoxy radicals derived from propene, 1-butene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethylbutene.[18,38,40,47,50,64] Vereecken et al.[18] have demonstrated that the barrier to decomposition for the two β-hydroxyalkoxy radicals derived from propene oxidation, $\mathrm{CH_3CH(OH)\text{-}CH_2O^{\bullet}}$ and $\mathrm{CH_3CH(O^{\bullet}){-}CH_2OH}$, is only about 7 kcal/mol, and that the majority of the dissociation for these species occurs via chemical activation. While chemical activation also likely plays a role in the decomposition of larger β-hydroxyalkoxy radicals as well,[183] the low barriers to decomposition imply a very rapid ($\geq 10^7$ s^{-1}) thermal dissociation process, which precludes the significant occurrence of any reaction with O_2. Atkinson has provided estimates of the dissociation rate coefficients for various hydroxyalkoxy radicals,[14] on the basis of the known ionization potentials for various $RC^{\bullet}HOH$ radicals and estimates of the enthalpy for dissociation of the β-hydroxyalkoxy radicals considered. However, it now appears[17-19,183] that both the enthalpy and the barrier height for many of these processes are lower and the dissociation processes are faster than previously predicted.[14]

While unimolecular dissociation is the sole atmospheric fate for most β-hydroxyalkoxy radicals, this is not the case for those β-hydroxyalkoxy radicals derived from long-chain 1-alkenes, such as 1-pentene:[40,44,135]

$$OH + CH_2{=}CHCH_2CH_2CH_3 + O_2 \rightarrow {}^{\bullet}OOCH_2{-}CH(OH)CH_2CH_2CH_3 \quad (23)$$

$$^{\bullet}OOCH_2CH(OH)CH_2CH_2CH_3 + NO \rightarrow {}^{\bullet}OCH_2CH(OH)CH_2CH_2CH_3 + NO_2 \quad (24)$$

In these cases, isomerization reactions via 1,5-H shifts can also occur in competition with the dissociation:

$$^{\bullet}OCH_2CH(OH)CH_2CH_2CH_3 \rightarrow HOCH_2CH(OH)CH_2CH^{\bullet}CH_3 \quad (25)$$

$$^{\bullet}OCH_2CH(OH)CH_2CH_2CH_3 \rightarrow CH_2O + {}^{\bullet}CH(OH)CH_2CH_2CH_3 \quad (26)$$

While these isomerization processes will be discussed in more detail below, in section 3.3, it is apparent that they must occur with rate coefficients in excess of 10^6 s^{-1} in order to compete with dissociation.

The atmospheric oxidation of many biogenic hydrocarbons (in particular, isoprene and the terpenes) is also expected to proceed via the formation of β-hydroxyalkoxy radicals. In the case of isoprene (2-methyl-1,3-butadiene), the relatively large yield of formaldehyde that has been observed in chamber studies, along with coproducts methyl vinyl ketone (MVK) and methacrolein,[48,119,208] indicates that unimolecular decomposition is an important pathway for the various β-hydroxyalkoxy radicals formed. One example is shown here for illustrative purposes:

$$OH + CH_2{=}CH{-}C(CH_3){=}CH_2 \rightarrow HOCH_2{-}C^{\bullet}H{-}C(CH_3){=}CH_2 \quad (27)$$

$$HOCH_2{-}C^{\bullet}H{-}C(CH_3){=}CH_2 + O_2 \rightarrow HOCH_2{-}CH(OO^{\bullet}){-}C(CH_3){=}CH_2 \quad (28)$$

$$HOCH_2{-}CH(OO^{\bullet}){-}C(CH_3){=}CH_2 + NO \rightarrow HOCH_2{-}CH(O^{\bullet}){-}C(CH_3){=}CH_2 + NO_2 \quad (29)$$

$$HOCH_2{-}CH(O^{\bullet}){-}C(CH_3){=}CH_2 + NO \rightarrow {}^{\bullet}CH_2OH + \mathbf{O{=}CH{-}C(CH_3){=}CH_2} \quad (30)$$

$$^{\bullet}CH_2OH + O_2 \rightarrow \mathbf{CH_2O} + HO_2 \quad (31)$$

Though the formaldehyde yield from the OH-initiated oxidation of isoprene is less than unity, this is believed to be due to the allylic nature of the OH–isoprene adducts, which leads to the formation of 1,4-hydroxyalkoxy radicals,[119,120,208]

$$HOCH_2{-}C^{\bullet}(CH_3){-}CH{=}CH_2 \leftrightarrow HOCH_2{-}C(CH_3){=}CH{-}CH_2^{\bullet} \quad (32)$$

$$HOCH_2{-}C(CH_3){=}CH{-}CH_2^{\bullet} + O_2 \rightarrow HOCH_2{-}C(CH_3){=}CH{-}CH_2O_2^{\bullet} \quad (33)$$

rather than to the existence of other reaction pathways for the β-hydroxyalkoxy radicals themselves.

The atmospheric oxidation of terpenes (a series of biogenic $C_{10}H_{16}$ compounds) is currently a topic of great interest, given the importance of the oxidation of these species to organic aerosol formation. Complete oxidation schemes, and specifically the nature of the products involved in aerosol nucleation and growth, have yet to be established. Many terpenes (for example, α-pinene; see Figure 9) possess cyclohexene skeletons, whose oxidation leads to the generation of cyclic β-hydroxyalkoxy radicals. Decomposition of either of the two possible β-hydroxyalkoxy radicals generated in the OH-initiated oxidation of α-pinene should lead to pinonaldehyde in large yield. However, it is currently believed that the pinonaldehyde yield is quite low, only ~30% or so,[121] implying that other reaction channels, including various isomerizations and ring-opening reactions (see Figure 9 for a couple of examples), may be available to these complex radicals.[136,177,178,184] A full description of the chemistry of the terpenes is beyond the scope of the present article, but details can be found in ref 177, for example.

3.2.3. Other Oxygen-Substituted Alkoxy Radicals

The atmospheric oxidation of ketones can proceed via the production of a β-oxo-substituted alkoxy radical, as shown below for 2-butanone:[56]

$$OH + CH_3CH_2C({=}O)CH_3\ ({+}O_2) \rightarrow CH_3CH(OO^{\bullet})C({=}O)CH_3 + H_2O \quad (34)$$

$$CH_3CH(OO^{\bullet})C({=}O)CH_3 + NO \rightarrow CH_3CH(O^{\bullet})C({=}O)CH_3 + NO_2 \quad (35)$$

Experiments have now demonstrated that the acetyl radical and other acyl fragments are very good leaving groups, consistent with their low ionization potentials, and that unimolecular dissociation of these species is rapid. For example, Cox et al.[56] have shown that decomposition is the sole fate of the $CH_3CH(O^{\bullet})C({=}O)CH_3$ radical at 298 K, leading to the production of acetaldehyde and an acetyl fragment with a rate coefficient $>10^6$ s^{-1}. Studies of acetone[22,112] indicate similar behavior for the acetonoxy radical, not only at 298 K but also at the very low temperatures representative of the upper troposphere:

$$CH_3C({=}O)CH_2O^{\bullet} \rightarrow CH_3C^{\bullet}O + CH_2O \quad (36)$$

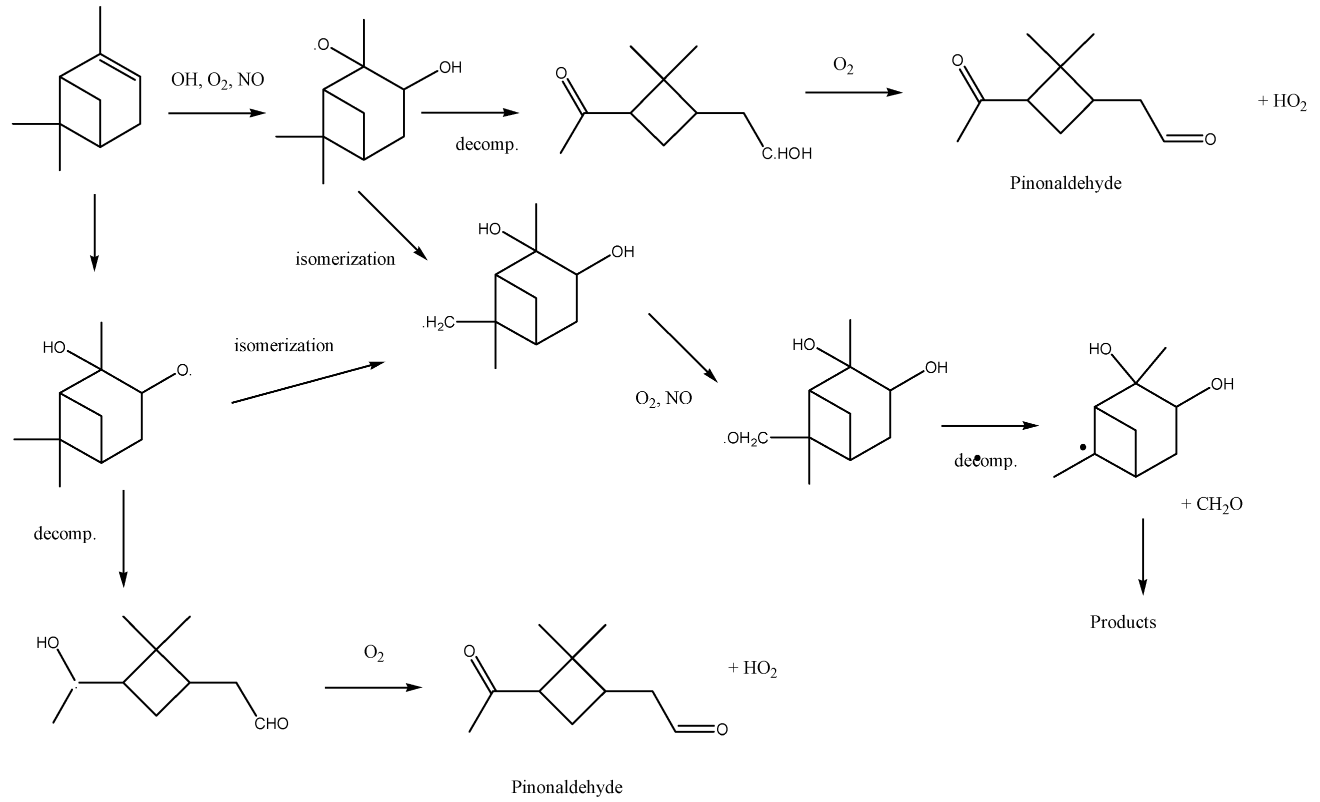


Figure 9. Partial oxidation scheme for α-pinene, showing decomposition pathways for the two β-hydroxyalkoxy radicals leading to pinonaldehyde production, and some potentially competing isomerization pathways.

The barrier for this dissociation process has been shown to be quite low (~6−7 kcal/mol), and again chemical activation plays a role in the dissociation process when acetonoxy radicals are produced from the exothermic acetonylperoxy radical/NO reaction.[22] Studies of larger ketones have also been conducted,[54] but in these cases OH attack occurs largely at sites that are distant from the carbonyl group, where the influence of the carbonyl moiety is not likely large.

The atmospheric oxidation of ethers leads in part to the production of α-alkoxy-substituted alkoxy radicals of general form $R{-}O{-}C(O^\bullet)<$, where R represents an organic fragment. In general, ester production dominates the chemistry of these species. For example, oxidation of methyl ethers leads to the formation of $R{-}O{-}CH_2O^\bullet$ radicals, whose major fate in most cases is reaction with O_2:[39,45,106,109,113,124]

$$CH_3{-}O{-}CH_2O^\bullet + O_2 \rightarrow CH_3OCHO + HO_2 \quad (37)$$

$$C(CH_3)_3{-}O{-}CH_2O^\bullet + O_2 \rightarrow C(CH_3)_3OCHO + HO_2 \quad (38)$$

$$CH_3CH_2C(CH_3)_2{-}O{-}CH_2O^\bullet + O_2 \rightarrow CH_3CH_2C(CH_3)_2OCHO + HO_2 \quad (39)$$

The one exception encountered to date is the $CH_3CH_2CH_2CH_2{-}O{-}CH_2O^\bullet$ radical, obtained in the oxidation of *n*-butyl methyl ether, which appears to undergo isomerization rather than reaction with O_2.[39]

The strong thermodynamic driving force to ester production in the chemistry of these α-alkoxy-substituted alkoxy radicals leads to a peculiarity in the chemistry of the $CH_3OCH_2O^\bullet$ radical generated from dimethyl ether oxidation. Jenkin et al.[109] showed that rupture of the C−H bond is surprisingly facile, with a rate coefficient of approximately 3000 s^{-1} at 298 K and 25 Torr total pressure:

$$CH_3OCH_2O^\bullet + M \rightarrow CH_3OCHO + H + M \quad (40)$$

Similar behavior has been demonstrated at slightly elevated temperature for the $HOCH_2O^\bullet$ radical, derived following reaction of HO_2 with CH_2O.[209] Given the likelihood of a faster rate coefficient for reaction 40 at atmospheric pressure than at 25 Torr, this reaction likely occurs to a certain extent in the lower atmosphere, in competition with reaction with O_2:

$$CH_3{-}O{-}CH_2O^\bullet + O_2 \rightarrow CH_3OCHO + HO_2 + M \quad (37)$$

Note, however, that this process (reaction 40) has no impact on atmospheric chemistry, since the H atom generated via decomposition will rapidly add to O_2. Nonetheless, the occurrence of this H atom elimination, with an estimated barrier of about 14 kcal/mol (assuming an *A*-factor near 5×10^{13} s^{-1} near atmospheric pressure), is in perfect keeping with Choo and Benson-type correlations of ΔH_{rxn} and E_a for H atom elimination processes. A similar occurrence of a facile H atom elimination in the chemistry of some of the larger alkoxy-substituted methoxy radicals (e.g., $(CH_3)_3COCH_2O^\bullet$), though not studied to date, is also likely.

Oxidation of ethyl (and larger) ethers can lead to the generation of radicals of the form R−O−CH(O•)−R′. For the most part, cleavage of the C−C bond to form esters is the most favorable process for these radicals, as the presence of the RO− substituent leads to a weakening of the neighboring C−R′ bond. For example, in the case of the 1-ethoxy-ethoxy radical obtained from diethyl ether,[67] the rate of decomposition via C−C bond cleavage (reaction 41) is believed to exceed the rates for reactions 42 and 43 by a factor of 15 or more at room temperature and 1 atm air:

$$CH_3CH_2O{-}CH(O^\bullet)CH_3 \rightarrow CH_3CH_2OCHO + {}^\bullet CH_3 \quad (41)$$

$$CH_3CH_2O{-}CH(O^\bullet)CH_3 \rightarrow CH_3CH_2O^\bullet + CH_3CHO \quad (42)$$

$$CH_3CH_2O{-}CH(O^\bullet)CH_3 + O_2 \rightarrow CH_3CH_2O{-}C({=}O)CH_3 + HO_2 \quad (43)$$

Similarly, decomposition via C−C bond cleavage has been shown to be the predominant fate of a variety of other similar radicals, as summarized by Aschmann and Atkinson[39] and highlighted in Table 2. The prevalence of C−C bond scission versus C−O bond scission can be understood from a simple consideration of the thermodynamics involved, as reaction 42 is endothermic by roughly 11 kcal/mol and reaction 41 is roughly thermoneutral. On the basis of the observed product yields reported by Eberhard et al.[67] and an assumed rate coefficient for reaction 43 on the order of 10^{-14} cm^3 molecule^{-1} s^{-1}, the barrier for reaction 41 can be estimated at approximately 11 kcal/mol, consistent with the correlations shown in Figure 7 for methyl as the leaving group. It should also be noted, however, that at least in one case, that of ethyl *tert*-butyl ether,[110] evidence for C−O bond rupture, reaction 45, as a minor process has been noted:

$$(CH_3)_3C{-}O{-}CH(O^\bullet)CH_3 \rightarrow (CH_3)_3COCHO + {}^\bullet CH_3 \quad (44)$$

$$(CH_3)_3C{-}O{-}CH(O^\bullet)CH_3 \rightarrow (CH_3)_3CO^\bullet + CH_3CHO \quad (45)$$

As discussed by Aschmann and Atkinson,[39] these C−O bond ruptures appear to be more rapid than would be anticipated on the basis of the thermodynamics involved and the ionization potentials of the alkoxy radical leaving groups.

Oxidation of larger ethers, such as methyl *tert*-butyl ether (MTBE),[45,106,113] ethyl *tert*-butyl ether (ETBE),[78,110] and *n*-butyl methyl ether,[39] can also lead to the production of β-oxy-substituted alkoxy radicals, as illustrated below for MTBE:

$$OH + CH_3OC(CH_3)_3 \rightarrow CH_3OC(CH_3)_2CH_2^\bullet \quad (46)$$

$$CH_3OC(CH_3)_2CH_2^\bullet + O_2 \rightarrow CH_3OC(CH_3)_2CH_2O_2^\bullet \quad (47)$$

$$CH_3OC(CH_3)_2CH_2O_2^\bullet + NO \rightarrow CH_3OC(CH_3)_2CH_2O^\bullet + NO_2 \quad (48)$$

The behavior of a representative set of these radicals, drawn mostly from the summary of Aschmann and Atkinson,[39] is outlined in Table 2. In general, it appears that the β-alkoxy substituents are rather good leaving groups, as might be expected from their low ionization potentials ($IP(CH_3OCH_2^\bullet) = 6.9$ eV). For example, Ferenac et al.[182] estimate from a theoretical study that the decomposition of $CH_3OCH_2CH_2O^\bullet$ occurs with a barrier of only ∼7−8 kcal/mol, much lower than the barrier for decomposition of the nonsubstituted 1-butoxy case. Decomposition is also thought to be the major fate of the $CH_3OC(CH_3)_2CH_2O^\bullet$, $CH_3CH_2OC(CH_3)_2CH_2O^\bullet$, and $CH_3CH_2CH(O^\bullet)CH_2OCH_3$ radicals encountered in the oxidation of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *n*-butyl methyl ether, respectively.[39]

The final class of oxygenates to be considered in this review are the esters, for which some end-product studies and theoretical analyses have now been conducted.[55,80,93,96,97,123,125,126,186] Although an extensive dataset has yet to be obtained, some general conclusions can be drawn from the available data. One common type of alkoxy radical, encountered in the oxidation of methyl esters, is the series of radicals of general formula $RC({=}O)OCH_2O^\bullet$.[80,93,96,97] Under tropospheric conditions, two pathways have been encountered for these species: reaction with O_2 to produce anhydrides,

$$RC({=}O)OCH_2O^\bullet + O_2 \rightarrow RC({=}O)OC({=}O)H + HO_2 \quad (49)$$

and a novel α-ester rearrangement process[55] that will be discussed in more detail below (see section 3.4),

$$RC({=}O)OCH_2O^\bullet \rightarrow RC({=}O)OH + H^\bullet CO \quad (50)$$

This rearrangement process seems to be even more rapid in the case of $RC({=}O)OCHRO^\bullet$ radicals, and represents the predominant fate of the $CH_3C({=}O)OCH(O^\bullet)CH_3$ radical,[55,123] although reaction with O_2, decomposition via C−C or C−O bond scission, or isomerization may also occur to a small degree.[123] In the event that no α-hydrogen is available, as in the case of the $CH_3C({=}O)OC(O^\bullet)(CH_3)_2$ radical derived from isopropyl acetate,[55,125,126] C−C bond cleavage to generate CH_3 radicals and acetic anhydride dominates,

$$CH_3C({=}O)OC(O^\bullet)(CH_3)_2 \rightarrow CH_3C({=}O)OC({=}O)CH_3 + {}^\bullet CH_3 \quad (51)$$

though C−O bond rupture and/or isomerization to generate acetone are also possible:

$$CH_3C(O)OC(O^\bullet)(CH_3)_2 \rightarrow CH_3C(O)O^\bullet + (CH_3)_2CO \quad (52)$$

$$CH_3C(O)OC(O^\bullet)(CH_3)_2 \rightarrow\rightarrow {}^\bullet OCH_2C(O)OC(OH)(CH_3)_2 \quad (53)$$

$${}^\bullet OCH_2C(O)OC(OH)(CH_3)_2\ (+O_2) \rightarrow CH_2O + CO_2 + (CH_3)_2CO + HO_2 \quad (54)$$

Longer chain alkyl esters can lead to the generation of radicals possessing acyloxy substituents located beta to the alkoxy site (or even farther away); for example, the oxidation of *n*-propyl acetate[123,125] results in the formation of $CH_3C(O)OCH_2CH(O^\bullet)CH_3$ and $CH_3C(O)OCH_2CH_2CH_2O^\bullet$ radicals. As might be expected by analogy to nonsubstituted radicals of similar structure, reaction with O_2 is a major fate in the latter case, while decomposition via C−C bond cleavage appears to dominate in the former case:

$$CH_3C(O)OCH_2CH(O^\bullet)CH_3 \rightarrow CH_3CHO + CH_3C(O)OCH_2^\bullet \quad (55)$$

$$\rightarrow CH_3C(O)OCH_2CHO + CH_3^\bullet \quad (56)$$

$$CH_3C(O)OCH_2CH_2CH_2O^\bullet + O_2 \rightarrow CH_3C(O)OCH_2CH_2CHO + HO_2 \quad (57)$$

Reaction of OH with esters can also occur on the acyl side of the molecule, although this appears to be a minor occurrence in the case of the acetates.[210] Attack on longer acyl groups is expected to occur to a greater extent, however, and product studies are available for a couple of these compounds, namely methyl propionate, $CH_3CH_2C(O)OCH_3$, and methyl pivalate, $(CH_3)_3C(O)OCH_3$.[96,97] For example, in a study of methyl propionate oxidation, Cavalli et al.[97] showed that, for the $CH_3CH(O^\bullet)C(O)OCH_3$ radical, reaction with O_2 and C−C bond cleavage occurred in competition, as in the case of the structurally similar 2-butoxy radical:

$$CH_3CH(O^\bullet)C(O)OCH_3 + O_2 \rightarrow CH_3C(O)C(O)OCH_3 + HO_2 \quad (58)$$

$$CH_3CH(O^\bullet)C(O)OCH_3 \rightarrow CH_3CHO + {}^\bullet C(O)OCH_3 \quad (59)$$

Oxidation of methyl pivalate proceeds in large part via the ${}^\bullet OCH_2C(CH_3)_2C(O)OCH_3$ radical, which leads in large part via reactions 60 and 61 to acetone production:

$${}^\bullet OCH_2C(CH_3)_2C(O)OCH_3 \rightarrow\rightarrow CH_2O + {}^\bullet OC(CH_3)_2C(O)OCH_3 \quad (60)$$

$${}^\bullet OC(CH_3)_2C(O)OCH_3 \rightarrow (CH_3)_2C(O) + {}^\bullet C(O)OCH_3 \quad (61)$$

3.2.4. Halogenated Alkoxy Radicals

Halogenated alkoxy radicals can be generated in the atmosphere via two different routes, either via the oxidation of an alkene initiated by halogen atom (Cl or Br) addition,

$$Cl + R{-}CH{=}CH{-}R \rightarrow R{-}CH(Cl){-}C^\bullet HR \quad (62)$$

$$R{-}CH(Cl){-}C^\bullet HR + O_2 \rightarrow R{-}CH(Cl){-}CHRO_2^\bullet \quad (63)$$

$$R{-}CH(Cl){-}CHRO_2 + NO \rightarrow R{-}CH(Cl){-}CHRO^\bullet + NO_2 \quad (64)$$

or via the OH-initiated oxidation of the various halocarbon species present in the atmosphere. In particular, the decision to eliminate the use of chlorofluorocarbons (CFCs) and replace these species with hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) provided the impetus for the study of a variety of these partially halogenated C1 and C2 alkoxy radicals. A number of chlorinated, brominated, and iodinated methanes and ethanes are also present in the atmosphere as the result of natural emissions, and their oxidation proceeds as well via the formation of halogen-substituted alkoxy radicals.

In addition to the possibility of unimolecular reaction via C−C bond cleavage, other routes, mostly involving C−X (where X refers to Cl or Br) bond cleavage, are also possible. Table 3 lists a number of halogenated alkoxy radicals of possible importance in the atmosphere, the dominant reaction pathways that these species undergo, and any available information related to the thermodynamics/reaction dynamics of these reactions. What follows is a general discussion of available rate coefficient data for the halogenated alkoxy radicals that have been studied to date, and some general reactivity trends for these species.

We will first consider the effect of halogen substitution in an α-position. The presence of a halogen in a position alpha to the alkoxy radical site opens up the possibility for cleavage of the carbon−halogen bond, for example in the case of bromomethoxy,

$$BrCH_2O^\bullet \rightarrow Br + CH_2O \quad (65)$$

In the case of fluorine, rupture of a C−F bond is not at all favorable and will not occur under atmospheric conditions. For example, decomposition of the $FCH_2O^\bullet$ radical to F and CH_2O is a highly endothermic process ($\Delta H_{rxn} = 34$ kcal/mol). The presence of F atoms in the α-position does, however, have a positive effect on the rate of the beta carbon−carbon bond scission process, much as was the case for the presence of an α-RO− substituent discussed above. For example, Somnitz and Zellner[169] have demonstrated theoretically that the endothermicity and concomitant barriers to carbon−carbon bond cleavage decrease quite dramatically with F atom substitution for the series of reactions (66−68) below:

$$CF_3CH_2O^\bullet \rightarrow CF_3^\bullet + CH_2O \qquad (66)$$

$$CF_3CHFO^\bullet \rightarrow CF_3^\bullet + CHFO \qquad (67)$$

$$CF_3CF_2O^\bullet \rightarrow CF_3^\bullet + CF_2O \qquad (68)$$

Similar trends can be arrived at from the consideration of the decomposition of ethoxy ($\Delta H_{rxn} = 13$ kcal/mol, $E_a = 18$ kcal/mol; see Table 1) and 1-fluoroethoxy ($\Delta H_{rxn} = 0$ kcal/mol, $E_a = 12$ kcal/mol[171]).

Cleavage of C−X bonds is much more favored in the cases where X = Cl, Br, or I. This can be understood from a simple consideration of the thermodynamics involved, since the enthalpies for rupture of the C−X bond in $X{-}CH_2O^\bullet$ radicals are +34, +6, −8, and −19 kcal/mol for X = F, Cl, Br, and I, respectively. In fact, in all cases where Br or I atoms are present in the α-position, rupture of the C−Br or C−I bond is the dominant process. For example, Orlando et al.[70] and Chen et al.[65] showed conclusively that CH_2O is formed in >90% yield in the Cl-atom-initiated oxidation of methyl bromide:

$$Cl + CH_3Br \rightarrow {}^\bullet CH_2Br + HCl \qquad (69)$$

$${}^\bullet CH_2Br + O_2 \rightarrow CH_2BrO_2^\bullet \qquad (70)$$

$$CH_2BrO_2^\bullet + NO \rightarrow CH_2BrO^\bullet + NO_2 \qquad (71)$$

$$CH_2BrO^\bullet \rightarrow Br + CH_2O \qquad (65)$$

Similarly, HCOBr and $COBr_2$ are the expected end-products in the Cl-atom-initiated oxidation of dibromomethane and bromoform, respectively.[72,187,188] Analogous alkoxy radical decomposition reactions via C−I bond cleavage have been inferred in studies of alkyl iodide oxidation by Cotter et al.[122] The low dissociation barriers to many of these dissociation processes (see Table 3) indicates that chemical activation may play a role when the brominated or iodinated alkoxy radical is generated from the exothermic reaction of the corresponding peroxy radical with NO, though studies of this possibility have not been conducted to date.

Carbon−chlorine bond cleavages are not as facile as is the case for C−Br and C−I, but these processes are still sufficiently rapid to occur in a number of cases, for example in the chemistry of $CF_2ClO^\bullet$ radical.[211] However, alkoxy radicals containing a single α-chlorine atom and at least one α-hydrogen atom, such as for $ClCH_2O^\bullet$ and $CH_3CHClO^\bullet$, provide something of a special case, as three-centered elimination of HCl has been demonstrated to be a favorable process for these species:[20,23,79,105,212]

$$CH_3CHClO^\bullet \rightarrow CH_3C^\bullet O + HCl \qquad (72)$$

$$CH_2ClO^\bullet \rightarrow HCO + HCl \qquad (73)$$

As will be discussed in more detail below, these processes can actually be thought of as C−Cl bond cleavages in their initial stages, but with a late occurrence of HCl formation. Thermal rate coefficients for reactions 72 and 73 are thought to be on the order of 10^6 and 10^4 s^{-1}, respectively, though chemical activation again plays a role in the chemistry of these species.

For alkoxy radicals possessing multiple chlorine atoms in the α-position, straightforward C−Cl cleavage dominates the chemistry, as in the case of $CHCl_2O^\bullet$ [58,170,213] and $CFCl_2O^\bullet$,[214] e.g.:

$$CHCl_2O^\bullet \rightarrow HCOCl + Cl \qquad (74)$$

Reaction 74 is highly exothermic (−10.5 kcal/mol[170]) and occurs through a rather low (2 kcal/mol) barrier.[170]

It should be noted that the presence of an α-chlorine atom does not guarantee that dissociation via C−Cl cleavage (or via HCl elimination) will be the dominant atmospheric process in all cases. For example, both the $CCl_3CCl_2O^\bullet$ [81,101] and $CF_3CHClO^\bullet$ [100] radicals are thought to undergo decomposition in part via C−C bond cleavage, and reaction with O_2 is thought to occur in part for both the $CF_3CHClO^\bullet$ [100] and $CH_2ClO^\bullet$ [20,79] radicals:

$$CCl_3CCl_2O^\bullet \rightarrow {}^\bullet CCl_3 + CCl_2O \qquad (75)$$

$$CCl_3CCl_2O^\bullet \rightarrow CCl_3COCl + Cl \qquad (76)$$

$$CF_3CHClO^\bullet \rightarrow {}^\bullet CF_3 + HCOCl \qquad (77)$$

$$CF_3CHClO^\bullet \rightarrow CF_3CO + HCl \qquad (78)$$

$$CF_3CHClO^\bullet + O_2 \rightarrow CF_3COCl + HO_2 \qquad (79)$$

$$CH_2ClO^\bullet \rightarrow H^\bullet CO + HCl \qquad (80)$$

$$CH_2ClO^\bullet + O_2 \rightarrow HCOCl + HO_2 \qquad (81)$$

As alluded to above, one way in which β-halogenated alkoxy radicals can arise in the atmosphere is via the Cl-atom (or Br-atom)-initiated oxidation of an alkene (see reactions 62−64 above). In contrast to β-hydroxyalkoxy radicals discussed earlier, dissociaton is not a particularly favorable processes for the β-chlorinated or β-brominated species. For example, the observation of large yields of chloroacetaldehyde from the Cl-initiated oxidation of ethene[17,66,111] has demonstrated that reaction with O_2 is the major fate of $ClCH_2CH_2O^\bullet$ radicals in the atmosphere:

$$Cl + CH_2CH_2 \rightarrow ClCH_2CH_2^\bullet \qquad (82)$$

$$ClCH_2CH_2^\bullet + O_2 \rightarrow ClCH_2CH_2O_2^\bullet \qquad (83)$$

$$ClCH_2CH_2O_2^\bullet + NO \rightarrow ClCH_2CH_2O^\bullet + NO_2 \qquad (84)$$

$$ClCH_2CH_2O^\bullet + O_2 \rightarrow ClCH_2CHO + HO_2 \qquad (85)$$

Similar chemistry is seen in the case of the Br addition to ethene.[66] The C−C bond scission process has been estimated to occur with a rate coefficient on the order of about 50 s^{-1}, and to proceed through a barrier of about 16 kcal/mol.[176] Even for larger β-chlorinated or brominated radicals, decomposition via C−C bond cleavage is not particularly favorable. In fact, as a general rule, the presence of a chlorine

Table 4. Summary of the Available Data Regarding the Chemistry of Alkoxy Radicals Derived from Fluorinated Ethers

radical	dominant reaction pathway(s)	products	activation energy (kcal/mol)	approximate rate (s^{-1})[a]	refs
$CF_3CH_2OCH(O^{\bullet})CF_3$	unimolecular dissociation	$CF_3CH_2OCHO + {}^{\bullet}CF_3$	<11	7×10^5	83
$CF_3OCH_2O^{\bullet}$	rxn. with O_2	$CF_3OCHO + HO_2$			85
n-$C_4F_9{-}O{-}CH_2O^{\bullet}$	rxn. with O_2	n-$C_4F_9OCHO + HO_2$			86
n-$C_3F_7{-}O{-}CH_2O^{\bullet}$	rxn. with O_2	n-$C_3F_7OCHO + HO_2$			87
$CF_3CF(O^{\bullet}){-}O{-}CF_3$	unimolecular dissociation	${}^{\bullet}CF_3 + FC(O)OCF_3$			88
$CF_3{-}O{-}CF_2O^{\bullet}$	unimolecular dissociation	$CF_3O^{\bullet} + COF_2$			89
$CH_2F{-}O{-}CH(O^{\bullet})F$	unimolecular dissociation, rxn. with O_2	$CH_2FO^{\bullet} + HCOF$ $CH_2F{-}O{-}C(O)F + H$ $CH_2F{-}OC(O)F + HO_2$	*b*		90
$R_2CF{-}OCH(O^{\bullet})CH_3$	rxn. with O_2	$R_2CF{-}O{-}C(O)CH_3 + HO_2$			91, 92
	unimolecular dissociation	$R_2CF{-}O{-}CHO + CH_3^{\bullet}$	~ 13	$\sim 1 \times 10^4$	
$CF_3CH(O^{\bullet}){-}O{-}CHF_2$	unimolecular dissociation	${}^{\bullet}CF_3 + HC(O)OCHF_2$	$<12^b$		84
	rxn. with O_2	$CF_3C(O)OCHF_2$			
$CF_3CCl(O^{\bullet}){-}O{-}CHF_2$	unimolecular dissociation	$CF_3C(O)OCHF_2 + Cl$			84

[a] Applies to conditions of the lower troposphere (298 K, 1 atm air). [b] Unimolecular dissociation process enhanced by chemical activation (see text section 3.5 and Table 6 for details).

or bromine atom in the β-position has little effect on the behavior of a given alkoxy radical relative to its non-halogenated counterpart.[73,176] For example, it was presented above that, at 298 K, the ratio of decomposition to O_2 reaction for the 2-butoxy radical is roughly 4×10^{18} molecules cm^{-3}, similar to the rate coefficient ratio obtained by Orlando et al.[73] for the $CH_3CH(Cl)CH(O^{\bullet})CH_3$ radical, which arises from the Cl-atom-initiated oxidation of *trans*-2-butene.

Other, more highly substituted chlorine- and fluorine-containing alkoxy radicals arise in the atmosphere from the oxidation of various CFC, HFC, and HCFC compounds, and thus some information is available regarding the behavior of the relevant alkoxy radicals under tropospheric conditions. However, this class of radicals has not been the subject of as much systematic study as is the case for the non-halogenated radicals, and thus the development of structure−reactivity relationships is less mature at this stage. From a general consideration of the data presented in Table 3, it is apparent that the substitution of multiple Cl atoms beta to the alkoxy radical site leads to a general decrease in the endothermicity of the C−C bond rupture process, but with only a very modest lowering of the barrier to decomposition (compare ethoxy radical decomposition, $\Delta H_r = 13$ kcal/mol,[14] $E_a = 18$ kcal/mol,[151,153,164,167] with that of 2,2,2-trichloroethoxy, $\Delta H_{rxn} = 6$ kcal/mol, $E_a = 14$ kcal/mol[76]). From the standpoint of the Choo−Benson relationship of ΔH_{rxn} to E_a, one might expect that chlorinated radicals would be very good leaving groups, given the decrease in ionization potential along the series ${}^{\bullet}CH_3$, ${}^{\bullet}CH_2Cl$, ${}^{\bullet}CHCl_2$, ${}^{\bullet}CCl_3$. However, as is shown in Figure 7, this is not the case; dissociation reactions involving chloromethyl and 1-chloroethyl radicals as leaving groups follow much the same trend as is the case for reactions involving methyl radical as the leaving group, despite the lower ionization potential of the chlorinated radicals.

One of the atmospheric consequences of the relative stability of these β-chlorinated alkoxy radicals (relative to the β-hydroxyalkoxy radicals) is that the Cl (or Br)-atom-initiated oxidation of alkenes leads to production of some rather complex and unique chlorinated, partially oxygenated species.[73,115−118,184] For example, Finalyson-Pitts and co-workers[117,118] have demonstrated the production of various chloro-methyl-butenal and chloro-methyl-butenone compounds from the Cl-atom-initiated oxidation of isoprene, and have proposed that the detection and quantification of these species in the atmosphere can be used as a marker for the occurrence of Cl chemistry.

Less extensive data are available for alkoxy radical unimolecular dissociation reactions involving fluorinated methyl radicals as the leaving group. Theoretical studies[168] of $CF_3CH_2O^{\bullet}$ radical decomposition suggest a very high barrier to this process, 25 kcal/mol, despite the fact that the endothermicity is not substantially different than for ethoxy radical decomposition. In contrast, consideration of the available data for decomposition of the series of radicals $CF_{3-n}H_nCHFO^{\bullet}$ (see Table 3) indicates a slight decrease in activation energy with increasing fluorine substitution, despite a fairly constant endothermicity. Clearly, a quantitative description of structure−reactivity relationships for these fluorinated radicals will not be possible without further data on the endothermicity and energy barriers to these processes. As a last point, we note that some C−C bond scissions reactions involving fluorinated alkoxy radicals are quite exothermic, such as in the case of $CF_3CF_2O^{\bullet}$ decomposition,[168] yet it appears that there is a minimum barrier in the neighborhood of 8 kcal/mol for these processes, regardless of the exothermicity.

A last class of compounds to be discussed is a group of fluorinated or partially fluorinated ethers[83−92] that are being used, or have been proposed for use, as CFC replacement compounds. The compounds studied to date, and the fate of the relevant alkoxy radicals under lower tropospheric conditions, are summarized in Table 4. The general behavior of this class of alkoxy radicals can be summarized as follows. Radicals of general formula $R{-}O{-}CH_2O^\bullet$ (where R is a fluorinated alkyl fragment) react predominantly with O_2 to generate a fluorinated formate,[85-87] in analogous fashion to the non-fluorinated analogues such as $CH_3OCH_2O^\bullet$. Elimination of an H atom may also play a role in the chemistry of these species, a process which leads to the same formate end-product as O_2 reaction. Radicals of the form $R{-}O{-}CH(O^\bullet)CH_3$ (where again R represents a fluorinated alkyl group) appear to undergo reaction via C−C bond scission and reaction with O_2, though bond scission processes appear to be of reduced importance in the case of fluorinated R groups than for non-fluorinated species.[91] (For example, recall that the $CH_3CH_2OCH(O^\bullet)CH_3$ and $CF_3CH_2OCH(O^\bullet)CF_3$[83] undergo C−C bond cleavage exclusively in 1 atm air at 298 K). Radicals possessing fluorine substitution either alpha or beta to the alkoxy radical site (e.g., $CH_2F{-}O{-}CHFO^\bullet$,[90] $CHF_2{-}O{-}CH(O^\bullet){-}CF_3$,[84] $CF_3{-}O{-}CF_2O^\bullet$,[89] etc.) enjoy a rich chemistry, with O_2 reaction (if an α-hydrogen is available) or decomposition via C−C, C−H, or C−O bond scission all potentially playing a role. For example, in the case of $CH_2F{-}O{-}CHFO^\bullet$,[90] three competing pathways have been observed:

$$CH_2F{-}O{-}CHFO^\bullet + O_2 \rightarrow CH_2F{-}O{-}CFO + HO_2 \quad (86)$$

$$CH_2F{-}O{-}CHFO^\bullet \rightarrow HCOF + CH_2FO^\bullet \quad (87)$$

$$CH_2F{-}O{-}CHFO^\bullet \rightarrow CH_2F{-}O{-}CFO + H \quad (88)$$

3.3. Isomerization Reactions

Isomerization of alkoxy radicals via an intramolecular 1,5-hydrogen shift, the so-called Barton reaction, has been known in the solution phase for more than 40 years,[215] and the possibility that the same reaction may occur in the gas phase under atmospheric conditions has also long been acknowledged. However, direct experimental evidence has been scant until recently, owing largely to the complex nature of the eventual end-products of the isomerizations and the fact that other rapidly occurring unimolecular processes often compete. Calculations by Carter et al.[43] and Baldwin et al.[204] showed that the entropy and strain energy terms are favorable for isomerization to occur for six-membered rings, particularly if the hydrogen atom being abstracted is a secondary hydrogen. Thus, the simplest system in which isomerization might be expected is the 1-butoxy radical:

$$CH_3CH_2CH_2CH_2O^\bullet \rightarrow {}^\bullet CH_2CH_2CH_2CH_2OH \quad (89)$$

This system was studied experimentally by Carter et al.,[42] Niki et al.,[60] and Cox et al.[56] by examining the competition between isomerization and reaction with O_2:

$$CH_3CH_2CH_2CH_2O^\bullet + O_2 \rightarrow HO_2 + CH_3CH_2CH_2CHO \quad (90)$$

Measurements of the butanal yields as a function of oxygen pressure led to estimates of the rate coefficient ratio k_{89}/k_{90} in the range $(1.5-1.9) \times 10^{19}$ molecules cm^{-3}. Niki et al.[60] found evidence for residual features in the FTIR spectrum which may belong to the 4-hydroxybutanal formed following a second isomerization:

$${}^\bullet CH_2CH_2CH_2CH_2OH + O_2 \rightarrow {}^\bullet O_2CH_2CH_2CH_2CH_2OH \quad (91)$$

$${}^\bullet O_2CH_2CH_2CH_2CH_2OH + NO \rightarrow {}^\bullet OCH_2CH_2CH_2CH_2OH + NO_2 \quad (92)$$

$${}^\bullet OCH_2CH_2CH_2CH_2OH \rightarrow HOCH_2CH_2CH_2C^\bullet HOH \quad (93)$$

$$HOCH_2CH_2CH_2C^\bullet HOH + O_2 \rightarrow HO_2 + HOCH_2CH_2CH_2CHO \quad (94)$$

This basic pattern conforms to what is expected for most simple oxy radicals formed from linear and branched alkanes. Atkinson has refined the earlier estimates of isomerization rates to derive empirical relationships relating the first-order rate coefficient to the structure of the radical (see later).[14]

The study of Eberhard et al.[68] was aimed at showing that isomerizations occurred for 2- and 3-hexoxy radicals. From the yields of the simple carbonyls formed, these workers concluded that these radicals do indeed isomerize, and they estimated relative rate coefficients for isomerization, decomposition, and reaction with O_2 for the two radicals. They also tentatively identified the hydroxycarbonyl 5-hydroxy-hexan-2-one and a hydroxynitrate formed from the reactions of the isomerized radicals.

Shortly thereafter, Atkinson and co-workers[41,52] were able to use atmospheric pressure ionization mass spectrometric (API-MS) methods to qualitatively identify hydroxycarbonyls formed in the oxidation of butane through octane, the first definitive in situ measurement of isomerization products. In these papers, the yields of primary carbonyls with the same number of carbon atoms as the alkanes was shown to decrease gradually, from 60−70% in the case of butane to <2% for octane. A semiquantitative analysis also showed that the hydroxycarbonyl yields increased substantially with the length of the carbon chain. All the available evidence thus points to rapid isomerization taking place, particularly if a secondary hydrogen is available for abstraction. Since OH abstraction at a terminal methyl group is not expected to be fast, it is clear that isomerizations would be expected to dominate for hexane and higher alkanes, since abstraction at the 2-position, followed by isomerization to the 5-position, is then possible. In the case of pentane, isomerization of the 1-pentoxy radical is rapid, but its yield from OH attack is low.[41] Relative yields for products from isomerization and

Table 5. Summary of Available Data Regarding Isomerization Reactions[a]

radical	product	approximate rate at 298 K, 1 atm (s^{-1})[b]	E_a (kcal/mol)[c]	ref
1-butoxy	${}^{\bullet}CH_2CH_2CH_2CH_2OH$	1.6×10^5		42
		1.5×10^5		56
		1.9×10^5		60
		2.0×10^5	8.4 sar	14
		1.3×10^5	9.4 b3lyp	175
		1.2×10^5	9.2 bac4	191
		1.1×10^5	9.9 g2	167
		1.7×10^5	8.8 dft	165
			9.9 b3lyp	182
2-pentoxy	${}^{\bullet}CH_2CH_2CH_2CH(OH)CH_3$	2.5×10^5		41
		2.0×10^5	8.4 sar	14
		5.0×10^5	8.8 g2	167
2-hexoxy	$CH_3C^{\bullet}HCH_2CH_2CH(OH)CH_3$	$(1.4-4.7) \times 10^6$		68
		2.0×10^6	6.8 sar	14
3-hexoxy	${}^{\bullet}CH_2CH_2CH_2CH(OH)CH_2CH_3$	$(1.8-4.3) \times 10^6$		68
		2.0×10^5	8.4 sar	14
δ-OH-isoprene	$HOC^{\bullet}HC(CH_3){=}CHCH_2OH$	8.5×10^7	5.4 mpw1k	180
		2.1×10^8	5.3 mpw1k	190
δ-OH-isoprene	$HOC^{\bullet}HCH{=}C(CH_3)CH_2OH$	1.0×10^8	5.2 mpw1k	180
		2.1×10^9	3.9 mpw1k	190
2-OH-1-butoxy	${}^{\bullet}CH_2CH_2CH(OH)CH_2OH$	1.8×10^2	12.2 dft	183
2-OH-1-pentoxy	$CH_3C^{\bullet}HCH_2CH(OH)CH_2OH$	3.8×10^6	9.4 dft	183
2-OH-1-hexoxy	$CH_3CH_2C^{\bullet}HCH_2CH(OH)CH_2OH$	3.7×10^6	9.0 dft	183

[a] Radicals that are thought to undergo a significant isomerization in the atmosphere. [b] If no activation energy is given, rate is experimental at 1 bar and 300 K, measured relative to O_2 reaction using $k(O_2) \approx 8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. [c] Activation energy, at 1 bar and 300 K when given, calculated at the level of theory shown, or from structure–activity relationship (sar) and appropriate A-factor.

reaction with O_2 for these alkoxy radicals have been tabulated by Kwok et al.[52] and are seen to be in broad agreement with those calculated. In addition to the hydroxycarbonyls, a number of hydroxynitrates are also seen, which presumably derive from the isomerized alkyl radicals.

$$ {}^{\bullet}CH_2CH_2CH_2CH_2OH + O_2 \rightarrow {}^{\bullet}O_2CH_2CH_2CH_2CH_2OH \quad (91) $$

$$ {}^{\bullet}O_2CH_2CH_2CH_2CH_2OH + NO \rightarrow O_2NOCH_2CH_2CH_2CH_2OH \quad (95) $$

Further evidence for the occurrence of isomerizations in simple alkoxy radicals comes from the work of Hornung et al.,[216] who used a novel variation of the neutralizaton–reionization mass spectroscopic technique. These authors noted the propensity for isomerization of 1-butoxy, 1-pentoxy, and 3-methyl-1-pentoxy radicals. Furthermore, using deuterium labeling in the 1-pentoxy radical, isomerization was shown to occur exclusively from the 4-position in the pentoxy, i.e., via a six-membered transition state.

Currently there are no published experimental studies on the temperature dependence of isomerization reactions. The Arrhenius parameters estimated by Atkinson[14] point to relatively low barriers for 1,5-shifts. Preliminary studies from the National Center for Atmospheric Research (NCAR) laboratory on the isomerization of 1-butoxy radicals certainly support this picture, yielding a barrier of 8–9 kcal mol^{-1}, in agreement with the estimated value.[14]

Similar behavior has been observed in the case of 1-alkenes, where the yields of both formaldehyde and the complementary carbonyl decrease with the length of the alkene chain.[40,44,135] For example, in the case of 1-hexene, the following competition is expected:

$$ HOCH_2CHO^{\bullet}CH_2CH_2CH_2CH_3 \rightarrow HOCH_2CH(OH)CH_2CH_2CH^{\bullet}CH_3 \quad (96) $$

$$ HOCH_2CH(OH)CH_2CH_2CH^{\bullet}CH_3 + O_2 \rightarrow\rightarrow \text{products including } HOCH_2C({=}O)CH_2CH_2CH(OH)CH_3 \quad (97) $$

$$ HOCH_2CHO^{\bullet}CH_2CH_2CH_2CH_3 \rightarrow {}^{\bullet}CH_2OH + CH_3CH_2CH_2CH_2CHO \quad (98) $$

$$ {}^{\bullet}CH_2OH + O_2 \rightarrow HO_2 + HCHO \quad (99) $$

The implied competition between these channels confirms the rapidity of the isomerizations, since decomposition of β-hydroxyalkoxy radicals is known to be very rapid ($>10^5$ s^{-1}). However, the rates of isomerization calculated for these radicals by Rayez and co-workers[165,183] are slower than for the analogous unsubstituted alkoxy radicals, as a result of the hydrogen bonding between the oxy radical and the adjacent –OH group.

The key factor in the mechanism for isomerizations of alkoxy radicals is the existence of an unstrained, slightly puckered, six-membered cyclic transition state which facilitates transfer of an aliphatic hydrogen atom to an oxygen atom four carbons distant.[165,167] It is interesting—but also critical—to consider what happens in larger, structurally more complex molecules. Perhaps the most important nonmethane hydrocarbon in the atmosphere is isoprene, and this molecule also offers an interesting scenario.

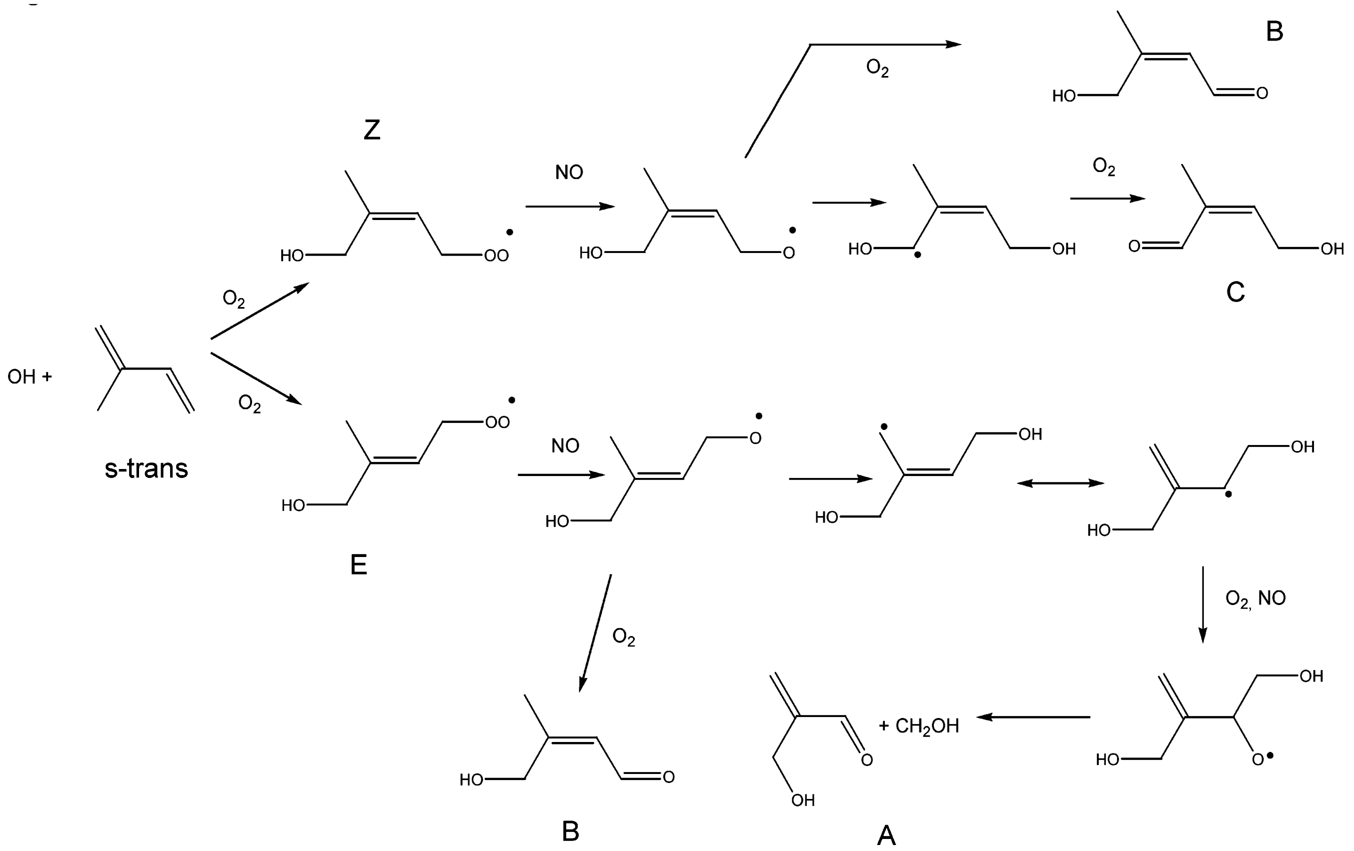


Figure 10. Formation of possible reaction products from the *E* and *Z* isomers of allylized radicals generated following reaction of OH with isoprene. Note the formation of isomeric products, B (3-methyl-4-hydroxybut-2-enal) and C (2-methyl-4-hydroxybut-2-enal), in addition to the unique isomerization to hydroxymethacrolein (A).

Isoprene is a conjugated 1,3-diene, and addition of OH can occur at either double bond.[11,119,120] As has been presented earlier (see reactions 27−33), addition at either of the outer carbon atoms (which is the expected mechanism) leads to the formation of an allylic radical, which can add O_2 in either of two distinct positions due to the resonance structure— either beta or delta to the OH site. The β-oxy radical will most likely decompose (to give formaldehyde and either MVK or methacrolein, all of which are observed), while the δ-radical, e.g., $HOCH_2{-}C(CH_3){=}CH{-}CH_2O^\bullet$, has the possibility to isomerize.[119] However, the isomerization now occurs across an internal double bond. The presence of the double bond will stiffen the molecule, and also hold it planar, so no puckering is possible. However, it will also reduce the number of degrees of freedom of the molecule and reduce the entropy of activation (essentially holding the oxy radical center in close proximity to the hydrogen atom to be abstracted). Dibble[180] calculated an *A*-factor for this type of isomerization that is a factor of 10 higher than that for loose, puckered rings. A further factor in this reaction may be the weakness of the abstracted hydrogen to form an allylic center (only 74 kcal for a C−H bond in the CH_2OH group according to Zhao et al.[190]). However, since the orbital of the abstracted hydrogen is necessarily oriented perpendicular to the π-system of the double bond, it is unlikely that there is any allylic nature to the transition state.[217]

There are other steric considerations when looking at the overall product distribution. Isoprene exists as a mixture of s-trans and s-cis forms. While these isomers interconvert readily at room temperature (barrier ∼4 kcal),[218] the thermalized allylic radicals are not expected to show internal rotation (barrier 15 kcal).[219] Dibble[180] has argued that, following the initial OH attack, the allyl radicals are chemically activated, and may rearrange, but once the radicals become thermalized it is likely that the conformation of the carbon skeleton is maintained throughout the rest of the reaction sequence. Thus, as shown in Figure 10, the *E* form of the allyl radical leads to the formation of formaldehyde and hydroxymethacrolein (compound A of Figure 10), while the *Z* form should give 2-methyl-4-hydroxybut-2-enal (compound C). The *Z*-radical also forms the isomeric 3-methyl-4-hydroxybut-2-enal (compound B) by reaction with O_2, and since these molecules are indistinguishable by present methods, it is not possible to say whether both isomerizations occur. However, a rapid isomerization would be expected to dominate over O_2 reaction.[180] Apparently, isomerization does occur to some extent, since hydroxymethacrolein (or one of its isomers) was observed by Kwok et al. using API-MS.[120] It can be seen that the number and complexity of products becomes large, and that the existence of different stereoisomers of the initially formed radicals can lead to chemically distinct products, not just isomers of the same product.

It is also interesting to speculate on the conditions under which other, more exotic isomerizations may occur. In the case of linear alkanes, the five-membered transition states are not expected because the internal strain energy is too high (5−6 kcal).[175,191,204] For the case of a seven-membered transition state, calculations by Houk et al.[220] indicate that the process is not favored on entropic grounds. However, if the hydrogen being abstracted is less strongly bound, as in the case of an aldehydic proton, it is feasible that the isomerization becomes favorable. There is some indirect evidence for this occurring in the study of Orlando et al. on cyclopentane.[71] The radical formed on cleavage of the cyclopentoxy radical eventually forms 5-oxopentoxy, for which two possible isomerizations are possible, one six-membered ring abstracting a $-CH_2-$ hydrogen, and one seven-membered ring abstracting an aldehydic hydrogen:

$$CH(O)CH_2CH_2CH_2CH_2O^\bullet \rightarrow CH(O)C^\bullet HCH_2CH_2CH_2OH \tag{100}$$

$$CH(O)CH_2CH_2CH_2CH_2O^\bullet \rightarrow {}^\bullet C(O)CH_2CH_2CH_2CH_2OH \tag{101}$$

Application of the standard oxidation reactions to the above radicals leads to the formation, as end-products, of CO from the first radical and CO_2 from the second. Orlando et al.[71] observed comparable amounts of CO and CO_2 below room temperature, and suggested that this may be evidence for the occurrence of a seven-membered isomerization.

In the oxidation of molecules with rigid frameworks such as terpenes, possibilities for unusual isomerizations also exist. In this case, the cyclobutane ring holds certain groups in proximity to one another, and it is possible that some seven-membered transition states are in fact less strained than six-membered ones when the three-dimensional configuration of the molecule is considered. One such possibility was proposed by Orlando et al.[136] to explain the acetone yield in their study of α-pinene oxidation, while other possibilities were noted by Peeters et al.,[177] including a 1,7-hydrogen transfer. A further consideration of these isomerizations is, as pointed out by Atkinson[15] and by Peeters et al.,[177] that their occurrence is contingent on the oxy group and the abstractable hydrogen both being on the same side of the ring. It is not clear at present what factors (if any) affect the stereochemistry of addition of OH (and subsequently O_2) to the ring in α-pinene and other terpenes, and what influence this has on the oxidation products observed.

The first attempts to calculate the rates of alkoxy radical isomerizations, by Carter et al.[43] and Baldwin et al.,[204] involved a simple thermochemical model, which considered the loss of entropy in forming an internal ring structure, coupled with the strain energy intrinsic to forming that ring. In this way, A-factors of the order of 10^{11} s^{-1} per hydrogen atom were estimated, along with activation energies of the order 6−7 kcal mol^{-1}, leading to isomerization rates of around 10^5 s^{-1} for 1-butoxy, and up to 10^7 s^{-1} for larger radicals. On the basis of the available experimental data, Atkinson[14] has modified the parameters and provided structure−reactivity rules, analogous to those for abstraction reactions of OH radicals with hydrocarbons. The currently recommended kinetic parameters, given in the work of Atkinson[14] and Aschmann and Atkinson,[39] for six-membered 1,5-isomerization reactions are as follows, where the rate constants are evaluated for conditions of 1 atm and 298 K:

$$\begin{array}{lll}
k(\mathrm{prim}) = 1.6 \times 10^5\ \mathrm{s}^{-1} & A(\mathrm{prim}) = 2.4 \times 10^{11}\ \mathrm{s}^{-1} & E/R = 4240\ \mathrm{K} \\
k(\mathrm{sec}) = 1.6 \times 10^6\ \mathrm{s}^{-1} & A(\mathrm{sec}) = 1.6 \times 10^{11}\ \mathrm{s}^{-1} & E/R = 3430\ \mathrm{K} \\
k(\mathrm{tert}) = 4.0 \times 10^6\ \mathrm{s}^{-1} & A(\mathrm{tert}) = 8.0 \times 10^{10}\ \mathrm{s}^{-1} & E/R = 2745\ \mathrm{K} \\
F(\mathrm{CH_3}) = 1.00 & F(\mathrm{alk}) = 1.27 & F(\mathrm{OH}) = 4.3
\end{array}$$

The rate coefficient, k(prim), k(sec), or k(tert), depends on the nature of the hydrogen atom being abstracted, and is multipied by the corresponding factors according to the presence of other groups attached to that carbon atom. These rate coefficients should allow the assessment of the importance of isomerization reactions for many alkanes over a range of atmospheric temperatures, at a pressure of 1 bar.

A number of papers based on quantum chemical calculations and RRKM theory have appeared over the past few years. In general, the height of the calculated isomerization barrier depends on the level of theory used, with differences of up to 2 kcal mol^{-1} common. However, most calculations put the barrier for 1-butoxy isomerization between 7 and 9 kcal mol^{-1},[165,167,175,182,191] in agreement with Atkinson's estimate and with activation energies estimated from the limited experimental data available. The limiting high-pressure A-factors tend to be higher than the original estimate made by Baldwin et al.[204] Values in the range of $(2-5) \times 10^{12}$ s^{-1} are found, which are still a factor of 10−20 lower than those for unimolecular decompositions described earlier, a result of the high entropy of activation. Ferenac et al.[182] also point out that tunneling can play a large role in the reaction, possibly increasing the 1-butoxy isomerization rate by a factor of 200.

The calculations by Somnitz and Zellner,[167] Méreau et al.,[165] and Lendvay and Viskolcz[191] all indicate that the isomerization reactions should be somewhat pressure dependent over the range of atmospheric conditions. The rate coefficient at 1 atm is calculated to be within a factor of 2 of the high-pressure value. The result of this is that the *apparent* A-factor at 760 Torr could be a factor of 10 lower than the high-pressure value, bringing it into closer agreement with the empirical value derived by Atkinson. At lower pressures, <100 Torr, the isomerization rate coefficient is predicted to be strongly dependent on P.

It is interesting to speculate whether isomerization reactions should be subject to chemical activation. As yet, no experimental studies have been conducted that were detailed enough to evaluate this effect. Caralp et al.[183] have performed theoretical studies on the β-hydroxyalkoxy radicals derived from 1-alkenes. They indicate that some activated isomerization should occur. However, in this case the radicals also have a competing channel, unimolecular decomposition, and the latter would be expected to dominate in the activated case, because of the higher A-factor (higher density of states) associated with the loose transition state for decomposition. Zhao et al.[190] also predict that the δ-hydroxyalkenoxy radicals from allylized isoprene−OH adducts in the *Z*-configuration should also be subject to chemical activation, with greater than 60% of the radicals dissociating before they can be collisionally stabilized.

At present, isomerization reactions still present many unknowns both experimentally and theoretically. In contrast to decomposition reactions, there have been no direct studies of isomerizations, and all of the experimental evidence is derived from relative product yields in chamber studies. In fact, other than the study of pentane by Atkinson et al.,[41] all of the reported yields are semiquantitative at best. Time-resolved experiments designed to detect either the oxy radicals or the products would be useful. One problem is that the isomerizations of interest are very rapid, and the slower ones often have competing channels that are faster. This leads to problems in preparing the radicals in a thermalized state more rapidly than the rate of isomerization. Furthermore, since the product formed is an alkyl radical, in the presence of O_2 it will also be removed rapidly and converted to a peroxy radical, which are also difficult to detect with any degree of specificity. One approach is to use the photolysis of a nitrite to form the alkoxy radical, as was done in the chamber study of the oxidation of 1-butoxy by Niki et al.[60] However, it is known that the UV photolysis of nitrites imparts substantial energy to the alkoxy radicals,[150] and that relatively large pressures of bath gas are needed to stabilize them. Since the barriers to alkoxy radical isomerization are so low, the activated radicals will also be subject to rapid isomerization. Nevertheless, Okumura and co-workers[221] have succeeded in detecting time-resolved spectra in the OH-stretching region following the photolysis of 1-butyl nitrite, which they attributed to the isomerized alkyl radical 4-hydroxy-1-butyl. Improvements in optical techniques, particularly in the infrared, should allow direct confirmation of the rates of isomerization and pressure and temperature dependences in coming years.

Further theoretical studies are also required to calculate the thermochemistry, particularly of some of the more “exotic” isomerizations from larger biogenic molecules, and to fully elucidate the role of tunneling. It is worth commenting that, for many of these systems, the barriers are only of the order of 5−10 kcal mol^{-1}. Subtle intramolecular forces such as hydrogen bonds or O−O lone pair repulsion can alter the energetics of such multifunctional radicals by up to 5 kcal mol^{-1},[17,22] and affect the most stable conformations of both the ground state and the transition state. Thus, particularly in reactions where a competition between two or more channels is evident, full account of the energetics needs to be taken.

In terms of understanding the atmosphere, it is of importance to understand the temperature dependence of isomerization reactions. As mentioned earlier, many of the reaction products from isomerization reactions are multifunctional oxygenates, which are candidates for deposition onto, or even nucleators of particles. Since these removal processes will be more efficient at low temperatures typical of the upper troposphere, the role of isomerizations in particle formation and growth needs to be fully explored.

3.4. Other Intramolecular Reactions

In addition to the standard reactions described above for alkoxy radicals (i.e., reaction with O_2, C−C bond fission, and 1,5-isomerization as illustrated in Figure 2), oxy radicals with highly electronegative substituents have been found to undergo a number of other reactions. These seem to be specific to the substituent present, and are very sensitive to the thermochemistry of the radical. The reactions involve constrained transition states, but have relatively low barriers. Since these reactions usually occur in competition with other simpler pathways, there is only a narrow range of radicals for which the reactions are important in the atmosphere.

3.4.1. HCl Elimination Reactions

This reaction occurs for radicals of the type $RCHClO^•$ formed from chlorinated hydrocarbons. It was first identified by Shi et al.[105] for the 1-chloroethoxy radical formed in the oxidation of chloroethane in air. Shi et al. noted the formation of HCl and CO_2, which was interpreted as evidence for the presence of $CH_3C^•(O)$ radicals:

$$CH_3CHClO^• + M \rightarrow HCl + CH_3C^•(O) + M \quad (72)$$

$$CH_3C^•(O) + O_2 + M \rightarrow CH_3C(O)O_2^• + M \quad (102)$$

$$CH_3C(O)O_2^• + RO_2^• \rightarrow CH_3CO_2^• + RO^• + O_2 \quad (103)$$

$$CH_3CO_2^• \rightarrow CH_3^• + CO_2 \quad (104)$$

Shi et al. showed that HCl elimination is actually the dominant channel under lower tropospheric conditions, faster than the O_2 reaction:

$$CH_3CHClO^• + O_2 \rightarrow CH_3C(O)Cl + HO_2 \quad (105)$$

Further evidence of the rapidity of the reaction came in a time-resolved study by Maricq et al.,[212] who measured the production of HCl directly. They derived a lower limit of $5 \times 10^5\ s^{-1}$ for the elimination. The effects of temperature and chemical activation have recently been investigated by Orlando and Tyndall.[23] In the absence of NO_x, reaction of $CH_3CHClO^•$ with O_2 and decompositon via HCl elimination were shown to be competing fates of the $CH_3CHClO^•$ radical, with $k_{72}/k_{105} = 3.3 \times 10^{23} \exp(-2230/T)$ molecules cm^{-3}. The $CH_3CHClO^•$ radical was also shown to be subject to a chemical activation effect; when produced in the exothermic reaction of $CH_3CHClO_2^•$ with NO, about 50% of the nascent $CH_3CHClO^•$ radicals decompose promptly via HCl elimination.

The most-studied reaction of this type is that of the chloromethoxy radical, $CH_2ClO^•$:

$$CH_2ClO^• + M \rightarrow HCl + H^•CO, \quad \Delta H = -11 \text{ kcal} \quad (73)$$

$$H^•CO + O_2 \rightarrow HO_2 + CO \quad (106)$$

Kaiser and Wallington[108] first studied the oxidation of CH_3Cl as a function of O_2 at room temperature, and found a competition between reaction 73 and reaction with O_2:

$$CH_2ClO^{\bullet} + O_2 \rightarrow HO_2 + HC(O)Cl \quad (107)$$

By measuring the ratio of CO/HC(O)Cl as a function of O_2, they found $k_{73}/k_{107} = 2.2 \times 10^{17}$ molecules cm^{-3} at 700 Torr. By varying the total pressure, they were also able to show that the unimolecular elimination was in the falloff region. At 1 atm, the decomposition rate coefficient is estimated to be 2000 s^{-1}.

The work was extended to other temperatures by Wallington et al.[79] Both these studies found that, in pure oxygen at room temperature, the majority of radicals were being scavenged by O_2, implying that the elimination reaction is somewhat slower than that of $CH_3CHClO^{\bullet}$. Wallington et al. also deduced an activation energy of 8.6 ± 1.9 kcal mol^{-1} for the HCl elimination, and confirmed the overall pressure dependence at 294 K.

In a later study by these same groups,[20] a reduced yield of HC(O)Cl was noted upon addition of NO to the system, due to enhanced decomposition of the $CH_2ClO^{\bullet}$ radicals formed chemically activated. This finding supports the low activation energy found by Wallington et al.[79]

The elimination of HCl from $CH_2ClO^{\bullet}$ radicals has also been studied in a series of papers by Wu and Carr[161,162] using flash photolysis and time-resolved photoionization mass spectrometry of the products HCl and HCOCl. They worked at pressures up to 35 Torr, and temperatures in the range 265−306 K, confirming a dependence on pressure, with an activation energy of 9.5 ± 1.4 kcal mol^{-1} at 10 Torr. These authors also used RRKM theory[192] to fit their data (which are at the low-pressure limit), and to extrapolate to 700 Torr (see next paragraphs). When combined with their measured rate coefficient for k_{107}, $2.0 \times 10^{-12} \exp(-934/T)$, a relative rate coefficient at 700 Torr of $k_{73}/k_{107} = 5.0 \times 10^{17}$ molecules cm^{-3} at 296 K is obtained, in reasonable agreement with that reported by Wallington et al.[79]

Elimination of HCl has also been observed in the chemistry of the $CH_2ClCHClO^{\bullet}$ [95] and $CCl_3CHClO^{\bullet}$ [171] radicals. In the case of the 1,2-dichloroethane oxidation, Wallington et al.[95] found $k(\mathrm{diss})/k(O_2) = 4.4 \times 10^{19}$ molecules cm^{-3} for thermalized $CH_2ClCHClO^{\bullet}$ radicals. All known cases of radicals which undergo the HCl elimination are included in Table 3.

The three-center mechanism for the HCl elimination is clearly quite unusual, and has provoked a number of theoretical studies. Catoire et al.[222] first examined the possibility of HCl elimination from $CH_2ClO^{\bullet}$ in 1994. They located a transition state for the elimination lying 19 kcal mol^{-1} above the ground state. This is clearly much higher than the experimentally measured values, and produces a rate coefficient much slower than those observed (although their experiments indirectly supported the HCl elimination). Hou et al.[172] conducted a theoretical study of the decomposition pathways of $CH_3CHClO^{\bullet}$, and concluded that HCl elimination should dominate the behavior of this radical at room temperature. The barrier to HCl elimination was found to be 5.7 (without tunneling) or 4.6 kcal mol^{-1} (including tunneling). In contrast, the fission to eliminate Cl atoms had a barrier of 6.4 (6.0 with tunneling) kcal mol^{-1}. They also explored the pressure dependence of the reaction and found that the reaction is about a factor of 10 below the high-pressure limit at 700 Torr. The limiting high-pressure *A*-factor for HCl elimination is estimated to be ~8×10^{13} s^{-1}, similar to what might be expected for a simple bond fission. Interestingly, this group had previously examined the reactions of $CH_2ClO^{\bullet}$,[173] but did not report parameters for the HCl elimination channel. However, in the later paper on $CH_3CHClO^{\bullet}$, they comment that HCl elimination should also be dominant for $CH_2ClO^{\bullet}$.

Wu and Carr[192] augmented their experimental studies with RRKM studies of the $CH_2ClO^{\bullet}$ radical. The barrier to HCl elimination was found to be 10.5 kcal mol^{-1}, in good agreement with the experiments of Wallington et al.[79] and Wu and Carr.[161,162] The reaction was found to be in the low-pressure region up to several atmospheres total pressure, with a limiting *A*-factor at high pressure of 5.8×10^{13} s^{-1}, similar to that found for $CH_3CHClO^{\bullet}$ by Hou et al.[172] Thus, it seems that the experimental results of Wallington et al., which roll off with pressure, are inconsistent with the calculations of Wu and Carr, and it seems reasonable that the rate coefficient should keep increasing linearly with pressure. The pressure dependence found by Wallington et al. gives a high-pressure *A*-factor of only 6.4×10^{9} s^{-1}, which seems physically much too low to be near k_{∞}.

It is interesting to examine the transition states for the two most likely decomposition channels:[192]

$$CH_2ClO^{\bullet} + M \rightarrow HCl + H^{\bullet}CO, \quad \Delta H = -11 \text{ kcal} \quad (73)$$

$$CH_2ClO^{\bullet} + M \rightarrow Cl + HCHO, \quad \Delta H = +4 \text{ kcal} \quad (108)$$

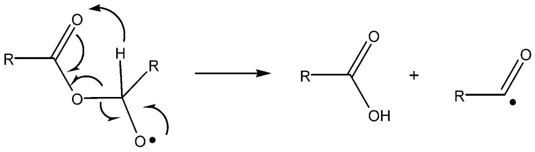
In both HCl elimination and C−Cl scission, the C−Cl bond length is about the same, 2.15 Å. In the C−Cl channel, the remaining HCHO group is essentially planar, while the transition state for HCl elimination is still pyramidal. (It is feasible that the C−Cl bond initially starts to lengthen, and then, depending on the orientation of the HCHO fragment, either channel could occur.) The rate coefficients for the two channels are predicted to differ by factors of 15−30 at 296 K, and no evidence for Cl elimination from thermalized $CH_2ClO^{\bullet}$ was found. However, for experiments done in the presence of NO, where the $CH_2ClO^{\bullet}$ was formed chemically activated, Bilde et al.[20] found evidence for promotion of both channels from the activated radicals. This suggests that the *A*-factors and activation energies are indeed similar.

Finally, it is worth addressing whether the analogous channel could occur in other radicals. Hou et al.[170] calculated that the elimination of HCl from $CHCl_2O^{\bullet}$ is exothermic by 23 kcal, with a barrier of 8 kcal. However, loss of chlorine is in this case exothermic, with a barrier of only 2 kcal. Thus, loss of a chlorine atom dominates this radical at all atmospherically relevant temperatures.[139]

In the case of bromine and fluorine substituents, the energetics probably preclude the occurrence of the HX elimination reaction for any of the radicals. For $CHF_2O^•$,[170] although the overall reaction to eliminate HF is 12 kcal exothermic, the barrier is ~33 kcal,[170] because of the strength of the C−F bond (elimination of F atoms is uphill by 24 kcal). In the case of Br, the elimination of HBr is ~7 kcal mol^{-1} exothermic. However, the presence of a very weak C−Br bond means that loss of Br is very rapid, and Orlando et al.[70] concluded that HBr elimination from $CH_2BrO^•$ probably did not occur (<5%).

3.4.2. The Ester Rearrangement Reaction

A further reaction that appears to be specific to one class of substituted oxy radicals is the so-called α-ester rearrangement. This reaction was first noted by Tuazon et al. in their study of ethyl acetate.[55] The reaction involves transfer of a hydrogen atom in a five-membered transition state from the alkyl chain of an ester to the carbonyl group in the acid function:



(109)

As a historical note, in the investigation of ethylene oxide oxidation made by Niki and co-workers,[137] the $HC(O)OCH_2O^•$ radical was formed, and gave a product distribution consistent with what is now known from methyl formate oxidation. However, the chemistry was not recognized as being a result of the ester rearrangement. The ester rearrangement is novel in mechanistic terms, and also interesting because it leads to the gas-phase production of a carboxylic acid, the atmospheric sources of which are not well known. The reaction is expected to mainly occur in urban regions, where esters are present both as solvents and as the breakdown products of ethers.

Since Tuazon's original paper, several others have confirmed the mechanism and extended it to other radicals. Picquet-Varrault et al.[123,126] studied a series of acetates and identified the occurrence of the ester rearrangement in primary radicals from ethyl, *n*-propyl, and isobutyl acetates. The oxidation of isopropyl and *tert*-butyl acetates also lead to secondary radicals which undergo the rearrangement. The overall product distribution obtained for ethyl acetate by Picquet-Varrault et al.[123] is in good agreement with that of Tuazon et al.,[55] and both conclude that, in air, the oxy radical undergoes rearrangement essentially 100% of the time (rate coefficient >10^6 s^{-1}), and that no reaction with O_2 to give acetic anhydride occurs:

$$CH_3C(O)OCH(CH_3)O^• + O_2 \rightarrow HO_2 + CH_3C(O)OC(O)CH_3 \quad (110)$$

Kerr and Stocker[125] also studied the oxidation mechanism of *n*-propyl acetate in 1986, and observed products consistent with those reported by Picquet-Varrault et al.[123]

Christensen et al.[93] carried out a systematic study of the oxidation of methyl acetate, varying the O_2 pressure, both with and without NO present, to give a more complete picture of the mechanism:

$$CH_3C(O)OCH_2O^• \rightarrow CH_3C(O)OH + H^•CO \quad (111)$$

$$CH_3C(O)OCH_2O^• + O_2 \rightarrow HO_2 + CH_3C(O)OCH(O) \quad (112)$$

By measuring the yields of acetic acid and acetic formic anhydride as a function of O_2 pressure, they derived a rate coefficient ratio of $k_{111}/k_{112} = 6 \times 10^{18}$ molecules cm^{-3}. Experiments with NO present also showed that the reaction is subject to chemical activation, with approximately 20% of the oxy radicals dissociating promptly under atmospheric conditions. These two results can thus be combined to infer (1) a rate coefficient at room temperature and pressure of around 10^5 s^{-1} (typically the first-order rate for reaction with O_2) and (2) a relatively low barrier (<12 kcal or so) for chemical activation to occur.

Other relevant studies are those by Cavalli et al.[97] (methyl propionate), Wallington et al.[80] (methyl formate), and Wallington et al.[96] (methyl pivalate, $(CH_3)_3C(O)OCH_3$). All these studies were more complex, since the parent molecule can be attacked at more than one site, but a consistent picture of the mechanisms could be obtained, allowing the rate of rearrangement to be obtained relative to the O_2 reaction. Cavalli et al.[97] showed that in air in the presence of NO, 60% of $C_2H_5C(O)OCH_2O^•$ radicals undergo rearrangement, identical to the fraction found by Christensen[93] for $CH_3C(O)OCH_2O^•$ under the same conditions. Wallington et al.[80] studied methyl formate over a wide range of oxygen pressures, and extracted a ratio of $k_{113}/k_{114} = 1.5 \times 10^{18}$ molecules cm^{-3}:

$$HC(O)OCH_2O^• \rightarrow HC(O)OH + H^•CO \quad (113)$$

$$HC(O)OCH_2O^• + O_2 \rightarrow HC(O)OCHO + HO_2 \quad (114)$$

They were also able to show that roughly one-third of the radicals are subject to chemical activation, meaning that under atmospheric conditions a formic acid yield of about 15% is expected (since abstraction of the methyl hydrogen accounts for roughly half of the total reaction). The study of methyl pivalate[96] found some evidence of the α-rearrangement, but the branching ratio for abstraction at the methoxy group was too low to be able to quantify the available pathways for that radical.

Maurer et al.[138] have also noted the occurrence of the ester rearrangement in ethylene glycol diformate, $HC(O)OCH_2CH_2OCHO$, a primary product in the oxidation of 1,4-dioxane. Interestingly, the oxy radical involved, $HC(O)OCHO^•CH_2OCHO$, has two available decomposition channels, a C−C bond dissociation and the α-rearrangement:

$$\mathrm{HC(O)OCHO^{\bullet}CH_2OCHO} \rightarrow \mathrm{HC(O)OCHO} + {}^{\bullet}\mathrm{CH_2OCHO} \quad (115)$$

$$\mathrm{HC(O)OCHO^{\bullet}CH_2OCHO} \rightarrow \mathrm{HC(O)OH} + \mathrm{HC(O)OCH_2C^{\bullet}(O)} \quad (116)$$

If the radicals are formed "cold" from the self-reaction of peroxy radicals, the rearrangement reaction accounts for 17% of the reaction. However, in the presence of NO, the activated radicals almost entirely undergo dissociation, in agreement with the higher density of states for the C−C scission.

A few general observations can be made from these experimental studies at room temperature (see entries in Table 2). Acetates appear to give the α rearrangement more readily than the corresponding formates. The more heavily substituted the alkoxy group, the more readily the rearrangement occurs (ethyl > methyl acetate). There does not appear to be a corresponding β-ester rearrangement of the form,

$$\mathrm{CH_3C(O)OCH_2CHO^{\bullet}CH_3} \rightarrow \mathrm{CH_3C(O)OH} + {}^{\bullet}\mathrm{CH_2C(O)CH_3} \quad (117)$$

presumably because there is no thermochemical driving force to break the β-C−H bond in a concerted mechanism.

Data regarding the temperature dependence of the α-rearrangement have recently become available at NCAR.[140] The oxidation mechanisms of methyl formate and methyl acetate were studied between 254 and 340 K, using methodology analogous to the previous room-temperature studies. The ratio k(rearr)/$k(\mathrm{O_2})$ varied with temperature, giving a difference in activation energies of 10 kcal $\mathrm{mol^{-1}}$ for both radicals. Assuming that the reaction with $\mathrm{O_2}$ has a weak positive activation energy of about 1 kcal leads to the conclusion that the α-rearrangement has an activation barrier of 10−11 kcal $\mathrm{mol^{-1}}$. This finding is consistent with the observation of chemical activation mentioned earlier.[80,93] These results also indicate that, within experimental uncertainty, there was no pressure dependence of the methyl acetate mechanism between 100 and 700 Torr at 296 K.

There have been a number of papers recently addressing theoretical aspects of the ester rearrangement. Good and Francisco[186] made the first calculations on one of these systems, and found a barrier of 13 kcal $\mathrm{mol^{-1}}$ for the radical derived from methyl formate $\mathrm{HC(O)OCH_2O^{\bullet}}$. More recently, Rayez et al.[185] and Ferenac et al.[182] have undertaken more detailed studies specifically targeting the rearrangement. Rayez et al.[185] investigated the $\mathrm{CH_3C(O)OCH(CH_3)O^{\bullet}}$ radical from ethyl acetate, finding a barrier of 6.5 kcal $\mathrm{mol^{-1}}$. They also did RRKM calculations, which gave an A-factor of 4.7×10^{12} $\mathrm{s^{-1}}$ and a high-pressure limiting rate coefficient of 7.4×10^{7} $\mathrm{s^{-1}}$. Furthermore, they predict that the reaction should be pressure dependent, with the rate coefficient at 1 bar being about a factor of 2 lower than k_{∞}. The transition state they identified for the rearrangement is a planar five-membered ring, with a distance of 1.499 Å between the carbonyl oxygen and the H atom being transferred.

Ferenac et al.[182] studied decomposition and isomerization in a series of structurally related radicals, including the $\mathrm{CH_3C(O)OCH_2O^{\bullet}}$ radical from methyl acetate. Depending on the level of calculation used, they found isomerization barriers in the range of 8.0−11.2 kcal $\mathrm{mol^{-1}}$. The most consistent agreement between theory and the chamber experiments[80,140] is with a barrier of around 10−12 kcal $\mathrm{mol^{-1}}$. Ferenac et al.[182] also showed a five-membered transition state, with a carbonyl O-to-H bond length of 1.36−1.43 Å, a little shorter than that reported by Rayez et al.[185] They describe the reaction in terms of a lengthening of the bond between the alkoxy C and the carboxylic O (as if decomposition to $\mathrm{CH_3C(O)O^{\bullet}} + \mathrm{CH_2O}$ would be occurring). However, as the C−O bond lengthens, the carbonyl O starts to acquire some radical character (since the $\mathrm{CH_3C(O)O^{\bullet}}$ radical is delocalized). It is this radical character that causes the α-ester rearrangement to occur (and presumably does not stabilize the β rearrangement). Ferenac et al. also comment that part of the difficulty in calculating the barrier accurately is in dealing with the partially delocalized nature of the transition state. Tunneling was also taken into account, but only played a small role (a factor of 1.5 or so) in determining the rate coefficient.

It seems reasonable that the α-ester rearrangement should occur in any ester that has hydrogen atoms available on the first carbon of the alkyl chain. Analogous radicals, for example $\mathrm{CH_3C(O)CH_2CH_2O^{\bullet}}$, in which the ester O atom is replaced by a $\mathrm{CH_2}$ group presumably do not show similar behavior because the thermodynamic driving force to make an acid is not there. Further experiments to understand the pressure and temperature dependence would be useful, as would calculations of a wider range of radicals to help to understand systematic reactivity trends.

3.5. Chemical Activation

Experimental[16−18,20−23,74,80,81,90,93,127] and computational[17−19,22,183,223] studies have shown that chemical activation plays an important role in the atmospheric chemistry of certain alkoxy radicals. As noted above, alkoxy radicals are formed in the atmosphere via reaction of peroxy radicals ($\mathrm{RO_2^{\bullet}}$) with either NO or other peroxy radicals (e.g., $\mathrm{CH_3O_2^{\bullet}}$):

$$\mathrm{RO_2^{\bullet}} + \mathrm{NO} \rightarrow \mathrm{RO^{\bullet}} + \mathrm{NO_2} \quad (1)$$

$$\mathrm{RO_2^{\bullet}} + \mathrm{CH_3O_2^{\bullet}} \rightarrow \mathrm{RO^{\bullet}} + \mathrm{CH_3O^{\bullet}} + \mathrm{O_2} \quad (2a)$$

$$\rightarrow \text{nonradical products (carbonyls, alcohols)} \quad (2b)$$

Reaction 2a is close to thermoneutral, and consequently the alkoxy radicals produced have little or no internal excitation. In contrast, reaction 1 is exothermic, with reaction enthalpies which range from −11 kcal $\mathrm{mol^{-1}}$ for simple unsubstituted alkyl peroxy radicals (e.g., $\mathrm{CH_3O_2^{\bullet}}$, $\mathrm{C_2H_5O_2^{\bullet}}$)[197] to approximately −17 kcal $\mathrm{mol^{-1}}$ for certain halogenated alkyl peroxy radicals (e.g., $\mathrm{CH_2FO_2^{\bullet}}$, $\mathrm{CF_3O_2^{\bullet}}$, $\mathrm{CF_3CFHO_2^{\bullet}}$).[128,223,224] Reaction 1 proceeds via the formation of a short-lived (10^{-10} s) vibrationally excited peroxy nitrite, ROONO*, which decomposes to give

Table 6. Alkoxy Radicals Showing Chemical Activation Effects in 1 atm of Air at 296 K

RO	decomposition pathway	barrier height (kcal/mol)[a]	fraction undergoing prompt decomposition[b]	refs
$CH_2ClO^\bullet$	$HC^\bullet O + HCl$ $Cl + CH_2O$	nd	0.44^e	20
$CBrCl_2O^\bullet$	$Cl + BrC(O)Cl$	nd	$\geq 0.21^c$	21
$CH_2ClCHClO^\bullet$	$CH_2ClC^\bullet(O) + HCl$	nd	$\geq 0.19^h$	127
$CH_3CHClO^\bullet$	$CH_3C^\bullet O + HCl$	6	~ 0.5	23, 172
$CCl_3CCl_2O^\bullet$	$^\bullet CCl_3 + COCl_2$	nd	$\geq 0.19^d$	81
$CF_3CFHO^\bullet$	$^\bullet CF_3 + HC(O)F$	7.5−9.0	$0.64^{+0.12}_{-0.23}$	16
$CF_3CF_2CFHO^\bullet$	$CF_3CF_2^\bullet + HC(O)F$	nd	$0.67^{+0.19}_{-0.22}$	74
$HC(O)OCH_2O^\bullet$	$HC^\bullet O + HC(O)OH$	nd	0.24 ± 0.03	80
$CH_3C(O)OCH_2O^\bullet$	$CH_3C(O)OH + HC^\bullet O$	nd	0.20 ± 0.08	93
$CH_3C(O)CH_2O^\bullet$	$CH_3C^\bullet(O) + CH_2O$	6−7	0.80	22
$CH_2FOCHFO^\bullet$	$^\bullet CH_2FO + HCOF$	nd	$\geq 0.31^g$	90
$CF_3CH(O^\bullet)OCHF_2$	$^\bullet CF_3 + HC(O)OCHF_2$	nd	0.75^i	84
$HOCH_2CH_2O^\bullet$	$^\bullet CH_2OH + HCHO$	10	0.31^f	17, 19, 183
$HOCH_2CH(O^\bullet)CH_3$	$CH_3CHO + CH_2OH$	7.1^j	0.775^j	18, 183
$CH_3CH(OH)CH_2O^\bullet$	$CH_3{}^\bullet CH(OH) + CH_2O$	7.2	0.75	183
$CH_3CH_2CH(OH)CH_2O^\bullet$	$CH_3CH_2{}^\bullet CH(OH) + CH_2O$	7.2	0.63	183
$CH_3(CH_2)_2CH(OH)CH_2O^\bullet$	$CH_3(CH_2)_2{}^\bullet CH(OH) + CH_2O$	6.9	0.47	183
$CH_3(CH_2)_3CH(OH)CH_2O^\bullet$	$CH_3(CH_2)_3{}^\bullet CH(OH) + CH_2O$	6.9	0.32	183

[a] nd = not determined. [b] Fraction of alkoxy radicals formed in RO_2 + NO reaction that undergo prompt decomposition. [c] Based on increased yield of BrC(O)Cl, ref 21. [d] Based on decreased yield of $CCl_3C(O)Cl$, ref 81. [e] Based on combined yield of HCHO and CO, ref 20. [f] Average from refs 17−19. [g] Based on increased HC(O)F yield, ref 90. [h] Based on $CH_2ClC(O)Cl$ yield, ref 127. [i] Estimated from data in Figure 7 in ref 84. [j] Average from refs 18 and 183.

$RO^\bullet + NO_2$. Although the lifetime of the vibrationally excited peroxy nitrite, ROONO*, is short (10^{-10}−10^{-9} s),[183] it is nevertheless long enough for efficient intramolecular energy transfer (occurring on a time scale of the order of 10^{-12} s). Thus, energy distributions among the reaction products are essentially statistical, and nascent alkoxy radicals formed following decomposition of ROONO* carry a significant fraction of the exothermicity of reaction 1. As discussed in section 3.2, for many alkoxy radicals the barrier to decomposition, or isomerization, is comparable to or less than the exothermicity of reaction 1. Under such conditions, it is likely that a significant fraction of the nascent $RO^\bullet$ radicals will decompose "promptly" (on a time scale $<10^{-9}$ s).[17−19,22,183,223] The remaining $RO^\bullet$ radicals will be thermalized by collisions with the diluent gas and will undergo thermal decomposition, thermal isomerization, or bimolecular reaction with O_2. The overall mechanism can be represented as follows:

$$RO_2^\bullet + NO \rightarrow ROONO^*$$

$$ROONO^* \rightarrow RO^{\bullet *} + NO_2$$

$$ROONO^* + M \rightarrow ROONO + M$$

$$ROONO \rightarrow RO^\bullet + NO_2$$

$$RO^{\bullet *} \rightarrow \text{decomposition or isomerization}$$

$$RO^{\bullet *} + M \rightarrow RO^\bullet + M$$

$$RO^\bullet \rightarrow \text{decomposition, isomerization, or reaction with } O_2$$

For chemical activation to play a significant role in the atmospheric chemistry of a given $RO^\bullet$ radical, three conditions must be met: (i) the lifetime of ROONO* must be long enough ($>10^{-12}$ s) to enable efficient intramolecular energy flow but short enough ($<10^{-9}$ s) that collisions with the diluent gas do not remove a significant fraction of the ROONO* excitation; (ii) the $RO^\bullet$ radical must possess a decomposition or isomerization pathway which has an activation barrier which is comparable to or lower than the excitation of the nascent $RO^{\bullet *}$ radical (determined by exothermicity of reaction 1 and the relative heat capacities of the $RO^\bullet$ and NO_2 fragments); and (iii) the overall rate of prompt decomposition of $RO^{\bullet *}$ must be sufficiently fast (i.e., the *A*-factor for decomposition must be sufficiently large) that collisions with the diluent gas do not remove a significant fraction of the $RO^{\bullet *}$ excitation prior to "prompt" decomposition.

For many radicals, it can be shown from a simple consideration of the thermodynamics that chemical activation cannot be of any importance. For example, the decomposition of $CH_3O^\bullet$ radicals via H atom elimination is endothermic by an amount (22 kcal mol^{-1}) that far exceeds the exothermicity of reaction 1. Similarly, inspection of the activation energies given in Table 1 reveals that chemical activation effects are not important for the majority of alkoxy radicals derived from alkanes (although the neopentoxy radical may represent an interesting exception). On the other hand, inspection of Tables 2 and 3 shows that many of the alkoxy radicals derived from OH radical addition to alkenes and hydrogen abstraction from oxygenated and halogenated organics have activation barriers which are sufficiently low that chemical activation effects may be important.

Table 6 provides a list of alkoxy radicals for which chemical activation effects have been reported. Consistent with the discussion above, in all cases the activation barriers for decomposition are modest (≤ 10 kcal mol^{-1}). For some alkoxy radicals, e.g., $CBrCl_2O^\bullet$, $CCl_3CCl_2O^\bullet$, and $CH_2FOCHFO^\bullet$, the effect of chemical activation is to alter the relative importance of competing decomposition pathways. In such cases, the experimentally observed change in product distribution provides a lower limit for the importance of chemical activation. For example, while it has been reported that chemical activation of $CCl_3CCl_2O^•$ radicals increases the relative importance of C−C bond scission at the expense of Cl atom elimination,[81] it is likely that chemical activation increases the rate of both processes. Hence, estimates of the importance of chemical activation in such systems derived from observed changes in product distributions provide lower limits for the importance of prompt decomposition of $RO^{•}*$ radicals. In at least one case, that of the $CH_2ClO^•$ radical referred to in the previous section, chemical activation allows for access to a dissociation channel not open to the thermalized radicals. While thermalized $CH_2ClO^•$ radicals decompose via three-centered elimination of HCl (in competition with their reaction with O_2), activated $CH_2ClO^•$ radicals can also undergo Cl atom elimination.[20]

It is worthwhile to highlight two practical ramifications of the effect for some important alkoxy radicals listed in Table 6. First, the formation of trifluoroacetic acid following the atmospheric degradation of CFC replacements such as CF_3CFH_2 (replacement for CFC-12 in air conditioning and refrigeration units) has been the subject of significant environmental research interest.[225] Assessments of the environmental impact of CF_3CFH_2 which do not include the chemical activation effect will overestimate the formation of $CF_3C(O)F$, and hence trifluoroacetic acid, by a factor of approximately 3.[16] Second, ethene is one of the more important volatile organic compounds released into the atmosphere. Atmospheric oxidation of ethene is initiated by reaction with OH radicals, which leads to the formation of $HOCH_2CH_2O^•$ radicals. HCHO is an important photolytic precursor to HO_x radicals in the upper troposphere. Neglecting chemical activation effects, it would be calculated that, for conditions relevant to the upper troposphere (220 K, 0.2 bar), only 2.5% of $HOCH_2CH_2O^•$ radicals decompose via C−C bond scission to give HCHO. Recognition of the occurrence of chemical activation leads to the conclusion that 25% of $HOCH_2CH_2O^•$ radicals decompose to give HCHO (see Figure 8).[17]

The importance of chemical activation in determining the atmospheric fate of alkoxy radicals has been recognized only very recently. There are large uncertainties associated with our understanding of the significance of this effect in the atmospheric chemistry of alkoxy radicals. At the time of this writing, all experimental data concerning chemical activation have been derived from product studies conducted using “smog” or environmental chamber systems. Direct, real-time studies are needed to confirm or refute the findings discussed above. As seen from inspection of Table 6, chemical activation appears to play an important role in the atmospheric fate of many oxygenated and halogenated alkoxy radicals. Further experimental and theoretical investigations are required to establish if chemical activation effects are a generic feature of the atmospheric fate of oxygenated and halogenated alkoxy radicals. Chemical activation may be important in the atmospheric chemistry of alkoxy radicals formed during the oxidation of sulfur-containing organics (e.g., CH_3SCH_3) and aromatic compounds. Further work to explore this possibility is needed.

4. Conclusions and Suggestions for Further Study

From the body of work just summarized, it is clear that great progess continues to be made toward an understanding of the chemistry of alkoxy radicals, particularly with regard to their behavior in the atmosphere. Through the combination of time-resolved measurements, end-product studies, and theoretical approaches, we now have quantitative knowledge regarding the end-products from most relatively small (four carbon or less) organic species encountered in the atmosphere (at least at 298 K, and in some cases at the lower temperatures of the upper troposphere), and hence an understanding of at least the relative rates of the various alkoxy radical processes involved. Furthermore, in the case of the nonsubstituted alkoxy radicals derived from C1−C4 alkanes, absolute rates and temperature dependences of major atmospheric reactions, unimolecular dissociation and reaction with O_2, have been obtained.

However, as has been alluded to throughout this review, many challenges still remain before a complete description of alkoxy radical chemistry, and hence of hydrocarbon oxidation, can be attained over the entire range of atmospheric conditions. In particular, absolute rate data are required for reactions of all but the simplest alkoxy radicals, and achieving this goal will require that direct detection methods for these alkoxy radicals be developed and implemented. The use of time-resolved mass spectometry, along the lines of the methods employed by Carr and co-workers,[161−163] seem promising in this regard. Direct detection of alkoxy radical isomerization reactions and of the effects of chemical activation in these processes would also be useful. End-product (environmental chamber) studies need to continue, with an emphasis on low-temperature oxidation mechanisms and on the oxidation of complex hydrocarbons, such as the terpenes. More sophisticated analytical techniques (such as the chemical ionization mass spectrometry employed by Atkinson and co-workers, e.g., refs 39 and 51) need to be developed for and employed in these chamber studies to quantify the many multifunctional products obtained in these processes. Furthermore, synthetic chemists need to be enlisted to generate standard samples of these multifunctional species for identification and calibration purposes. Finally, theoretical studies need to continue to be used to provide reliable data on series of related radicals so that reactivity trends can be developed, and to aid in the development of mechanisms for complex hydrocarbons.

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CR020527P