# Kinetics and Mechanisms of the Oxidation of Oxygenated Organic Compounds in the Gas Phase

A. Mellouki,*,† G. Le Bras,† and H. Sidebottom§

*Laboratoire de Combustion et Systèmes Réactifs, Centre National de Recherche Scientifique, 1C Avenue de la recherche scientifique, 45071 Orléans Cedex 02, France, and University College Dublin, Dublin 4, Ireland*

*Received June 4, 2003*

## Contents

## 1. Introduction

The degradation of volatile organic compounds (VOCs) in the troposphere leads to the production of a range of secondary pollutants such as ozone, peroxyacyl nitrates, and secondary organic aerosols. Ozone formation is of particular concern since it is known to have adverse effects on human health, vegetation, and a variety of materials, and it is also a greenhouse gas. Indeed, strategies for the control of emissions of VOCs have been based on their individual contribution to the photochemical formation of ozone.[1]

Field measurements indicate that oxygenated VOCs form a major component of the trace gases found in the troposphere.[2] They are emitted directly into the atmosphere from biogenic sources and from solvent and fuel additives use, and are also formed in the tropospheric oxidation of all hydrocarbons. It is now accepted that a change from aromatic and halocarbon solvents to oxygenated compounds is inevitable both in terms of toxicity problems and in the case of aromatic compounds as a means of reducing the levels of oxidant formation in the troposphere. It is apparent that oxygenated compounds will thus play an increasing role in determining the oxidizing capacity of the troposphere both on a regional and a global scale.

A considerable body of experimental data on the gas-phase oxidation of small-chain oxygenated compounds such as alcohols, ethers, carbonyl compounds, and esters has been reported.[3−7] However, degradation pathways for loss of higher molecular weight and polyfunctional oxygenated species have not been well characterized. The available evidence suggests that the oxidation of saturated oxygenated compounds is largely initiated by their reaction with hydroxyl radicals, and the kinetics and mechanisms for these reactions have been comprehensively reviewed.[3−7] In addition, photolysis of aldehydes and ketones can also play a significant role in their atmospheric degradation.[8−12] Oxidation of unsaturated oxygenated compounds may be initiated by reaction with ozone,[5,13−16] nitrate[5,17,18] and hydroxyl radicals.[3−7]

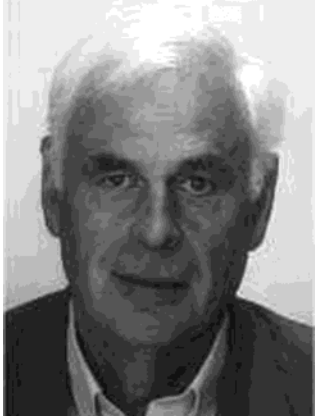
In the present work the available kinetic and mechanistic data for the oxidation of oxygenated organic compounds under tropospheric conditions are reviewed. Analysis of the reported experimental results enables the development of structure−activity relationships for the kinetics and mechanisms of the various possible oxidation channels of these compounds. The relationships can be employed to determine the tropospheric lifetimes and initial oxidation products of a range of oxygenated organic compounds and to predict the degradation pathways and atmospheric fate of the primary products. Not only is information on the fate of oxygenated compounds in the troposphere important in terms of oxidant formation, but oxidation of simple oxygenated compounds often leads to the generation of polyfunctionalized species. These compounds can be of low reactivity in the gas phase, and thus their relatively high solubil-

---

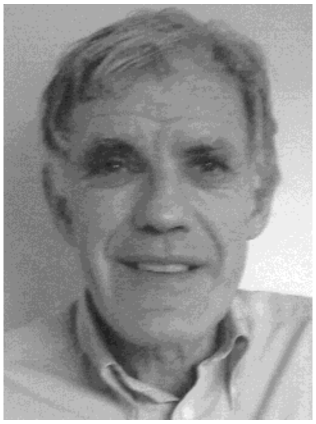
[†] LCSR/CNRS.
[§] UCD.

10.1021/cr020526x CCC: $44.00 © 2003 American Chemical Society
Published on Web 10/28/2003

Abdelwahid Mellouki obtained his Ph.D. from the University of Paris 7 (1989). After a postdoctoral fellowship with Dr. A. R. Ravisankara at the National Oceanic and Atmospheric Administration in Boulder, he joined the Centre National de Recherche Scientifique (1991), where he is presently a researcher at the Laboratoire de Combustion et Systèmes Réactifs at Orléans. His research interests are principally in the areas of kinetics and photochemistry, including the kinetics and mechanisms for the oxidation of organic compounds under atmospheric conditions.



Georges Le Bras graduated from the University of Paris (1965), and he obtained his Ph.D. from the University of Orléans (1972). He joined the Centre National de la Recherche Scientifique (CNRS) in 1969, and he is currently Directeur de Recherche at the Laboratoire de Combustion et Systèmes Réactifs at Orléans. His research interests are mainly free radical reactions and atmospheric kinetics. He has been very much involved in European atmospheric research over the past 15 years.



Howard Sidebottom obtained his B.Sc. (1966) and Ph.D. (1969) from the University of St. Andrews, working under the direction of Professor J. M. Tedder. After a postdoctoral fellowship with Professor J. G. Calvert at The Ohio State University, he returned to St. Andrews as an I.C.I. research fellow before joining the Chemistry Department at University College Dublin, where he is currently Associate Professor of Chemistry. His research interests are principally in the areas of kinetics and photochemistry, including the kinetics and mechanisms for the oxidation of halogenated compounds under atmospheric conditions.

ity and low vapor pressures may lead to uptake in cloud and fog droplets or to formation of secondary organic aerosols. Hence, anthropogenic emissions of oxygenates may impact on wet deposition and also on climate by increasing the levels of tropospheric aerosol.

## *2. Kinetics and Mechanisms of the OH-Initiated Oxidation of Oxygenated Compounds*

### 2.1. Alcohols

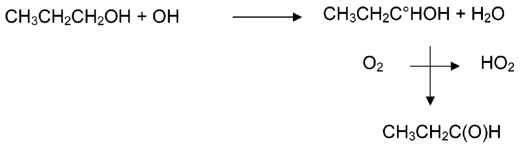
The gas-phase oxidation of aliphatic alcohols in the atmosphere is initiated mainly by reaction with OH radicals, reactions with $NO_3$ and $O_3$ and photolysis being negligible.[5]

#### *2.1.1. Rate Constants of OH Reactions*

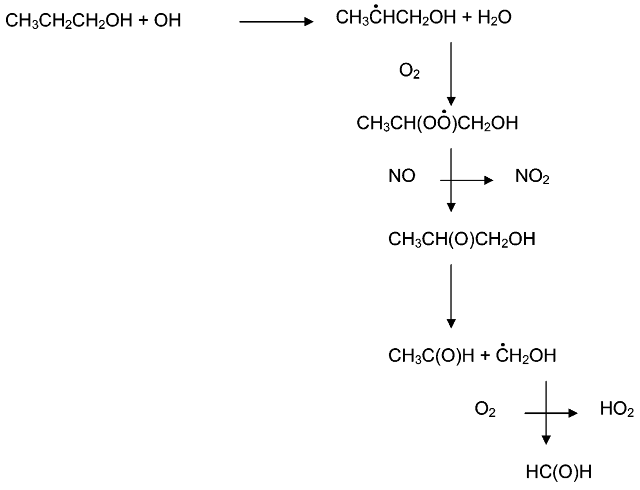
Rate constant data for the OH reaction with alcohols are available mainly at room temperature, although data at lower temperatures which are of atmospheric interest (below ~300 K) also exist for alcohols containing up to five carbons.[19-21] The increase in reactivity shown for the reaction of OH radicals with $CH_3OH$, $CH_3CH_2OH$, and $(CH_3)_2CHOH$ compared to reaction with the corresponding alkanes can, at least in part, be rationalized in terms of the lowering of the α-carbon hydrogen bond strength.[7] At $T \approx 298$ K, for linear straight-chain alcohols, the rate constant values increase by a factor of ~5 from ethanol ($k_{OH} \approx 3 \times 10^{-12}$) to *n*-octanol ($k_{OH} \approx 15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).[19,22] The increase in the rate constants with chain length indicated that $-CH_2-$ groups in the $\beta$ and $\gamma$ positions with respect to the OH group also have higher reactivities than $-CH_2-$ groups in unsubstituted alkanes, with a slight reduction in reactivity per $-CH_2-$ group on going from the $\beta$- to the $\gamma$-carbon atom. Hence, the activating effect of the alcohol group for reaction with the OH radical appears to extend over around three carbon atoms.[19,22] For further increases in the chain length, the reactivity of the $-CH_2-$ groups is essentially the same as that found in unsubstituted alkanes. The observed long-range activating effect of the alcohol group cannot be explained in terms of bond energy or inductive effects and indicates an alternative reaction pathway to the direct concerted hydrogen atom abstraction process observed for alkanes.[22]

#### *2.1.2. Mechanisms of the OH-Initiated Oxidation of Alcohols*

Reaction of OH radicals with alcohols proceeds by a H-atom abstraction process either from the C−H bonds of the $CH_3-$, $-CH_2-$, and $>CH-$ groups in the alkyl chain or from the $-OH$ group. However, from a consideration of the thermochemical data for methanol, $D(H-CH_2OH) \approx 92$ kcal mol$^{-1}$ and $D(CH_3O-H) \approx 104$ kcal mol$^{-1}$, it is expected that H-atom abstraction from the OH group will be of minor importance at room temperature. It is likely that this contribution will decrease for $C_2H_5OH$ and $(CH_3)_2CHOH$, since the C−H bond strength at the α-carbon atom in these compounds is considerably weaker than that in $CH_3OH$. It has been shown experimentally that ∼85% of the OH reaction with methanol proceeds at room temperature by H-atom abstraction from the methyl group and the remaining 15% occurs by abstraction from the OH group.[23,24] Meir et al.[25] reported that, for the reaction of OH with ethanol, abstraction occurs mainly from the $-CH_2-$ group (75 ± 15%), while abstraction from the $CH_3$ and OH groups represents approximately 5% for each channel.[7] For linear-chain alcohols with three or more carbon atoms, H-atom abstraction from the α-carbon atom is likely to be the main reaction pathway, while abstraction from *β*-, *γ*-, and *δ*-carbon atoms will also make a significant contribution to the reaction products. Reaction at the OH or terminal methyl groups will be unimportant for long-chain alcohols. A number of product distribution studies on the reaction of OH radicals with long-chain alcohols in the presence of $NO_x$ in air have been reported. Azad and Andino[26] have shown that the main oxidation products from the reaction of OH with *n*-propanol are propionaldehyde (71.9 ± 5.8%) and acetaldehyde (18.4 ± 3%), which arise from H-atom abstraction from $-CH_2-$ groups in the α and *β* positions, respectively:



and



The reaction products observed from the OH-initiated oxidation of 1-butanol and 1-pentanol[27,28] suggest that the degradation mechanisms are similar to that of 1-propanol with the predominant reaction site at the $\alpha$-$CH_2-$ group, leading to 1-butanal and 1-pentanal, respectively. Significant yields of shorter-chain aldehydes in these systems indicate that abstraction from the *β*- and *γ*-$CH_2-$ groups make an important contribution to product formation. Thus, butanal (51.8 ± 7.1%), propanal (23.4 ± 3.5%), acetaldehyde (12.7 ± 2.2%), and formaldehyde (43.4 ± 2.4%) are products of the OH-initiated oxidation of 1-butanol,[28] while reaction of OH with 1-pentanol leads to the following aldehydes: pentanal (40.5 ± 8.2%), butanal (16.1 ± 3.7%), propanal (8.1 ± 1.9%), acetaldehyde (18.1 ± 4.2%), and formaldehyde (25.1 ± 1.3%).[27] Cavalli et al.[27,28] suggested that isomerization of the intermediate oxy radicals may also be important in the oxidation of long-chain alcohols leading to the formation of hydroxyketones and hydroxyaldehydes.

The available mechanistic data for the OH reaction with alcohols containing a tertiary carbon bonded to the −OH group, such as 2-propanol, 2-butanol, and 2-pentanol, show that H-atom abstraction from the C−H group is the dominant reaction channel at room temperature:[29,30]

$$RR'CHOH + OH \rightarrow RR'COH + H_2O$$

and the RR′COH radical generated in the system forms the corresponding carbonyl compound:

$$RR'COH + O_2 \rightarrow RC(O)R' + HO_2$$

Baxley and Wells[29] showed that methyl ethyl ketone produced in the OH-radical-initiated oxidation of $^{18}O$ isotopically labeled $CH_3CH_2C(^{18}OH)CH_3$ contained the isotopic label, indicating that the alcoholic oxygen remains in the carbonyl compound generated in the system.[29] Abstraction of hydrogen from secondary alcohols can also occur from $CH_x$ groups ($x = 1-3$), other than at the α-CH< site, leading to carbonyl and hydroxycarbonyl compounds by decomposition, reaction with $O_2$, and isomerization:

$$RCH_2CH(R')OH + OH\ (O_2/NO) \rightarrow RCH(O)CH(R')OH + H_2O + NO_2$$

$$RCH(O)CH(R')OH \rightarrow RC(O)H + R'CH(OH)$$

$$\downarrow O_2$$

$$R'C(O)H + HO_2$$

$$RCH_2CH_2CH_2CH(R')OH + OH(O_2/NO) \rightarrow RCH(O)CH_2CH_2CH(R')OH + H_2O + NO_2$$

$$RCH(O)CH_2CH_2CH(R')OH \rightarrow RC(O)H + CH_2CH_2CHR'OH$$

$$RCH(O)CH_2CH_2CH(R')OH + O_2 \rightarrow RC(O)CH_2CH_2CH(R')OH + HO_2$$

$$\rightarrow RCH(OH)CH_2CH_2C(R')OH$$

$$\downarrow O_2$$

$$RCH(OH)CH_2CH_2C(O)R' + HO_2$$

Baxley and Wells[29] have reported that reaction of OH with 2-butanol gave methyl ethyl ketone (60 ± 2%) and acetaldehyde (29 ± 4%) as the major products, while the products of the corresponding reaction with 2-pentanol were 2-pentanone (41 ± 4%), propionaldehyde (14 ± 2%), and acetaldehyde (40 ± 4%).

The reaction of OH with tertiary alcohols arises mainly by H-atom abstraction from the $\beta$ position. The reaction of OH with *tert*-butyl alcohol has been investigated by Japar et al.[31] and proceeds by H-atom abstraction from the methyl groups, leading to the production of acetone and formaldehyde:

$$(CH_3)_3COH + OH\ (+O_2,\ NO) \rightarrow (CH_3)_2C(OH)CH_2O + H_2O + NO_2$$

$$(CH_3)_2C(OH)CH_2O \rightarrow HC(O)H + (CH_3)_2COH$$

$$(CH_3)_2COH + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$

The product distribution yields from the OH-radical-initiated oxidation of 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol have been reported.[32] For 2,4-dimethyl-2-pentanol, the product yields were as follows: acetone, 0.92 ± 0.15%; 2-methylpropanal, 0.21 ± 0.02%; 4-methyl-2-pentanone, 0.05 ± 0.01%; and 4-hydroxy-4-methyl-2-pentanone, 0.12 ± 0.02%. The proposed mechanisms leading to these compounds involve H-atom abstraction from the $\beta$-$CH_3$, $\beta$-$CH_2$−, and $\gamma$ >CH− groups, followed by the formation of the corresponding hydroxyalkoxy radical after reaction with $O_2$ and NO. Degradation of these alkoxy radicals accounts for the various products detected.

Abstraction from a $\beta$-$CH_3$ group:

$$(CH_3)_2CHCH_2C(CH_3)(OH)CH_2O \rightarrow HC(O)H + (CH_3)_2CHCH_2C(CH_3)OH$$

$$(CH_3)_2CHCH_2C(CH_3)OH + O_2 \rightarrow (CH_3)_2CHCH_2C(O)CH_3 + HO_2$$

Abstraction from the $\beta$-$CH_2$− group:

$$(CH_3)_2CHCHOC(CH_3)_2OH \rightarrow (CH_3)_2CHC(O)H + (CH_3)_2COH$$

$$(CH_3)_2COH + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$

Abstraction from the $\gamma$ >CH− group:

$$(CH_3)_2COCH_2C(CH_3)_2OH \rightarrow CH_3C(O)CH_3 + CH_2C(CH_3)_2OH$$

$$CH_2C(CH_3)_2OH\ (+O_2,\ NO) \rightarrow OCH_2C(CH_3)_2OH + NO_2$$

$$OCH_2C(CH_3)_2OH \rightarrow HC(O)H + (CH_3)_2COH$$

$$\downarrow O_2$$

$$CH_3C(O)CH_3 + HO_2$$

and

$$(CH_3)_2COCH_2C(CH_3)_2OH \rightarrow (CH_3)_2C(OH)CH_2C(CH_3)(OH)CH_2$$

$$(CH_3)_2C(OH)CH_2C(CH_3)(OH)CH_2\ (+O_2,\ NO) \rightarrow (CH_3)_2C(OH)CH_2C(CH_3)(OH)CH_2O + NO_2$$

$$(CH_3)_2C(OH)CH_2C(CH_3)(OH)CH_2O \rightarrow HC(O)H + (CH_3)_2C(OH)CH_2C(CH_3)OH$$

$$(CH_3)_2C(OH)CH_2C(CH_3)OH + O_2 \rightarrow (CH_3)_2C(OH)CH_2C(O)CH_3 + HO_2$$

The authors concluded that formation of 4-hydroxy-4-methyl-2-pentanone from the OH-initated degradation of 2,4-dimethyl-2-pentanol provides evidence for isomerization of the $(CH_3)_2COCH_2C(CH_3)_2OH$ alkoxy radical via a 1,5-H-atom shift to give $(CH_3)_2C(OH)CH_2C(CH_3)(OH)CH_2$. Subsequent reactions of this radical generate the hydroxy pentanone.

## 2.2. Diols

The dominant loss process for diols in the atmosphere is reaction with OH radicals. The available kinetic data show that the rate constants for the reaction of OH with diols are significantly higher than those with monoalcohols, indicating an activating effect of the second OH group.[33−36] For example, the OH reaction rate constants for $HOCH_2CH_2OH$ ($k_{OH} \approx 15 \times 10^{-12}$)[33] and $HOCH_2CH_2CH(OH)CH_3$ ($k_{OH} \approx 33 \times 10^{-12}$)[35] are somewhat higher than the values estimated using the structure−activity relationships developed by Atkinson,[37] in which the rate constant for H-atom abstraction from a carbon atom depends only on the nature of the α-substituent groups. Thus, it appears that abstraction of a hydrogen atom from a carbon atom α to the hydroxy group is enhanced by the presence of a second hydroxy group at the $\beta$ or $\gamma$ position in a diol. Mechanistic studies have shown that the main products of the OH-initiated oxidation of diols are the corresponding hydroxyketones:[35,36] $CH_3CH_2C(O)CH_2OH$ (66%) from $CH_3CH_2CH(OH)CH_2OH$; $CH_3C(O)CH(OH)CH_3$ (89%) from $CH_3CH(OH)CH(OH)CH_3$; $CH_3C(O)CH_2CH_2OH$ (50%) from $CH_3CH(OH)CH_2CH_2OH$; and $(CH_3)_2C(OH)CH_2C(O)CH_3$ (47%) from $(CH_3)_2C(OH)CH_2CH(OH)CH_3$. The products are consistent with H-atom abstraction from the $-CH_2OH$ or >CHOH groups in these molecules, followed by reaction of the α-hydroxyalkyl radicals with $O_2$ to give the corresponding α-hydroxycarbonyl compounds.

## 2.3. Ethers, Diethers, and Cyclic Ethers

Oxidation of ethers, polyethers, and cyclic ethers in the troposphere is predominantly initiated by reaction with OH radicals. Reaction with $NO_3$ may also contribute, to a small extent, to the removal of some ethers during night-time,[38,39] while photolysis[40] and reaction with $O_3$ [13] are negligible. A number of kinetic and mechanistic studies on the OH-radical-initiated degradation of aliphatic ethers, diethers, and cyclic ethers have been reported. However, analysis of the data reveals unexpected patterns of reactivity, particularly for multifunctional compounds.

### 2.3.1. Monoethers

**2.3.1.1. Rate Constants of OH Reactions.** Rate constant data for the reaction of OH radicals with aliphatic ethers show that ethers are considerably more reactive than the corresponding alkanes. The enhanced reactivities of $CH_3OCH_3$, $C_2H_5OC_2H_5$, and $(CH_3)_2CHOCH(CH_3)_2$ compared to ethane, butane, and 2,3-dimethylbutane have been rationalized in terms of a reduction in the α-carbon hydrogen bond energy.[22] The available rate constant data at room temperature for reactions of OH with linear chain ethers show a large increase in reactivity with increasing chain length. The reported OH rate constants at room temperature for $CH_3OCH_3$, $C_2H_5OC_2H_5$, $n$-$C_3H_7OC_3H_7$, and $n$-$C_4H_9OC_4H_9$ (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ units), are 2.8, 13.6, 21.7, and 26.9, respectively. This increase in reactivity compared to the corresponding alkanes ($k_{OH+C_2H_6} = 2.5 \times 10^{-13}$, $k_{OH+n-C_4H_{10}} = 2.4 \times 10^{-12}$, $k_{OH+n-C_6H_{14}} = 5.5 \times 10^{-12}$, and $k_{OH+n-C_8H_{18}} = 8.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)[41] indicates that abstraction at carbon atoms remote from the ether group is more facile than expected and that the activating effect of the ether group extends over about three carbon atoms.[22,42,43] Nelson et al.[22] suggested that this long-range activating effect of the ether linkage could not be explained considering bond energy or inductive effects alone but indicates an alternative pathway to the direct H-atom abstraction process observed for $n$-alkanes.[22] Porter et al.[44] have proposed that the enhanced reactivity shown by ethers may be due to formation of a ring transition state resulting from the interaction of the attacking OH radical with the O atom of the ether group and adjacent $-CH_2-$ groups. Smith and Ravishankara[45] have recently discussed reactions of OH radicals with oxygenated organic compounds in terms of hydrogen-bonded complexes, which result in a lowering of the activation energy for reaction. Moriaty et al.[46] have proposed that the initial step in the reaction of OH with an ether also involves the formation of a hydrogen-bonded complex, and the reaction then involves intramolecular H atom transfer to form $H_2O$ and an oxygenated alkyl radical. The reported temperature dependence measurements of the rate constants show a slight positive temperature dependence for dimethyl ether and methyl *tert*-butyl ether, whereas the more reactive ethers have negative temperature factors.[42,43,47,48] These temperature dependences provide some support for formation of a weakly bound complex between the OH radical and the ether group, which can either decompose back to reactants or eliminate $H_2O$.

**2.3.1.2. Mechanisms of the OH-Initiated Oxidation of Monoethers.** The reaction of OH radicals with *aliphatic ethers* proceeds via abstraction of a hydrogen atom from $CH_3$, $-CH_2-$, or $>CH-$ groups in the alkyl chain. Product distribution studies have shown that, when abstraction occurs at the α-carbon atom under atmospheric conditions, oxidation leads predominantly to the corresponding esters. Oxidation of dimethyl ether has been shown to give methyl formate with a yield close to unity.[31] This is consistent with H-atom abstraction by $O_2$ from the alkoxy radical $CH_3OCH_2O$, formed by successive reactions of the primary $CH_3OCH_2$ radical with $O_2$ and NO.[31] Studies carried out in the absence of NO also give methyl formate as the major product, but the hydroperoxide, $CH_3OCH_2OOH$, was also formed in significant amounts.[49,50] Ethyl formate was the main product observed in the oxidation of diethyl ether, together with small yields of acetaldehyde and ethyl acetate.[51,52] These results indicate that the dominant degradation pathway involves H-atom abstraction from the $-CH_2-$ group and that the alkoxy radical, formed after successive reaction with $O_2$ and NO, decomposes predominantly by carbon−carbon bond scission. Presumably, acetaldehyde and ethyl acetate are generated from the $CH_3CH_2OCHOCH_3$ alkoxy radical by C−O bond fission and reaction with $O_2$, respectively. Sempeles and Andino[53] recently reported that the main products of the OH-initiated oxidation of di-$n$-propyl ether were $n$-propyl formate, acetaldehyde, $n$-propionaldehyde, and $n$-propyl propionate with yields of 61 ± 4.4%, 60 ± 5.7%, 15 ± 6.2%, and 4.3 ± 1.5%. These products are consistent with abstraction mainly at the α-$CH_2-$ group, generating the $n$-$C_3H_7OCHOC_2H_5$ alkoxy radical, which decomposes largely by C−C bond cleavage, with minor loss by C−O bond-breaking or by reaction with $O_2$. A number of investigations have also been conducted on the oxidation of the longer linear-chain ethers di-$n$-butyl ether,[54] methyl $n$-butyl ether,[55] and ethyl $n$-butyl ether.[54] These studies, where the majority of the end products were identified and quantified, indicate that the alkoxy radicals generated in the reactions can react with $O_2$, decompose, or isomerize. For example, Aschmann and Atkinson[55] have determined the products from the OH-radical-initiated oxidation of methyl $n$-butyl ether in the presence of $NO_x$. The results show that H-atom abstraction can occur from α-, $\beta$-, and $\gamma$-$CH_2-$ groups in the $n$-butyl chain. The main reactions of the radicals generated in the system are C−C bond fission for $CH_3OCHOCH_2CH_2CH_3$ and $CH_3OCH_2CHOCH_2CH_3$, and reaction with $O_2$ for the $CH_3OCH_2CH_2CHOCH_3$ radical. Further details on the radicals formed in the oxidation of long-chain ethers are available from the work of Johnson and Andino[54] and Aschmann and Atkinson.[55]

Product distribution studies have been reported for the *branched ethers*, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and di-isopropyl ether (DIPE). The major product arising from the OH-radical-initiated oxidation of MTBE in the presence of NO was *tert*-butyl formate, with smaller amounts of $H_2CO$ and $CH_3C(O)CH_3$.[31,56,57] The data provide strong evidence that H-atom abstraction by OH radicals occurs mainly from the α-methyl group, while the minor products result from OH attack on the *tert*-butyl group. *tert*-Butyl formate has been shown to be the major oxidation product observed in the OH reaction with ETBE, while the minor products include $H_2CO$, $CH_3$-

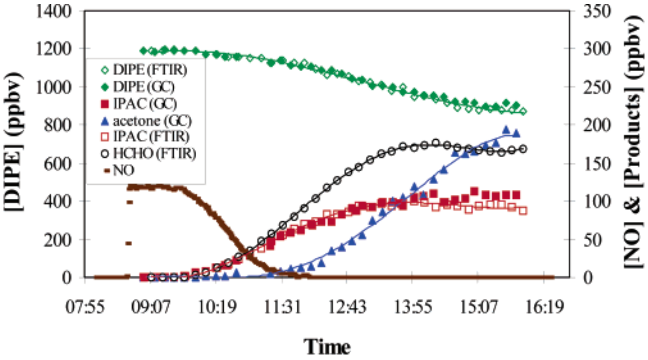


**Figure 1.** Concentration−time profile for the photooxidation of diisopropyl ether (DIPE) in the presence of NO under sunlight conditions (EUPHORE) (IPAC = isopropyl acetate).[61]

OCHO, and $(CH_3)_3COC(O)CH_3$.[51,58] The product distributions indicate that H-atom abstraction occurs largely from $-CH_2-$ in the $-C_2H_5$ group and that the alkoxy radical $CH_3CH(O)OC(CH_3)_3$ decomposes by carbon−carbon bond scission. The OH-initiated oxidation of TAME, in the presence of NO, leads to *tert*-amyl formate, methyl acetate, and acetaldehyde as major products which are formed in nearly equal amounts. This suggests that H-atom abstraction occurs about equally from the α-$CH_3$ group and from the $\beta$-$CH_2-$ group in the *tert*-amyl chain. Acetone, *tert*-amyl alcohol, and 3-methoxy-3-methylbutanal are also formed in small amounts.[59]

The OH-initiated oxidation of di-isopropyl ether (DIPE) gave isopropyl acetate with a yield of unity, indicating that the main reaction channel is H-atom abstraction from >CH− groups, followed by carbon−carbon bond cleavage of the alkoxy radical produced after reaction with $O_2$ and NO.[60,61] However, Wenger et al.[61] have shown that the OH-initiated oxidation of DIPE in the absence of $NO_x$ leads mainly to production of acetone (Figure 1) and proposed that acetone could be formed either by C−O bond cleavage of the alkoxy radical or via decomposition of the hydroperoxide formed in the reaction of the peroxy radical with $HO_2$. The OH-initiated oxidation of di-*tert*-butyl ether, $(CH_3)_3COC(CH_3)_3$, in the presence of NO gave *tert*-butyl acetate, $(CH_3)_3COC(O)CH_3$,[62] as the main product, which provides evidence that the dominant fate of the alkoxy radical generated from this ether is also C−C bond scission and that reaction with $O_2$ is a minor channel.

### 2.3.2. Diethers

**2.3.2.1. Rate Constants of OH Reactions.** At room temperature, the reaction rate constants of OH with dimethoxymethane ($CH_3OCH_2OCH_3$), 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$), 1,3-dimethoxypropane ($CH_3OCH_2CH_2CH_2OCH_3$), and 1,4-dimethoxybutane ($CH_3O(CH_2)_4OCH_3$) are (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ units) 4.9, 27, 51, and 30, respectively.[44,63] As discussed by Porter et al.,[44] the rate coefficient for the reaction of OH with dimethoxymethane at room temperature is somewhat lower than might be expected on the basis of the reactivity of the $-CH_2-$ groups in diethyl ether. It seems likely that the relatively low reactivity of the $-CH_2-$ group in dimethoxymethane, which is α to two oxygen atoms, is largely related to strengthening of the C−H bond compared to the α-$CH_2-$ group in monoethers. It is reasonable to assume that the C−H bond strength in the $-CH_2-$ groups in diethers of structure $CH_3O(CH_2)_nOCH_3$ ($n = 2-4$) is similar to that in an α-$CH_2-$ group in monoethers. The enhancement in the reactivity of the $-CH_2-$ groups in $CH_3OCH_2CH_2OCH_3$ and $CH_3OCH_2CH_2CH_2OCH_3$ compared to that of the α-$CH_2-$ groups in *n*-alkyl ethers is suggested to arise largely by activation of the H atoms by both ether groups as a result of the initial formation of a hydrogen-bonded adduct, followed by formation of a cyclic transition state.[46] A further increase in the chain length on going from $CH_3O(CH_2)_3OCH_3$ to $CH_3O(CH_2)_4OCH_3$ would be expected to increase the reaction rate constant due to the presence of an additional $-CH_2-$ group. However, the possibility that transfer of a H atom from the α-$CH_2-$ groups may occur by ring formation involving a hydrogen bond to the other ether group is less likely as the ring size increases, due to entropy restrictions, and provides an explanation for why the rate constant for reaction of OH radicals with $CH_3O(CH_2)_4OCH_3$ is lower than that for reaction with $CH_3O(CH_2)_3OCH_3$.[46]

The OH reaction rate constants with linear-chain diethers ($ROCH_2OR$) are $5 \times 10^{-12}$, $20 \times 10^{-12}$, $27 \times 10^{-12}$, and $37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for R = $CH_3$, $C_2H_5$, *n*-$C_3H_7$, and *n*-$C_4H_9$, respectively, higher than those of the corresponding ethers,[44,48,64] which suggests that the *n*-alkyl groups may be activated by both ether groups.

**2.3.2.2. Mechanisms of the OH-Initiated Oxidation of Diethers.** The major products identified in the OH-initiated oxidation of dimethoxy methane are methoxy methyl formate ($CH_3OCH_2OCHO$) and dimethyl carbonate ($CH_3OC(O)OCH_3$).[63,65] The data indicate that the reaction proceeds by H-atom abstraction from either $-CH_2-$ or $CH_3-$ groups to produce radicals which will react with $O_2$ and NO, leading to the corresponding alkoxy radicals $CH_3OCH(O)OCH_3$ and $CH_3OCH_2OCH_2O$. The reported yields of $CH_3OCH_2OCHO$ and $CH_3OC(O)OCH_3$, ∼75% and ∼25%, respectively, indicate that the fate of the intermediate alkoxy radicals is to react with $O_2$.

The major product formed in the OH-initiated oxidation of $CH_3OCH_2CH_2OCH_3$ is $CH_3OCHO$.[65,66] A small yield of methoxyethyl formate has also been observed by Wenger et al.[65] These data indicate that the reaction of OH with dimethoxyethane proceeds essentially by H-atom abstraction from a $-CH_2-$ group (∼85%), leading to the oxy radical $CH_3OCH(O)CH_2OCH_3$ after reaction with $O_2$ and NO. The observation of methyl formate as the main reaction product suggests that the alkoxy radical decomposes through C−C bond cleavage. Observation of small yields of $CH_3OCH_2CH_2OCHO$ shows that the H-atom abstraction from $-CH_3$ is of minor importance.

Dimethyl carbonate was found to be the major product (∼80%) in the OH-initiated oxidation of trimethoxymethane.[67] Upon comparing the reactivity of OH with the $CH_3O-$ groups in $CH_3OCH_3$, $CH_3OCH_2OCH_3$, and $(CH_3O)_4C$, it was suggested that the reactivity of an individual $CH_3O-$ group in trimethoxymethane is close to the average of the $CH_3O$ reactivity observed in $CH_3OCH_3$, $CH_3OCH_2OCH_3$, and $(CH_3O)_4C$. Hence, Platz et al.[67] estimated that approximately 80% of the OH reaction with $(CH_3O)_3CH$ proceeds via attack on the $CH_3O-$ groups and concluded that dimethyl carbonate is formed through the decomposition of the $(CH_3O)_2CHOCH_2O$ radical by C−O bond scission:

$$(CH_3O)_2CHOCH_2O \rightarrow (CH_3O)_2CHO + HC(O)H$$

$$(CH_3O)_2CHO + O_2 \rightarrow CH_3OC(O)OCH_3 + HO_2$$

### 2.3.3. Cyclic Ethers

**2.3.3.1. Rate Constants of OH Reactions.** The rate constants for reaction of OH radicals with the cyclic ethers, tetrahydrofuran, 1,3-dioxolane, tetrahydropyran, 1,3-dioxane, 1,4-dioxane, and 1,3-dioxepane are in the range $(6-20) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[44,46,68,69] Although cyclic ethers are more reactive toward OH radicals than the analogous cycloalkanes, in general, they are less reactive than their linear analogues, indicating that the long-range activating effects of the ether group are minimal.[46] From the work of Moriarty et al.[46] on a series of cyclic ethers, it appears that α-$CH_2-$ groups in cyclic ethers show slightly reduced reactivity compared to those in linear-chain ethers. The variation in reactivity of the $-CH_2-$ groups, which depends on both ring size and the number of ether groups in the ring, is probably largely a consequence of slight differences in C−H bond strengths. While the $-OCH_2O-$ group appears to have similar reactivity within cyclic and aliphatic ethers, cyclic systems containing $-O(CH_2)_nO-$ group ($n = 2-4$) structural units exhibit much lower reactivity than the analogous linear-chain compounds. It is proposed that this lower reactivity results from the difficulty in forming ring-stabilized transition states in cyclic ethers. The slightly negative temperature dependencies of the rate constants for the reaction of OH with cyclic ethers are consistent with facile direct H-atom-transfer reactions involving OH and reactive hydrocarbons.[41] The $A$ factors are also in the range expected for reactions of this type.

**2.3.3.2. Mechanisms of the OH-Initiated Oxidation of Cyclic Ethers.** Mechanistic studies have shown that OH-initiated oxidation of cyclic ethers under atmospheric conditions leads, in general, to ring opening with the resultant radicals containing the formate functional group. The OH-initiated oxidation of 1,4-dioxane, a cyclic diether with four equivalent α-$CH_2-$ groups, in the presence of $NO_x$ has been shown to form ethylene glycol diformate ($HC(O)OCH_2CH_2OC(O)H$) with a yield close to unity.[70,71] The reaction proceeds by H-atom abstraction, followed by reaction with $O_2$ and NO, to form a cyclic alkoxy radical which decomposes through C−C cleavage, leading to the $HC(O)OCH_2CH_2OCH_2$ radical. Ethylene glycol diformate is formed after successive reactions of $HC(O)OCH_2CH_2OCH_2$ with $O_2$ and NO to give the corresponding alkoxy radical, which reacts with molecular oxygen to generate the diformate. In a similar series of reactions, β-formyloxypropionaldehyde is formed as the major product in the oxidation of tetrahydrofuran.[71] Abstraction of a H atom from an α-$CH_2-$ group leads to the generation of the $HC(O)CH_2CH_2OCH_2O$ via a C−C bond cleavage ring-opening process. The corresponding diformate, $HC(O)CH_2CH_2C(O)H$, is formed by reaction with $O_2$. Sauer et al.[72] have reported that the oxidation of 1,3-dioxolane, which contains both $-OCH_2O-$ and $-OCH_2CH_2O-$ groups, leads to ethylene carbonate and methylene glycol diformate ($HC(O)OCH_2OC(O)H$) with close to 50% yields. The formation of these two products shows that the primary reaction of OH with 1,3-dioxolane occurs by H-atom abstraction from both $-OCH_2O-$ and $-OCH_2CH_2O-$ groups. The alkoxy radical generated by abstraction from the $-OCH_2O-$ group reacts with $O_2$ to produce the cyclic carbonate, while the alkoxy radical produced by abstraction from the $-OCH_2CH_2O-$ group breaks the C−C bond and leads to the subsequent formation of the diformate. The major oxidation product detected in the reaction of OH with 1,3-dioxane, a six-membered-ring diether containing both $-OCH_2O-$ and $-OCH_2CH_2CH_2O-$ groups, is the ester aldehyde $HC(O)OCH_2OCH_2C(O)H$.[54] It was proposed that the alkoxy radical generated by H-atom abstraction from an α-$CH_2-$ in the $-OCH_2CH_2CH_2O-$ group ring opens following C−C fission to give the $HC(O)OCH_2OCH_2CH_2$ radical, which after consecutive reactions with $O_2$ and NO forms the $HC(O)OCH_2OCH_2CH_2O$ alkoxy radical. Reaction of this radical with $O_2$ yields the ester aldehyde observed. Oxidation of 1,3,5-trioxane, a six-membered cyclic triether with three $-OCH_2O-$ groups, forms methyl glycol diformate, $HC(O)OCH_2OC(O)H$.[51] The cyclic alkyl radical produced by hydrogen atom abstraction from a $-CH_2O-$ group in the cyclic ether reacts successively with $O_2$ and NO to form the corresponding cyclic alkoxy radical. This alkoxy radical ring opens by carbon−oxygen bond cleavage to form the $HC(O)OCH_2OCH_2$ radical. Reaction with $O_2$ and NO forms the alkoxy radical $HC(O)OCH_2OCH_2O$, which reacts with $O_2$ to produce the final oxidation product.

## 2.4. Carbonyls

### 2.4.1. Aldehydes

Aldehydes play a central role in the chemistry of the troposphere since they are precursors of free radicals and peroxyacyl nitrates, which may lead to transport of $NO_x$ to remote areas.[5] The atmospheric degradation of aldehydes is controlled by photolysis and by reaction with OH radicals, for which the loss rates are of comparable magnitude. Photodissociation quantum yields for linear-chain aldehydes are relatively low compared with those for branched-chain aldehydes. As a consequence, reaction with OH radicals is generally the dominant loss process for linear-chain aldehydes, while for branched-chain aldehydes photolysis and reaction with OH occur at similar rates. The reported rate constants for reaction of $NO_3$ radicals with aldehydes show that atmospheric removal by this pathway will be minimal.[73−76] Reaction with $O_3$ for aldehydes that contain no carbon−carbon double bond system is also negligible.[13]

**2.4.1.1. Photolysis.** There are only a limited number of direct studies concerning the photolysis of aldehydes under atmospheric conditions. Absorption cross-section data are available for a range of aldehydes;[7,8,11,40] however, photodissociation quantum yields have been reported for only a few wavelengths in the actinic region.[7] Many of the photolysis rates for aldehydes used in atmospheric models have been calculated using the measured UV/visible absorption cross sections, assuming a photolysis quantum yield of unity. Hence, if the quantum yields are significantly less than unity, the estimated photodissociation rates will be seriously overestimated. The photolyses of a series of aldehydes have recently been investigated at the outdoor European simulation chamber in Valencia, Spain.[77] The results showed that the effective quantum yields for photodissociation ranged from around 0.05 for acetaldehyde to 0.28 for propionaldehyde. Further increases in chain length for the *n*-alkyl aldehydes up to nonanal indicated that the quantum yield remained essentially constant at 0.25. The quantum yields for dissociation of the branched-chain aldehydes, isobutyraldehyde and 2-methylbutyraldehyde, were shown to be considerably higher, with values of approximately 0.7, while that for the 1,2-dialdehyde, glyoxal, was 0.038. Although the unsaturated aldehydes methacrolein, acrolein, and *trans*-crotonaldehyde possess relatively high absorption cross sections in the actinic region, their quantum yields of $<0.004$, $<0.004$, and 0.03, respectively, are low. The products detected from the photolysis experiments carried out in sunlight showed that the products from acetaldehyde, propionaldehyde, and the branched-chain aldehydes could be explained in terms of a primary dissociation step leading to radical formation:

$$\mathrm{RCHO} + h\nu \rightarrow \mathrm{R} + \mathrm{HCO}$$

The products resulting from photolysis of longer-chain *n*-alkyl aldehydes provide evidence for the importance of the photodissociative molecular channel, which was found to increase in significance as the chain length increased:

$$\mathrm{CH_3CH_2CH_2C(O)H} + h\nu \rightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_3C(O)H}$$

**2.4.1.2. Rate Constants of OH Reactions.** Rate constants for the reaction of OH radicals with linear- and branched-chain aliphatic aldehydes have been reported at 298 K.[7,78,79] The rate constants for all the aldehydes fall in the small range $(1-3) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and increase only to a small extent with the length of the alkyl group. The facile nature of the reaction is consistent with the weakness of the aldehydic C−H bond, which is essentially independent of the nature of the substituent group.[7] The rate constant for reaction of OH with formaldehyde is virtually independent of temperature in the region of atmospheric relevance, while the higher aldehydes all show a slight negative temperature dependence.[5,80−83] It is unclear from the observed temperature dependence of the rate constants whether the reaction proceeds by direct hydrogen atom abstraction or addition to the >C=O double bond system, or involves the initial formation of a hydrogen-bonded complex, followed by H-atom abstraction.[78,79,84] Ab initio calculations indicate that the reaction channel involving addition to the carbonyl group has a significantly higher activation energy than the other two proposed reaction pathways.[83,85,86] Vandemberk and Peeters[83] proposed that a reaction pathway involving a hydrogen-bonded complex was consistent with the temperature dependence of the rate constants if the barrier for decomposition of the complex is higher than that for intramolecular H-atom transfer to form the reaction products.

**2.4.1.3. Mechanisms of the OH-Initiated Oxidation of Aldehydes.** The available kinetic and mechanistic data show that the reaction of OH radicals with aldehydes proceeds predominantly by overall H-atom abstraction from the −C(O)H group to form an acyl radical and water:[5,80−83]

$$\mathrm{RC(O)H} + \mathrm{OH} \rightarrow \mathrm{RC(O)} + \mathrm{H_2O}$$

The aldehydic C−H bond is sufficiently weak that hydrogen atom abstraction from the C−H bonds of the alkyl chain is of minor importance. For example, reaction at the $CH_3$ group in acetaldehyde represents, at most, a few percent of the reaction at room temperature.[81−83] It is interesting to note that the reaction of OH with the α-hydroxy aldehyde, glycolaldehyde, involves abstraction from both the α-$CH_2$− (∼20%) and the −C(O)H (∼80%) groups. Presumably, the strengths of the C−H bonds in the −C(O)H and $HOCH_2$− groups are quite similar in this molecule.[87]

### *2.4.2. Ketones*

Although ketones absorb quite strongly in the actinic region, photolysis studies carried out under atmospheric conditions show that, except for acetone, degradation by this pathway is minor compared to removal by OH-initiated oxidation.[8,12,40] Atmospheric loss of acetone by reaction with OH dominates at low altitudes, while photolysis is the major degradation process in the upper troposphere.[88] Reactions of $O_3$ [30] and $NO_3$ [34,35] with saturated ketones are negligible under atmospheric conditions.[13,18]

**2.4.2.1. Rate Constants of OH Reactions.** It is apparent from the kinetic data that a carbonyl group appears to have little effect on the reactivities of $-CH_3$ and $-CH_2CH_3$ groups in ketones, which are quite similar to their reactivities in alkanes.[4,5] This result may be expected in terms of bond dissociation energies since C−H bond strengths in the α position of ketones are approximately equal to those for the analogous groups in alkanes.[7] However, the carbonyl group is strongly electron withdrawing, and hence reaction of the electrophilic OH radical with a ketone at the α position may be expected to be considerably less facile than that with the corresponding group in an alkane. It is interesting to note that the rate constant for the electrophilic reaction of Cl atoms with acetone is around 4 times smaller than the rate constant for reaction with ethane.[89] Although the

$-CH_3$ and $-CH_2CH_3$ groups in ketones have reactivities similar to those in alkanes, there is considerable enhancement in the reactivity of alkyl groups containing ≥3 carbon atoms in carbonyl compounds compared to their reactivities in alkanes.[90-93] In particular, the reactivity of C−H bonds at the $\beta$-carbon atom appears to be quite pronounced. The increase in rate constants with chain length for linear-chain ketones indicates that the $-CH_2-$ group in the $\gamma$ position is also more reactive than expected, although there is a reduction in reactivity along the chain from the $\beta$- to the $\gamma$-carbon atoms. Wallington and Kurylo[91] tentatively proposed that this enhanced reactivity arises from the coordination of the attacking OH radical to the carbonyl group through an O−O interaction between the attacking OH radical and the carbonyl group. Formation of six- and seven-membered-ring transition states then facilitates H-atom abstraction from the $\beta$- and $\gamma$-carbon atoms, respectively. Smith and Ravishankara[45] have rationalized the enhanced reactivity exhibited by carbonyl compounds in terms of the initial formation of a weakly bound hydrogen-bonded adduct between the OH radical and the carbon group, which leads to intramolecular H-atom abstraction from sites in the alkyl group via cyclic transition states. On this basis, the transition state for reaction of OH with acetone is stablilized by hydrogen-bonding in the six-membered transition state, and hence the deactivating inductive effect of the carbonyl group is offset to some extent by the stabilizing effect of hydrogen bonding. As the chain length in the carbonyl compound increases, the deactivating inductive effect of the carbonyl group will diminish, while the transition states for H-atom abstraction at sites quite remote from the carbonyl group may be stabilized by hydrogen bond formation.

A number of theoretical studies on the reaction of OH radicals with acetone have been reported.[94,95] The results indicate that the activation energy for the reaction channel involving addition of OH to the carbonyl group is sufficiently high that this reaction will be insignificant at 298 K. The calculations provided strong support for the argument that the reaction of OH with acetone proceeds via formation of a hydrogen-bonded adduct, followed by intramolecular transfer of a hydrogen atom. Recent investigations on the temperature dependence of the OH reaction with acetone by Le Calvé et al.,[92] Wollenhaupt at al.,[96] and Gierczak et al.[97] indicate that the reaction shows a strong non-Arrhenius behavior, with the overall rate constant increasing above 298 K but becoming essentially constant below 250 K. This behavior, together with the large primary isotopic effect observed by Gierczak et al.,[97] provides support for a mechanism involving a H-bonded complex between acetone and OH. The rate constants for reaction of OH radicals with 2-butanone, 3-methyl-2-butanone, and 3-pentanone show little dependence on temperature, whereas the rate constants for reaction with 4-methyl-2-pentanone have strongly negative temperature dependencies.[91,92] The variation in the rate constants with temperature exhibited by ketones appears to be significantly less than that for reaction with the analogous alkanes, which provides support for the suggestion that the reactions proceed through different mechanisms.

**2.4.2.2. Mechanisms of the OH-Initiated Oxidation of Ketones.** It has generally been assumed that the reaction of OH radicals with acetone leads to the formation of the $CH_3C(O)CH_2$ radical following H-atom abstraction:

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

Recently, Wollenhaupt and Crowley[98] and Vasvári et al.[95] reported indirect experimental evidence which indicated that OH addition to the carbonyl group, followed by methyl radical elimination at 298 K, could be an important channel to generate acetic acid:

$$CH_3C(O)CH_3 + OH \rightarrow CH_3C(OH)OCH_3 \rightarrow CH_3COOH + CH_3$$

However, Talukdar et al.[99] have provided compelling evidence that the reaction of OH with $CH_3C(O)CH_3$ occurs through a hydrogen-bonded complex that leads almost exclusively to $CH_3C(O)CH_2$ and $H_2O$, independent of temperature between 242 and 350 K. The channel leading to acetic acid has been shown to be negligible at temperatures of atmospheric interest (less than 1% between 237 and 353 K).[80,94,99] In the atmosphere, H-atom abstraction is followed by reaction with $O_2$ and NO, leading to the acetonoxy radical, $CH_3C(O)CH_2O$, which predominantly decomposes to $CH_3C(O)$ and $CH_2O$, even at low temperature.[100] The available kinetic data for the reaction of OH with ketones suggest that the reactions proceed by H-atom abstraction from the alkyl chain. For 2-butanone, the major oxidation products in the presence of $NO_x$ are acetaldehyde and 2,3-butadione, indicating that the H-atom abstraction from the $\alpha$-$CH_2-$ dominates and that the $CH_3C(O)CH(CH_3)O$ alkoxy radical generated decomposes by C−C bond fission and by reaction with $O_2$.[101-103] The oxidation of methyl isobutyl ketone in the presence of $NO_x$ has been found to lead mainly to acetone, which shows that the reaction occurs predominantly through abstraction from the $\beta$-CH< group and that the $CH_3C(O)CH_2C(CH_3)_2O$ alkoxy radicals decompose by C−C bond cleavage.[92,101] Atkinson and Aschmann[103] have investigated the products observed in the OH-initiated oxidation of 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone and showed that isomerization of the alkoxy radicals generated in these systems is important. Isomerization rates of the alkoxy radicals formed from the ketones were found to depend markedly on whether the H atom abstracted in the isomerization process is on a carbon atom $\alpha$ or $\beta$ to the carbonyl group, with H-atom abstraction from C−H bonds on the $\beta$-carbon atom being significantly faster than that from C−H bonds on the $\alpha$-carbon atom.[103]

### *2.4.3. Esters*

As for most saturated organic compounds, reaction with OH radicals is the main atmospheric degradation process for esters. Photolysis and reaction with other oxidants, such as $O_3$ and $NO_3$ radicals, are expected to be of minor importance.[3,5]

**2.4.3.1. Rate Constants of OH Reactions.** The available rate constant data show that the increase in reactivity of an alkyl ester as the chain length of the alkyl group RC(O)O− increases from methyl to *n*-butyl is considerably smaller than the increase in reactivity of the *n*-alkyl formates, acetates, propionates, and butyrates as the chain length of the alkoxy group (−OR′) increases.[104−106] These results show that the OH radical reaction with esters mainly involves the alkoxy group.[3,104−106] The rate constants for reaction of OH with esters indicate that the alkoxy groups in these compounds are slightly more reactive than the corresponding *n*-alkyl group in alkanes; however, they are less reactive than in ethers. The significant reduction in the reactivity of the alkoxy group in esters compared to that in ethers is presumably a result of the deactivating inductive effect of the carbonyl on the alkoxy group. It is interesting to note that the rate constants for reaction of OH with alkyl formates are lower than those for the analogous acetates. It is suggested that replacement of the electron-donating methyl group in the acetates by a hydrogen atom leads to an increase in the deactivating effect of the carbonyl group. The increase in the rate constants with chain length of the alkoxy group in esters shows that $-CH_2-$ groups in the $\beta$ position, and to a slight extent in the $\gamma$ position, have higher reactivities than in unsubstituted alkanes. Thus, as has been discussed previously for the reaction of OH with alcohols, ethers, and ketones, the activating effect of the ester functional group appears to extend over several carbon atoms. This observation provides some support for the occurrence of an indirect H-atom-transfer mechanism involving the initial formation of a hydrogen-bonded adduct between the OH radical and the esters. Measurements of the variation of the rate constants with temperature for reaction of OH with esters are somewhat limited; however, the available data suggest that the rate constants of the reactions have only a small temperature dependence, which may indicate an alternative pathway to direct H-atom abstraction.

**2.4.3.2. Mechanisms of OH-Initiated Oxidation of Esters.** Mechanistic studies are available for the oxidation of a number of esters: methyl,[107−109] ethyl,[108,110,111] *n*-propyl,[108,111,112] isopropyl,[110,112,113] isobutyl,[113] *n*-butyl,[114] and *tert*-butyl[110,113] acetates and methyl and ethyl formates.[108] Christensen et al.[107] have investigated the Cl-atom-initiated oxidation of methyl acetate in the presence of $NO_x$. The major products reported were acetic acid and acetic formic anhydride. Hydrogen-atom abstraction occurs mainly from the $-OCH_3$ group, leading to the $CH_3C(O)OCH_2$ radical, which generates the $CH_3C(O)OCH_2O$ alkoxy radical. This radical then undergoes a unimolecular α-ester rearrangement via a five-membered-ring transition state or reacts with $O_2$:

$$CH_3C(O)OCH_2O \rightarrow CH_3C(O)OH + HCO$$

$$CH_3C(O)CH_2O + O_2 \rightarrow CH_3C(O)OC(O)H + HO_2$$

It was found that the importance of the α-ester rearrangement channel relative to that of the biomolecular reaction with $O_2$ depends on the reaction pathway by which the alkoxy radical has been generated from the peroxy radical. Formation of $CH_3C(O)OCH_2O$ by reaction of $CH_3C(O)OCH_2O_2$ with NO is considerably exothermic, whereas production by the self-reaction of peroxy radicals is close to thermoneutral. The data show that the relative yield of $CH_3C(O)OH$ was significantly higher when the alkoxy radical was generated by reaction with NO. The results were rationalized in terms of formation of vibrationally excited $CH_3C(O)OCH_2O$ radicals in the reaction of $CH_3C(O)OCH_2O_2$ with NO which possess sufficient internal energy to overcome the barrier for α-ester rearrangement. Some fraction of the excited alkoxy radicals undergo prompt α-ester rearrangement, while the remainder are thermalized by collision. The thermalized alkoxy radicals can decay either by reaction with $O_2$ or via α-ester rearrangement.[107] It was suggested that the OH-initiated oxidation of methyl acetate would lead to the same products, and Christensen et al.[107] have calculated that, under atmospheric conditions, the yields of acetic acid and acetic formic anhydride will be about 65% and 35%, respectively. Acetic acid (>70%) has been shown to be the major oxidation product formed from the reaction of OH with ethyl acetate in the presence of NO.[110,111] This observation is consistent with α-ester rearrangement of the alkoxy radical $CH_3C(O)OCH(CH_3)O$ produced in the system after H-abstraction from the $-OCH_2-$ group. The major products observed in the OH-initiated oxidation of *n*-propyl acetate were acetaldehyde and propanaldehyde,[111,112] which suggests that the $CH_3C(O)OCH(CH_2CH_3)O$ alkoxy radical formed following H-atom abstraction at the α-$CH_2$ group decomposes by both C−O and C−C bond cleavage. In addition, Picquet-Varrault et al.[111] have reported the formation of acetic acid and peroxypropionyl nitrate, which indicates that α-ester rearrangement of the alkoxy radical $CH_3C(O)OCH(CH_2CH_3)O$ may also occur. In their mechanistic study of the OH-initiated oxidation of *n*-butyl acetate ($CH_3C(O)OC_4H_9$), Veillerot et al.[114] identified the two products, 2-oxobutyl acetate ($CH_3C(O)OCH_2C(O)CH_2CH_3$) and 3-oxobutyl acetate ($CH_3C(O)OCH_2CH_2C(O)CH_3$), which arise by H-atom abstraction from $\beta$- and $\gamma$-$CH_2-$ groups in the $OC_4H_9$ chain, respectively. However, each of these products accounts for only about 15% of the overall reaction, which indicates that the reaction probably occurs mainly by abstraction from the α-$CH_2-$ group, leading to the formation of acetic butionic anhydride and acetic acid.

Oxidation of the branched-chain isopropyl, isobutyl, and *tert*-butyl acetates has been the subject of a number of studies.[110,112,113] The main products observed in the OH-initiated oxidation are acetic anhydride (∼70%) and acetone (∼25%) from isopropyl acetate; acetone (∼78%), formic acetic anhydride (∼50%), acetoxyacetaldehyde (∼18%), and acetic acid (∼8%) from isobutyl acetate; and acetic anhydride (∼50%) and acetone (∼25%) from *tert*-butyl acetate.[71,113] These product studies clearly show that

H-atom abstraction from the $CH_3C(O)O-$ group in these acetates is of minor importance and that abstraction occurs mainly from the alkoxy groups in the esters. Abstraction of the hydrogen atom from the $\alpha$ >CH− group in isopropyl acetate leads to the production of the $CH_3C(O)OC(CH_3)_2O$ radical, which undergoes both C−C and C−O bond fission to give acetic anhydride and acetone, respectively. Reaction of OH with isobutyl acetate can occur at both the $\alpha$-$CH_2-$ and $\beta$ >CH− groups to generate the alkoxy radicals $CH_3C(O)OCH(CH(CH_3)_2)O$ and $CH_3C(O)OCH_2C(CH_3)_2O$, respectively. The $CH_3C(O)OCH(CH(CH_3)_2)O$ radical decomposes by C−C bond fission to give acetic formic anhydride and the $(CH_3)_2CH$ radical, which provides a source of acetone in the system. Carbon−carbon cleavage of the $CH_3C(O)OCH_2C(CH_3)_2O$ radical leads to the formation of acetone and the $CH_3C(O)OCH_2$ radical, which produces the $CH_3C(O)OCH_2O$ alkoxy radical, which is a source of acetic acid and acetic formic anhydride. The production of acetoxyacetaldehyde from the OH-initiated oxidation of isobutyl acetate could arise by H-atom abstraction from a $\gamma$-$CH_3$ group, generating the alkoxy radical $CH_3C(O)OCH_2CH(CH_3)CH_2O$, which following elimination of HC(O)H generates the $CH_3C(O)OCH_2CH(CH_3)O$ radical in subsequent reactions. This radical decomposes by carbon−carbon bond-breaking to form acetoxyacetaldehyde. *tert*-Butyl acetate reacts with the OH radical by abstraction of a hydrogen atom from the *tert*-butyl group, leading to production of the alkoxy radical $CH_3C(O)OC(CH_3)_2CH_2O$. Loss of formaldehyde gives the $CH_3C(O)OC(CH_3)_2$ radical, which, as previously outlined for the oxidation of isopropyl acetate, generates acetic anhydride and acetone.

The Cl-atom-initiated oxidation of methyl[108,109] and ethyl[108] formates has been reported. Observation of formic acid in these systems indicates that the alkoxy radicals $HC(O)OCH_2O$ and $HC(O)OCH(CH_3)O$ decompose by an $\alpha$-ester rearrangement to give formic acid, as well as by reaction with $O_2$ to form an acid anhydride. As outlined previously for the oxidation of methyl acetate, when the alkoxy radical is generated by reaction of the peroxy radical with NO, the energy-rich alkoxy radical undergoes $\alpha$-rearrangement rather than reaction with $O_2$. Thus, Wallington et al.[109] found that the yield of HC(O)OH compared to that of HC(O)C(O)H was higher when the oxidation of methyl formate was carried out in the presence of NO than when the oxidation took place in the absence of NO when this alkoxy radical was generated from self-reaction of the peroxy radical. Evidence was also provided that H-atom abstraction from the $HC(O)O-$ group was also an important reaction channel.

## 2.5. Unsaturated Oxygenates

The atmospheric degradation of the unsaturated oxygenates is controlled mainly by chemical reaction with OH and $NO_3$ radicals and $O_3$, while photolysis plays a negligible role.[15,16,115−122]

### 2.5.1. OH Reaction with Unsaturated Oxygenates

The available rate constant data at room temperature for the reaction of OH with unsaturated alcohols having the $CH_2{=}CHROH$ structure, such as $CH_2{=}CHCH_2OH$, $CH_2{=}CHCH_2CH_2OH$, $CH_2{=}CHCH(OH)CH_3$, $(CH_3)_2C(OH)CH{=}CH_2$, and $CH_2{=}CHCH(OH)CH_2CH_3$, are similar ($k_{OH} \approx (5.5 \pm 1.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).[117,119] The rate constant of the OH reaction with $CH_3CH_2CH{=}CHCH_2OH$ has been found to be higher ($k_{OH} \approx 10.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).[119] These rate constant values are around 2 times higher than those for the corresponding alkenes, which indicates that the substituents "ROH" activate the C=C bond.[117,119]

Mechanistic studies have shown that these reactions proceed mainly by addition of the OH radical to the carbon atoms of the >C=C< double bond and that H-atom abstraction from the "ROH" groups is negligible.[117,119] It has also been suggested that the OH addition occurs mainly to the side of the C=C double bond adjacent to the hydroxyl group.[119]

The OH reaction rate constants with vinyl ethers ($ROCH{=}CH_2$) increase with the alkyl chain length from methyl to propyl vinyl ($k_{OH} \approx 4.5$-, 6.8-, and $10 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for methyl, ethyl, and propyl vinyl ether).[121,123,124] The higher vinyl ethers seem to show a reactivity toward OH radicals similar to that of propyl vinyl ether.[124] The rate constant values for vinyl ethers are a factor 2−3 higher than those for the corresponding alkenes, indicating an activating effect of the RO− group for the addition of OH radicals to the >C=C< double bond. Product studies confirm that the reactions proceed mainly by OH addition to the double bound. The OH initial reaction with vinyl ethers ($ROCH{=}CH_2$) in air leads essentially to the corresponding formate (ROC(O)H) and formaldehyde ($H_2CO$).

The OH reaction rate constants with unsaturated aldehydes are higher than the corresponding saturated ones ($k_{OH} \approx 2$-, 2.8-, and $3.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for acrolein ($CH_2{=}CHCHO$), methacrolein ($CH_2{=}C(CH_3)CHO$), and *trans*-crotonaldehyde ($CH_3CH_2{=}CHCHO$), respectively).[120,122] From their product studies, Orlando and Tyndall reported that the rate constants of the reactions involving H-atom abstraction from the carbonyl group of these three unsaturated aldehydes are very similar, and are quite similar to the rate constant for the reaction of OH with acetaldehyde.[125] They have also concluded that the rate constant for OH addition to acrolein (around $6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) is lower than that for the addition of OH to methyl-substituted alkenes (about $1.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), which was attributed to the enhancement of the reactivity of the >C=C< double bound due to the presence of the methyl group.[125−127] As expected, the presence of the adjacent carbonyl group (>C=O) lowers the contribution of the addition channel to the overall rate constants compared to that of the corresponding alkenes propene, 2-methylpropene, and 2-butene. It has been speculated that, for acrolein and methacrolein, about 80% of the addition reaction occurs at the $\beta$-carbon, while for *trans*-crotonaldehyde about 40% of the addition occurs on the $\alpha$-carbon (adjacent to the carbonyl group).[125]

The OH-intiated oxidation of acrolein, methacrolein, and *trans*-crotonaldehye in air in the presence of $NO_x$ may also lead to the formation of PAN-type species ($CH_2{=}CHCOO_2NO_2$, $CH_2{=}C(CH_3)COO_2NO_2$, and $CH_3CH{=}CHCOO_2NO_2$, respectively).[122,125−127]

Unsaturated esters such as allyl acetate ($CH_3C(O)OCH_2CH{=}CH_2$), isopropenyl acetate ($CH_3C(O)OC(CH_2){=}CH_2$), penten-1-yl acetate ($CH_3C(O)O(CH_2)_3CH{=}CH_2$), and *cis*-3-hexenyl acetate ($CH_3C(O)O(CH_2)_2CH{=}CHCH_2CH_3$) are much more reactive toward OH than their saturated analogues ($k_{OH} = 2.7$-, 7-, 4.3-, and $7.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively),[118,128,129] and their rate coefficients are close to those of the corresponding alkenes.[41] This indicates that the reactions of OH with unsaturated acetates proceed essentially by OH addition to the $>C{=}C<$ bond.

### 2.5.2. $O_3$ Reaction with Unsaturated Oxygenates

While unsaturated ethers react faster with ozone than their alkene structural homologues ($k_{alkene}/k_{ether} < 5 \times 10^{-2}$),[124] the reverse is observed for unsaturated carbonyls and unsaturated esters ($k_{alkene}/k_{carbonyl} < 2$).[15] The reactivity of unsaturated alcohols is about the same as that of the corresponding alkenes. Grosjean et al.[14−16] have discussed the reactivity of $O_3$ with unsaturated oxygenates as functions of the nature, number, and position of the oxygen-containing substituents −CHO, −C(O)R, −C(O)OR, and −OC(O)R. The reaction of $O_3$ with unsaturated compounds proceeds by electrophilic addition to the $>C{=}C<$ double bond. It is expected that the reactivity of ozone with unsaturated oxygenates reflects the electronic density at the $>C{=}C<$ double bond and depends on the nature and number of substituents as well as on the position of the oxygen-containing group relative to carbon−carbon double bond.[15]

The lower reactivity of unsaturated carbonyls compared to that of alkenes is consistent with the electron-withdrawing effect of the −CHO and −C(O)R groups, α,*β*-unsaturated ketones being more reactive than the corresponding aldehydes.[15] For esters, the electron-withdrawing effect of the −C(O)R is stronger than that of the −OC(O)R group. This electron-withdrawing effect is lowered when the carbonyl groups are separated by more than two $-CH_2-$ groups from the $>C{=}C<$ double bond.[16] The existing data indicate that, as for alkenes, reactivity of ozone with unsaturated oxygenates increases with the degree of substitution.[15] In the case of unsaturated ethers, the ether group enhances the reactivity of the $>C{=}C<$ double bond toward ozone compared to the alkenes.

Product studies have led Grosjean and Grosjean[15,16] to suggest a general mechanism for the reaction of ozone with oxygenated compounds:

$$O_3 + R_1R_2C{=}CR_3X \rightarrow \alpha(R_1COR_2 + R_3C(X)OO) + (1 - \alpha)(R_3COX + R_1C(R_2)OO)$$

where $R_1$, $R_2$, and $R_3$ = H or alkyl, X is the oxygen-containing substituent, $R_1COR_2$ and $R_3COX$ are the primary products, $R_3C(X)OO$ and $R_1C(R_2)OO$ are the carbonyl oxide biradicals, and α depends on the number and the nature of the alkyl and oxygen-containing substituents.[16] The fate of the carbonyl oxide biradicals $R_3C(X)OO$ and $R_1C(R_2)OO$ depends also on the nature of the substituents: they may rearrange or form hydroperoxides or organic aerosols. The production of OH radicals from the ozonolysis of unsaturated oxygenates has been reported for a number of compounds.[16,128]

### 2.5.3. $NO_3$ Reaction with Unsaturated Oxygenates

The reaction of $NO_3$ with unsaturated carbonyls proceeds by addition to the $>C{=}C<$ double bond (and by H-atom abstraction from the −CHO group for unsaturated aldehydes). Comparison of the measured rate constants shows that, similar to the reaction with $O_3$, the presence of the carbonyl group decreases the reactivity of $NO_3$ toward the $>C{=}C<$ double bond ($k_{NO_3} \approx 1 \times 10^{-15}$ for acrolein, $4 \times 10^{-15}$ for methacrolein, and $<1 \times 10^{-16}$ for methyl vinyl ketone, in cm$^3$ molecule$^{-1}$ s$^{-1}$ units).[130,131] Both steric and inductive effects influence the reactivity of $NO_3$ with unsaturated alcohols, as was suggested for 2-methyl-3-butene-2-ol, the latter being slightly less reactive than 1-butene.[130]

The reaction of $NO_3$ with unsaturated oxygenates proceeds by addition to either one of the carbon atoms of the $>C{=}C<$ double bond, preferentially leading to the most substituted radical. In the presence of $NO_x$, the reaction may ultimately lead to organic nitrates among the first-generation products.

## 3. Structure−Activity Relationships

### 3.1. Kinetics

Atkinson and co-workers[3,37,132] have developed a structure−activity relationship (SAR) which allows calculation of rate constants for hydrogen-atom abstraction in the gas phase from C−H bonds in organic compounds. The method is based on the estimation of $-CH_3$, $-CH_2-$, and $-CH<$ group rate constants, assuming that the group rate constants depend on the identity of α-substituent groups. Agreement between experimental and calculated values for the rate constants is in general good, although in some cases the effect of *β*-substituents must be taken into account to improve the accuracy of the predicted rate constants.

The products arising from the reaction of hydroxyl radicals with saturated oxygen-containing compounds are consistent with hydrogen-atom abstraction from the reactants.[3−5] The available rate coefficient data for reaction with alcohols,[19,22,133] ethers,[22,133−135] ketones,[90−92,136] and esters[105,106,137,138] clearly indicate that the oxygenated functional groups have long-range activating effects with respect to H-atom abstraction at sites remote from the substituent group. It is hence not surprising that agreement between experimental rate data and values calculated using the SAR method for reactions of OH with compounds containing oxygenated functional groups is in general rather poor. In particular, the estimated rate constants for polyfunctionalized compounds show significant deviations from the experi-

**Table 1. Reactivity of *n*-Alkyl Groups (R) in Alkanes, Alcohols, Ethers, Ketones, and Acetates at 298 K (in $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ Units)**

| R group | R−R[a] | HO−R[b,c] | RO−R[d] | $CH_3C(O)-R$[e] | $CH_3C(O)O-R$[g] | $R-C(O)OCH_3$[g] |
|---|---|---|---|---|---|---|
| $CH_3$ | 0.12 | 0.79[b] | 1.4 | 0.1[b] | 0.22 | 0.10 |
| $C_2H_5$ | 1.2 | 3.1[b] | 6.8 | 1.1[b] | 1.57 | 0.61 |
| *n*-$C_3H_7$ | 2.7 | 5.5[b] | 10.9 | 4.8[b] | 3.32 | 3.08 |
| *n*-$C_4H_9$ | 4.4 | 8.1[b] | 13.5 | 9.0[b] | 5.42 | 4.61 |
| *n*-$C_5H_{11}$ | 5.6 | 11.1[c] | 17.3 | 8.8[f] | 7.24 | 6.93 |
| *n*-$C_6H_{13}$ | 6.9 | 12.6[c] | | | | |
| *n*-$C_7H_{15}$ | 9.0 | 13.7[c] | | | | |
| *n*-$C_8H_{17}$ | 11.5 | 14.4[c] | | | | |

[a] From OH rate coefficient data for alkanes, $k_{OH}(R) = 0.5k_{OH}(R-R)$.[41] [b] From Atkinson et al.[7] [c] From Atkinson.[5] [d] From OH rate coefficient data for ethers, $k_{OH}(R) = 0.5k_{OH}(R-O-R)$.[42,43] [e] From OH rate coefficient data for ketones, $k_{OH}(R) = k_{OH}(CH_3C(O)R) - 0.5k_{OH}(CH_3C(O)CH_3)$.[5,7] [f] From Wallington et al.[104] [g] From OH rate coefficient data for esters, $k_{OH}(R) = k_{OH}(RC(O)OCH_3) - k(CH_3)$, where $k(CH_3) = 2.2 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$,[37] and $k_{OH}(R) = k_{OH}(CH_3C(O)OR) - k'(CH_3)$, where $k'(CH_3) = 1 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.[138] Data for esters are taken from El Boudali et al.[105] and Le Calvé et al.[106,138,159]

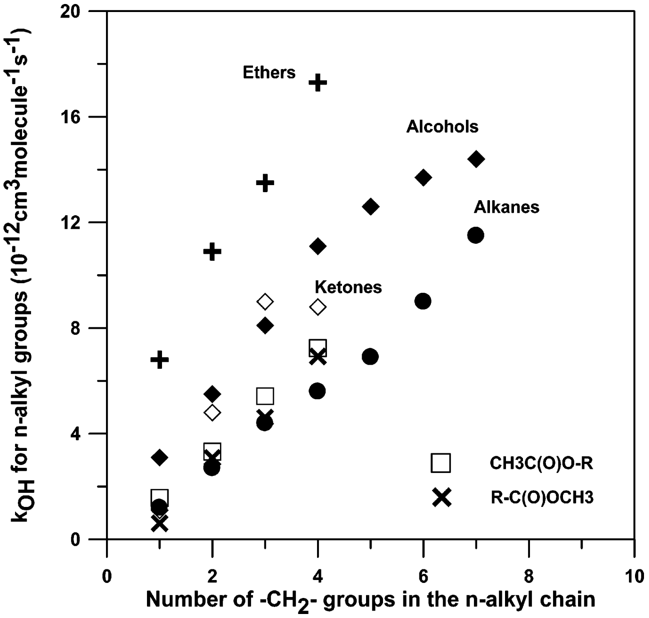


**Figure 2.** Plot of the rate constants for reaction of OH radicals with *n*-alkyl groups versus the number of $-CH_2-$ groups in the alkyl chain for alkanes, alcohols, ethers, ketones, and esters.

mental values. Reported rate constants for the reactions of OH radicals with aldehydes are virtually independent of the nature of the alkyl group, suggesting that these reactions proceed almost entirely by H-atom abstraction from the aldehyde group.[139] The data in Table 1 give the *n*-alkyl group rate coefficients derived from the literature for the reactions of OH radicals with linear-chain alkyl groups in alkanes, alcohols, ethers, ketones, and acetates. Plots of rate coefficients as a function of the number of $-CH_2-$ groups in the *n*-alkyl chain are shown in Figure 2. If it is assumed that electronic influences of the functional groups are largely restricted to H-atom abstraction from the α-carbon atom, it would be expected that, as the chain length increases, the reactivity of additional $-CH_2-$ groups would be virtually the same as that found in unsubstituted alkanes. The plots shown in Figure 2 for each series of compounds show distinct curvature up to around four $-CH_2-$ groups, with a gradual reduction in the reactivities of the $-CH_2-$ groups as the *n*-alkyl chain length increases. Hence, the activating effect of the oxygenated functional groups appears to extend over about three carbon atoms, after which the plots become linear when the $-CH_2-$ groups show the same level of reactivity as in *n*-alkanes.

The long-range activating effect of oxygenated functional groups cannot be explained in terms of bond energy or inductive effects alone and indicates an alternative pathway to the direct concerted hydrogen abstraction process observed for alkanes. Smith and Ravishankara[45] have recently discussed reactions of OH radicals with oxygenated organic compounds in terms of the formation of hydrogen-bonded complexes. These authors concluded that formation of such complexes can significantly influence the dynamics of the reaction by affecting the potential energy surface near the transition state. Formation of a hydrogen-bonded complex results in a lower activation energy for reaction compared to the direct H-atom abstraction pathway and provides an explanation for the unusual temperature dependence observed for the rate constants of OH reactions with oxygenated compounds.[42,43,47,92,96,104] Theoretical calculations on the possible energy profiles for the reaction of OH with acetone provide support for the involvement of a H-bonded complex in the initial stages of abstraction of a H atom from acetone by OH.[86,94,95] Although Smith and Ravishankara[45] limited their discussion on the role of hydrogen-bonded intermediates in the reaction of OH with oxygenated compounds to carboxylic acids, aldehydes, and ketones, it is suggested that the reactivity of aliphatic alcohols, ethers, and esters with OH radicals can also be rationalized in a similar manner. In all cases, the initial step in the reaction involves the formation of a complex in which a hydrogen bond exists between the H atom of the attacking OH radical and the O atom of the oxygenated substrate. A second hydrogen bond is then formed in the complex between the O atom of the OH radical and a H atom in the hydrocarbon chain, resulting in intermolecular H-atom transfer via a cyclic transition state. For example, the reaction of OH with alcohols and ethers involves the hydrogen-bonded complex forming a five-membered-ring system for abstraction of a H atom from the α-carbon atom, while abstraction of a H atom from the *β*- or *γ*-carbon atom involves six- and seven-membered-ring structures, respectively. As the ring size increases beyond six, ring strain is unlikely to increase significantly; however, entropy for ring

**Table 2. $CH_x$ ($x$ = 1, 2, or 3) Group Rate Constants (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ Units) for the Reaction of OH Radicals with Alkyl Alcohols at 298 K**

| $CH_x$ group | α position | $\beta$ position | $\gamma$ position | $\geq\delta$ position |
|---|---|---|---|---|
| $-CH_3$ | 0.79[a] | 0.36[b] | 0.25[c] | 0.12[d] |
| $-CH_2-$ | 2.9[e] | 2.2[f] | 1.6[c] | 1.2[d] |
| $>CH-$ | 4.2[g] | 6.4[h] | 4.3[c] | 2.9[d] |

[a] From $k(\mathrm{OH} + \mathrm{CH_3OH})$[7] $- k(-\mathrm{OH})$, where $k(-\mathrm{OH}) = 0.14 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[7,37] [b] From $^1/_3[k(\mathrm{OH} + \mathrm{(CH_3)_3COH})$[47] $- k(-\mathrm{OH})]$ and $k(\mathrm{OH} + \mathrm{CH_3CH_2OH})$.[7] [c] Assuming a monotonic decrease in the value of $k(-\mathrm{CH}_x)$ on going from the $\beta$- to the $\delta$-carbon atom. [d] Assuming $k(\delta\text{-}\mathrm{CH}_x)$ has the same value as in an alkane.[37] [e] From $k(\mathrm{OH} + \mathrm{CH_3CH_2OH})$.[7] [f] From $k(\mathrm{OH} + \mathrm{CH_3CH_2CH_2OH})$[7] $- [k(-\mathrm{OH}) + k(\alpha\text{-}\mathrm{CH_2}-) + k(\gamma\text{-}\mathrm{CH_3})]$. [g] From $k(\mathrm{OH} + \mathrm{(CH_3)_2CHOH})$[7] $- [k(-\mathrm{OH}) + 2k(\beta\text{-}\mathrm{CH_3})]$. [h] From $k(\mathrm{OH} + \mathrm{(CH_3)_2CHCH_2OH})$[160] $- [k(-\mathrm{OH}) + k(\alpha\text{-}\mathrm{CH_2}-) + 2k(\gamma\text{-}\mathrm{CH_3})]$.

**Table 3. $CH_x$ ($x$ = 1, 2, or 3) Group Rate Constants (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ Units) for the Reaction of OH Radicals with Alkyl Ethers at 298 K**

| $CH_x$ group | α position | $\beta$ position | $\gamma$ position | $\geq\delta$ position |
|---|---|---|---|---|
| $-CH_3$ | 1.4[a] | 0.6[b] | 0.39[c] | 0.12[d] |
| $-CH_2-$ | 6.2[e] | 4.3[f] | 2.9[c] | 1.2[d] |
| $>CH-$ | 3.9[g] | 6.5[h] | 4.7[c] | 2.9[d] |

[a] From $^1/_2[k(\mathrm{OH} + \mathrm{CH_3OCH_3})]$.[7] [b] From $^1/_3[k(\mathrm{OH} + \mathrm{CH_3OC(CH_3)_3})$[47] $- k(\alpha\text{-}\mathrm{CH_3})]$. [c] Assuming a monotonic decrease in the value of $k(\mathrm{CH}_x)$ on going from the $\beta$- to the $\delta$-carbon atom. [d] Assuming $k(\delta\text{-}\mathrm{CH}_x)$ has the same value as in an alkane.[37] [e] From $\{[k(\mathrm{OH} + \mathrm{CH_3CH_2OCH_2CH_3})]/2\}$[43] $- k(\beta\text{-}\mathrm{CH_3})$. [f] From $\{[k(\mathrm{OH} + \mathrm{CH_3CH_2CH_2OCH_2CH_2CH_3})]/2\}$[43] $- [k(\alpha\text{-}\mathrm{CH_2}-) + k(\gamma\text{-}\mathrm{CH_3})]$. [g] From $\{[k(\mathrm{OH} + \mathrm{(CH_3)_2CHOCH(CH_3)_2})]/2\}$[43] $- 2k(\beta\text{-}\mathrm{CH_3})$. [h] From $\{[k(\mathrm{OH} + \mathrm{(CH_3)_2CHCH_2OCH_2CH(CH_3)_2})]/2\}$[43] $- [k(\alpha\text{-}\mathrm{CH_2}-) + 2k(\gamma\text{-}\mathrm{CH_3})]$.

**Table 4. $CH_x$ ($x$ = 1, 2, or 3) Group Rate Constants (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ Units) for the Reaction of OH Radicals with Alkyl Ketones at 298 K**

| $CH_x$ group | α position | $\beta$ position | $\gamma$ position | $\geq\delta$ position |
|---|---|---|---|---|
| $-CH_3$ | 0.10[a] | 0.37[b] | 0.27[c] | 0.12[d] |
| $-CH_2-$ | 0.7[e] | 3.5[f] | 2.4[c] | 1.2[d] |
| $>CH-$ | 2.0[g] | 12.7[h] | 7.8[c] | 2.9[d] |

[a] From $^1/_2k(\mathrm{OH} + \mathrm{CH_3C(O)CH_3})$.[7] [b] From $^1/_3[k(\mathrm{OH} + \mathrm{CH_3C(O)C(CH_3)_3})$[91] $- k(\alpha\text{-}\mathrm{CH_3})]$. [c] Assuming a monotonic decrease in the value of $k(-\mathrm{CH}_x)$ on going from the $\beta$- to the $\delta$-carbon atom. [d] Assuming $k(\delta\text{-}\mathrm{CH}_x)$ has the same value as in an alkane.[37] [e] From $k(\mathrm{OH} + \mathrm{CH_3C(O)CH_2CH_3})$[7] $- [k(\alpha\text{-}\mathrm{CH_3}) + k(\beta\text{-}\mathrm{CH_3})]$. [f] From $k(\mathrm{OH} + \mathrm{CH_3C(O)CH_2CH_2CH_3})$[91] $- [k(\alpha\text{-}\mathrm{CH_3}) + k(\alpha\text{-}\mathrm{CH_2}-) + k(\gamma\text{-}\mathrm{CH_3})]$. [g] From $k(\mathrm{OH} + \mathrm{CH_3C(O)CH(CH_3)_2})$[92] $- [k(\alpha\text{-}\mathrm{CH_3}) + 2k(\beta\text{-}\mathrm{CH_3})]$. [h] From $k(\mathrm{OH} + \mathrm{CH_3C(O)CH_2CH(CH_3)_2})$[91,92] $- [k(\alpha\text{-}\mathrm{CH_3}) + k(\alpha\text{-}\mathrm{CH_2}-) + 2k(\gamma\text{-}\mathrm{CH_3})]$.

**Table 5. $CH_x$ ($x$ = 1, 2, or 3) Group Rate Constants (in $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ Units) for the Reaction of OH Radicals with Alkyl Esters at 298 K**

| $CH_x$ group | α position | $\beta$ position | $\gamma$ position | $\delta$ position |
|---|---|---|---|---|
| $CH_x$ in the Acyl Group | | | | |
| $-CH_3$ | 0.10[a] | 0.37[b] | 0.27[c] | 0.12[d] |
| $-CH_2-$ | 0.34[e] | 2.5[f] | 1.9[c] | 1.2[d] |
| $>CH-$ | 2.1[g] | | | 2.9[d] |
| $CH_x$ in the Alkoxy Group | | | | |
| $-CH_3$ | 0.22[h] | 0.17[i] | 0.17[c] | 0.12[d] |
| $-CH_2-$ | 1.4[j] | 1.9[k] | 1.6[c] | 1.2[d] |
| $>CH-$ | 3.3[l] | 4.5[m] | 3.7[c] | 2.9[d] |

[a] From $^1/_2k(\mathrm{OH} + \mathrm{CH_3C(O)CH_3})$.[7] [b] From $^1/_3[k(\mathrm{OH} + \mathrm{(CH_3)_3CC(O)CH_3})$[91] $- k(-\mathrm{C(O)OCH_3})]$, where $k(-\mathrm{C(O)OCH_3}) = k(\mathrm{OH} + \mathrm{CH_3C(O)OCH_3})$[105] $- k(-\mathrm{C(O)CH_3})$. [c] Assuming a monotonic decrease in the value of $k(-\mathrm{CH}_x)$ on going from the $\beta$- to the $\delta$-carbon atom. [d] Assuming $k(\delta\text{-}\mathrm{CH}_x)$ has the same value as in an alkane.[37] [e] From $k(\mathrm{OH} + \mathrm{CH_3CH_2C(O)OCH_3})$[104,159] $- [k(-\mathrm{C(O)OCH_3}) + k(\beta\text{-}\mathrm{CH_3})]$. [f] From $k(\mathrm{OH} + \mathrm{CH_3CH_2CH_2C(O)OCH_3})$[104,159] $- [k(-\mathrm{C(O)OCH_3}) + k(\alpha\text{-}\mathrm{CH_2}-) + k(\gamma\text{-}\mathrm{CH_3})]$. [g] From $k(\mathrm{OH} + \mathrm{(CH_3)_2CHC(O)OCH(CH_3)_2})$[161] $- [k(-\mathrm{C(O)OCH(CH_3)_2}) + 2k(\beta\text{-}\mathrm{CH_3})]$. [h] From $k(\mathrm{OH} + \mathrm{CH_3OC(O)CH_3})$[105] $- k(-\mathrm{C(O)CH_3})$, where $k(-\mathrm{C(O)CH_3}) = {}^1/_2k(\mathrm{OH} + \mathrm{CH_3C(O)CH_3})$.[7] [i] From $^1/_3[k(\mathrm{OH} + \mathrm{(CH_3)_3COC(O)CH_3})$[138] $- k(-\mathrm{C(O)CH_3})]$. [j] From $k(\mathrm{OH} + \mathrm{CH_3CH_2OC(O)CH_3})$[105] $- [k(-\mathrm{C(O)CH_3}) + k(\beta\text{-}\mathrm{CH_3})]$. [k] From $k(\mathrm{OH} + \mathrm{CH_3CH_2CH_2OC(O)CH_3})$[105] $- [k(-\mathrm{C(O)CH_3} + k(\alpha\text{-}\mathrm{CH_2}-) + k(\gamma\text{-}\mathrm{CH_3})]$. [l] From $k(\mathrm{OH} + \mathrm{(CH_3)_2CHOC(O)CH_3})$[138] $- [k(-\mathrm{C(O)CH_3}) + 2k(\beta\text{-}\mathrm{CH_3})]$. [m] From $k(\mathrm{OH} + \mathrm{(CH_3)_2CHCH_2OC(O)CH_3})$[138] $- [k(-\mathrm{C(O)CH_3}) + k(\alpha\text{-}\mathrm{CH_2}-) + 2k(\gamma\text{-}\mathrm{CH_3})]$.

formation in the complex will be less favorable. Hence, as abstraction takes place at sites increasingly remote from the alcohol or ether group in the OH−alcohol or OH−ether adduct, the probability of H-atom transfer will become progressively smaller. In contrast to H-atom abstraction from an α-carbon in alcohols or ethers, where intramolecular H-atom transfer in the hydrogen-bonded adduct involves a strained five-membered-ring, abstraction from the α-carbon atom in ketones or in the alkoxy group in an ester involves the formation of six- and seven-membered cyclic transition states, respectively.

From the available rate constant data at 298 K for the reactions of OH radicals with alcohols, ethers, ketones, and esters, it is possible to derive group rate constants for each $CH_x$ ($x$ = 1, 2, or 3) group in these compounds as a function of their position in the alkyl group chain relative to the functional group. Consideration of the reported rate constants for the reactions of OH with ethers, ketones, and esters suggests that the reactivities of the groups on either side of the ether and carbonyl groups are reasonably independent and additive.[4,5] This approximation has been employed to estimate the group rate constants for H-atom abstraction from α and $\beta$ sites in oxygenated compounds, given in Tables 2−5. These group rate constants clearly demonstrate that oxygenated functional groups activate both α and $\beta$ sites in the molecules. In principle, it is possible to calculate group rate constants from the available kinetic data base for reactivities at $\gamma$ and $\delta$ sites in oxygenated compounds. However, the absolute values of the derived group rate constants at the $\gamma$- and $\delta$-carbon atoms are subject to considerable error since they are calculated from a series of subtractions of several measured rate constants, which are subject to experimental error. It is suggested that the activating effect of the oxygenated functional group at $\gamma$ and $\delta$ sites is probably best estimated by assuming that there is a monotonic decrease in group rate constants on going from the $\beta$ to the $\delta$ position, where the $\delta$ group is expected to have the same reactivity as that shown by the group in an unsubstituted alkane. This approximation can be justified from the data given in Figure 2, which clearly shows that the activating effect of an oxygenated functional group extends at least to the $\gamma$-carbon atom. The estimated $CH_x$ group rate constants given in Tables 2−5 are of use in predicting the possible sites of attack in the reactions of OH radicals with acyclic alcohols, ethers, ketones, and esters, and hence the likely product distribution yields in the reactions. It also seems reasonable to assume that the alkyl group chains in aldehydes, esters, and carboxylic acids will have approximately similar group reactivities as for the same groups in ketones. The calculated group rate constant data given in Table 5 for the $CH_x$ groups in the alkyl chain of esters (RC(O)−) provide support for this argument. Although it is probable that the reaction of OH radicals with cyclic alcohols, ethers, ketones, and esters involves the initial formation of a hydrogen-bonded complex, intramolecular H-atom transfer via cyclic transition states is unlikely on steric grounds, and enhancement of reactivity at sites remote from the functional group is not observed experimentally.[44,46,68−70,72,133,136] Thus, apart from abstraction at the α-carbon atom, where the reactivity is expected to be similar to that found in a linear molecule, the remaining sites exhibit approximately the same level of reactivity as those observed in unsubstituted alkanes.

Rate constant data are available for the reactions of OH radicals with a limited number of difunctionalized oxygenated compounds, in which the two functional groups are separated by one or two $-CH_2-$ groups. The rate constants reported for reaction with dimethoxymethane, $CH_3OCH_2OCH_3$,[44,63] and 2,4-pentanedione, $CH_3C(O)CH_2C(O)CH_3$,[136] indicate that the $-CH_2-$ groups in these compounds have reactivities fairly similar to those shown by α-$CH_2-$ groups in monoethers and ketones. Hence, it appears that the activating effect of the two functional groups is not additive. It has been suggested that the lower-than-expected reactivity of the $-CH_2-$ bridging group is largely related to strengthening of the C−H bond in the $-CH_2-$ bridging group compared to their strength in α-$CH_2-$ groups in ethers or ketones.[46,140] In a similar manner, the reactivities of the $-CH_2-$ group in hydroxyacetone,[141] methoxyacetone[141] and methoxymethyl acetate[108] are little changed from those found in the parent alcohol, ether, and ester compounds. In contrast, the rate constants determined for the reaction of OH with $HOCH_2CH_2OH$,[4] $CH_3OCH_2CH_2OCH_3$,[44,63] and $CH_3C(O)CH_2CH_2C(O)CH_3$,[136] and with the mixed functionalized compounds $HOCH_2CH_2OCH_3$[141] and $CH_3OCH_2CH_2OC(O)CH_3$,[108] show that the bridging $-CH_2-$ groups have reactivities that are considerably enhanced compared to that expected on the basis of a simple addition of the rate constants for reaction of the two α-$CH_2-$ groups in the parent compounds. It seems reasonable to assume that the C−H bond strengths in the bridging $-CH_2-$ groups are similar to those in monofunctionalized compounds. The increased reactivity of the bridging $-CH_2-$ groups can be rationalized in terms of activation by both functional groups since they are in the α position to one group and in the β position with respect to the other group.

## 3.2. Alkoxy Radical Chemistry

Reactions of OH and $NO_3$ radicals with saturated and unsaturated oxygenated compounds lead to the generation of alkyl- and β-hydroxy- or β-nitroxy-substituted alkyl radicals, respectively. Under tropospheric conditions, the dominant reaction pathway for these species is rapid addition to molecular oxygen to form the corresponding peroxy radicals.[4,5,41] The reactions of α-hydroxy radicals, which are produced by H-atom abstraction from the α-carbon atom in alcohols, are unusual in that they react directly with $O_2$ to generate a carbonyl compound:[4,5]

$$CH_2OH + O_2 \rightarrow HC(O)H + HO_2$$

$$RCHOH + O_2 \rightarrow RC(O)H + HO_2$$

$$RR'COH + O_2 \rightarrow RR'C(O) + HO_2$$

The major reaction channels available in the troposphere for peroxy radicals are reaction with NO, $HO_2$, $NO_3$, and other peroxy radicals ($RO_2$).[4,5,41] The relative importance of these reaction pathways depends on the ambient concentrations of these species, although the reaction with NO is dominant for NO concentrations in excess of $1 \times 10^9$ molecules $cm^{-3}$.[4,5,41] Alkoxy radicals are formed in high yield in the reactions of peroxy radicals with NO, $NO_3$, and $RO_2$ and are also produced in subsequent degradation pathways of hydroperoxides, which are the main products arising from the reactions of peroxy radicals with $HO_2$. Thus, alkoxy radicals are key intermediates in the atmospheric degradation of organic compounds and have three major loss processes: reaction with $O_2$, thermal decomposition, and 1,5-H shift isomerization through a six-membered transition state.[142] The relative importance of these three reaction channels plays a major role in determining both the ozone formation potential of a compound and its ability to generate secondary organic aerosols. Reaction of alkoxy radicals with $O_2$ and isomerization generally lead to an increase in the number of oxygen-containing functional groups in the primary oxidation products compared to the reactants and hence generate compounds which may have low vapor pressures, whereas decomposition results in lower molecular weight products.

The available experimental data for the degradation of alkoxy radicals have been comprehensively reviewed by Atkinson and co-workers[5,142,143] and have been used to develop estimation methods to predict the relative importance of the various possible loss processes of these radicals.[5,142,144−146] For alkoxy radicals derived from alkanes and those where the substituent group is at the δ-carbon atom or more remote sites, the predicted and the experimental results are in good agreement. The data show that, for linear-chain alkoxy radicals, reaction with $O_2$ dominates over decomposition; however, decomposition occurs at a comparable rate for branched-chain alkoxy radicals. Where it is possible for isomerization to occur by a 1,5-H atom shift, this channel is generally dominant, particularly where H-atom abstraction occurs from δ-$CH_2-$ or δ-$CH<$ groups. Isomerization is also expected to dominate where H-atom abstraction from the δ-carbon atom in the alkoxy radical is activated by a substituent hydroxy or ether group. The results from recent quantum chemical calculations on the relative importance of the degradation pathways for unsubstituted alkoxy radicals are in line with those observed experimentally and with those predicted by the estimation methods.[147−153] The relative importance of both the unimolecular dissociation and isomerization reaction pathways is expected to decrease compared to the bimolecular reaction with $O_2$ at the lower temperatures prevalent in the upper troposphere, although isomerization reactions involving abstraction at $\delta$-$CH_2$− and $\delta$-CH< sites are predicted to dominate in all regions of the troposphere.

In principle, the general estimation methods derived in order to predict the degradation patterns for unsubstituted alkoxy radicals can be applied to alkoxy radicals generated from compounds which contain oxygenated functional groups. The relative importance of the three main degradation pathways for oxygenated alkoxy radicals—reaction with $O_2$, thermal decomposition, and 1,5-H shift—has been shown in a number of cases to depend on whether the alkoxy radicals are generated by the reaction of peroxy radicals with NO or via peroxy−peroxy radical reactions. In the former case, the alkoxy radicals are produced with excess vibrational energy and are more likely to undergo unimolecular reactions rather than reaction with $O_2$, which has a much lower activation energy.[107,109,154]

As mentioned previously, α-hydroxy alkyl radicals react directly with $O_2$ to form the corresponding carbonyl compound and $HO_2$. $\beta$-Hydroxy alkoxy radicals are generated in the atmosphere by addition of OH radicals to alkenes or by H-atom abstraction from a $\beta$-carbon atom in an alcohol. Decomposition of these radicals by C−C bond fission to give a carbonyl compound and an α-hydroxy alkyl radical appears to be their major reaction channel:

$$R'CH(OH)CH(R)O \rightarrow RC(O)H + R'CHOH$$

However, where isomerization can occur by abstraction from $\delta$-$CH_2$− or $\delta$-CH< groups, this reaction appears to compete effectively with decomposition.[142] Importantly, the alkoxy radical formed by addition of OH to ethene shows behavior significantly different from that of other $\beta$-hydroxy alkoxy radicals and degrades by both reaction with $O_2$ and decomposition:[153−156]

$$\begin{aligned} HOCH_2CH_2O + O_2 &\rightarrow HOCH_2C(O)H + HO_2 \\ &\rightarrow HOCH_2 + HC(O)H \end{aligned}$$

Carbon−carbon bond cleavage is relatively more important when the alkoxy radical is generated by the reaction of $HOCH_2CH_2O_2$ with NO than when it is formed by the peroxy radical self-reaction. Presumably, the excited alkoxy radical generated by reaction of $HOCH_2CH_2O_2$ with NO decomposes more readily than the thermalized radical.

The products obtained from the reaction of $NO_3$ radicals with alkenes indicate that the $\beta$-nitroxy alkoxy radicals generated in these systems both react with $O_2$ to give $\beta$-nitroxy carbonyl compounds and undergo unimolecular decomposition by C−C bond cleavage, generating carbonyl compounds and $NO_2$:[157,158]

$$RCH(ONO_2)CH(R')O + O_2 \rightarrow RCH(ONO_2)C(O)R' + HO_2$$

$$RCH(ONO_2)CH(R')O \rightarrow R'C(O)H + RCH(ONO_2)$$

$$RCH(ONO_2) \rightarrow RC(O)H + NO_2$$

Decomposition of primary $\beta$-nitroxy alkoxy radicals represents only a minor reaction pathway; however, the available data show that, for secondary $\beta$-nitroxy alkoxy radicals, both reaction with $O_2$ and decomposition are of about equal importance, while the only available pathway for tertiary radicals is C−C bond fission.[157,158]

Hydrogen atom abstraction from an α-carbon atom in an ether generates an α-alkoxy alkoxy radical. Primary alkoxy radicals lead to the production of formate esters by the bimolecular reaction with $O_2$:[31,49,50]

$$ROCH_2O + O_2 \rightarrow ROC(O)H + HO_2$$

Jenkin et al.[49] have provided evidence that the ester may also be formed via elimination of a hydrogen atom:

$$ROCH_2O \rightarrow ROC(O)H + H$$

Secondary and tertiary α-alkoxy alkoxy radicals have been shown to degrade mainly by C−C bond cleavage to give formate and alkyl esters, respectively:

$$ROCH(R')O \rightarrow ROC(O)H + R'$$

$$ROC(R')(R'')O \rightarrow ROC(O)R' + R''$$

Long-chain alkyl ethers may also degrade by a 1,5-H shift isomerization to give a $\beta$-carbonyl hydroxy ether:[54,55]

$$CH_3CH_2CH_2OCH(R)O \rightarrow CH_3CHCH_2OCH(R)OH$$

$$CH_3CHCH_2OCH(R)OH\ (+O_2/NO) \rightarrow CH_3CH(O)CH_2OCH(R)OH + NO_2$$

$$CH_3CH(O)CH_2OCH(R)OH + O_2 \rightarrow CH_3C(O)CH_2OCH(R)OH + HO_2$$

The degradation reactions of alkoxy radicals generated from diethers have been shown to be strongly structure dependent. Thus, an alkoxy radical which is in the α position relative to both ether groups reacts with $O_2$ to form a carbonate:[63,65]

$$ROCH(O)OR' + O_2 \rightarrow ROC(O)OR' + HO_2$$

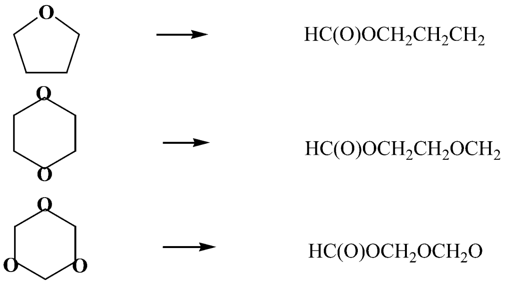
When the radical is α to one ether linkage and $\beta$ with respect to the other ether group, C−C bond fission is the major reaction channel:[65,66]

$$ROCH(O)CH_2OR' \rightarrow ROC(O)H + R'OCH_2$$

However, the $(CH_3O)_2CHOCH_2O$ radical produced by H-atom abstraction from trimethoxy methane decomposes by C−O bond fission:[67]

$$(CH_3O)_2CHOCH_2O \rightarrow (CH_3O)_2CHO + HC(O)H$$

Alkoxy radicals formed following H-atom abstraction from cyclic mono-, di-, and triethers decompose mainly by C−C or C−O bond fission, leading to ring-opening and the production of alkyl radicals containing the formate group:[69,70,72]



Carbonyl alkoxy radicals are formed directly by abstraction of the acidic hydrogen atom from carboxylic acids and are also generated from acyl radicals produced by abstraction of the aldehydic hydrogen from aldehydes or by degradation of α-carbonyl alkoxy radicals. Acyl radicals react with $O_2$ to give the corresponding peroxy acyl radicals, which form carbonyl alkoxy radicals following their reaction with $O_2$ and NO:

$$RCO + O_2 \rightarrow RC(O)O_2$$

$$RC(O)O_2 + NO \rightarrow RC(O)O + NO_2$$

The reaction of HCO with $O_2$ exhibits a different reaction pathway and reacts by H-atom transfer:

$$HCO + O_2 \rightarrow CO + HO_2$$

Carbonyl alkoxy radicals rapidly decompose to give $CO_2$ and alkyl radicals:[5]

$$RC(O)O \rightarrow R + CO_2$$

Mechanistic studies of the reactions of α-carbonyl alkoxy radicals indicate that these radicals decompose to yield an acyl radical and a carbonyl compound:[100,101]

$$RC(O)CH(O)R' \rightarrow RCO + R'C(O)H$$

Atkinson and Aschmann[103] have shown that isomerization is an important reaction channel for β-carbonyl alkoxy radicals produced by H-atom abstraction from the β-carbon atoms in ketones:

$$CH_3C(O)CH_2C(CH_3)_2O \rightarrow CH_2C(O)CH_2C(OH)(CH_3)_2$$

A number of product studies have been carried out on the OH-radical-initiated oxidation of esters.[110,111] The product distribution yields indicate that H-atom abstraction arises mainly from the alkoxy group. The dominant reaction channel for α-alkoxy ester radicals containing a hydrogen atom at the α position is a unimolecular α-ester rearrangement via a five-membered-ring transition state to give a carboxylic acid and an acyl radical:[110]

$$RC(O)OCH(R')O \rightarrow RC(O)OH + R'CO$$

Recent quantum chemical calculations on the possible reaction pathways for this rearrangement provide evidence that the reaction involves a concerted process rather than proceeding through formation of the intermediate RC(OH)OC(O)R′ radical.[152] For systems where there is no hydrogen atom at the α position, the α-alkoxy ester radical decomposes by C−C bond fission to form an acid anhydride and an alkyl radical:[107−110]

$$RC(O)OC(R')(R'')O \rightarrow RC(O)OC(O)R' + R''$$

Abstraction of a hydrogen atom from the β-carbon atom of the alkoxy group by OH radicals may be expected to lead to a β-ester rearrangement via a less strained six-membered-ring structure:

$$RC(O)OCH_2CH(R')O \rightarrow RC(O)OH + R'C(O)CH_2$$

However, this reaction appears to be unimportant, and β-alkoxy esters degrade by C−C bond cleavage:[110]

$$RC(O)OCH_2CH(R')O \rightarrow RC(O)OCH_2 + R'C(O)H$$

Ferenac et al.[152] have shown from theoretical calculations that β-ester rearrangement is unlikely since the carbonyl oxygen atom has insufficient radical character for the reaction to occur.

## 4. Atmospheric Implications

The present review shows that a significant amount of kinetic and mechanistic data on the gas-phase atmospheric oxidation of oxygenated organic compounds has recently been reported. An extensive data base is now available for alcohols, diols, monoethers, diethers, cyclic ethers, aldehydes, ketones, esters, and a range of unsaturated compounds containing oxygenated functional groups. The data base has been reviewed in this work and has been used to develop and improve existing structure−activity relationships for the kinetics of reactions of OH radicals with saturated oxygenated compounds and also in determining the degradation pathways of the intermediate alkoxy radicals generated in the oxidation of oxygenated VOCs.

A number of important general conclusions can be drawn from the available data concerning the reactivities and degradation mechanisms for oxygenated VOCs. The lifetimes of aldehydes are typically less than about 10 h, and oxidation results mainly in the production of acyl radicals, which either react to give shorter-chain aldehydes and ketones or form acylperoxynitrates. Oxidation of ketones is largely by reaction with OH radicals, resulting in lifetimes of the order of several days, and also produces acyl radicals. Alcohols have lifetimes similar to those of ketones and form aldehydes or ketones. Kinetic data suggest that ethers have residence times of less than 1 day, and oxidation leads to the formation of esters which have lifetimes about a factor of 10 longer than those of the precursor ethers. Oxidation of esters results in the production of organic acids and anhydrides. Unsaturated oxygenates rapidly degrade in the troposphere by reaction with $O_3$, OH, and $NO_3$, forming mainly carbonyl compounds. Thus, in general, the primary oxidation products of oxygenated VOCs are considerably less reactive than their parent compounds.

Photochemical trajectory models have been employed to describe the production of ozone and other oxidants from the atmospheric oxidation of a variety of VOCs.[1] Such calculations allow the derivation of ozone formation potentials, which show the relative importance of a compound in ozone formation. The detailed chemistry of the atmospheric oxidation of VOCs provides the major input into these models. Calculations have shown that oxygenated compounds such as acetone, 2-propanol, *tert*-butyl alcohol, and methyl acetate have low ozone formation potentials and hence are, for example, potential candidates for substitution of hydrocarbon and aromatic compounds as solvents in order to reduce ozone formation.

Despite the rapid progress in the understanding of the atmospheric chemistry of oxygen-containing VOCs, there are still areas of uncertainty which require further investigation. The fate of long-chain and polyfunctionalized oxygenated alkoxy radicals has received relatively little attention and may lead to isomerization reactions resulting in the production of low-vapor-pressure products. Formation of products having relatively low reactivity and low vapor pressure suggests that uptake of these species into cloudwater and formation of secondary organic aerosols is likely to be important in the atmospheric chemistry of oxygenates. An assessment of the impact of long-lived primary and secondary oxygenated compounds such as acetone on the chemistry of the upper troposphere is also required, since these compounds will provide a major source of $HO_x$ radicals and peroxyacyl nitrates in this region. Thus, investigations on the oxidation of persistent oxygenates at the low temperatures pertinent to the upper troposphere are required.

## 5. Acknowledgments

The authors are grateful for the support by the European Commission (project IALSI, EVR1-2001-40013). Thanks are due to T. Kelly for her assistance in the production of this manuscript.

## 6. References

(1) Derwent, R. G.; Jenkin, M. E.; Saunders, S. M. *Atmos. Environ.* **1996**, *30*, 181.
(2) Singh, H.; Chen, Y.; Standt, A.; Jacob, D.; Blake, D.; Heikes, B.; Snow, J. *Nature* **2001**, 1078.
(3) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69.
(4) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, Monograph 1.
(5) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, Monograph 2.
(6) Jenkin, M. E.; Saunders, S. M.; Pilling, M. J. *Atmos. Environ.* **1997**, *31*, 81.
(7) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1999**, *28*, 191.
(8) Martinez, R. D.; Buitrago, A. A.; Howel, N. W.; Hearn, C. H.; Joens, J. A. *Atmos. Environ.* **1992**, *26A*, 785.
(9) Raber, W. H.; Moortgart, G. K. *Adv. Ser. Phys. Chem.* **1996**, *3*, 318.
(10) Plum, I. C.; Sanhneza, E.; Atkinson, R.; Carter, W. P. L.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1983**, *17*, 479.
(11) Meller, R.; Moortgat, G. K. *J. Geophys. Res.* **2000**, *105*, 7089.
(12) Yujing, M.; Mellouki, A. *J. Photochem. Photobiol. A: Chem.* **2000**, *134*, 31.
(13) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437.
(14) Grosjean, E.; Grosjean, D. *J. Atmos. Chem.* **1997**, *27*, 271.
(15) Grosjean, E.; Grosjean, D. *Int. J. Chem. Kinet.* **1998**, *30*, 21.
(16) Grosjean, E.; Grosjean, D. *J. Atmos. Chem.* **1999**, *32*, 205.
(17) Atkinson, R. *J. Phys Chem. Ref. Data* **1991**, *20*, 459.
(18) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgart, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, *25A*, 1.
(19) Wallington, T. J.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1987**, *19*, 1015.
(20) Yujing, M.; Mellouki, A. *Chem. Phys. Lett.* **2001**, *333*, 63.
(21) Jiménez, E.; Gilles, M. K.; Ravishankara, A. R. *J. Photochem. Photobiol.* **2003**, *157*, 237.
(22) Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1990**, *22*, 1111.
(23) Meier, U.; Grotheer, H. H.; Just, T. *Chem. Phys. Lett.* **1984**, *106*, 97.
(24) Hägele, J.; Lorenz, K.; Rhäsa, D.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1023.
(25) Meier, U.; Grotheer, H. H.; Riekert, G.; Just, T. *Chem. Phys. Lett.* **1985**, *115*, 221.
(26) Azad, K.; Andino, J. M. *Int. J. Chem. Kinet.* **1999**, *31*, 810.
(27) Cavalli, F.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2000**, *34*, 4111.
(28) Cavalli, F.; Geiger, H.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2002**, *36*, 1263.
(29) Baxley, J. S.; Wells, J. R. *Int. J. Chem. Kinet.* **1998**, *30*, 745.
(30) Grosjean, D. *J. Braz. Chem. Soc.* **1997**, *8*, 433.
(31) Japar, S. M.; Wallington, T. J.; Richert, J. F. O.; Ball, J. C. *Int. J. Chem. Kinet.* **1990**, *22*, 1257.
(32) Atkinson, R.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 528.
(33) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1998**, *30*, 533.
(34) Neavyn, R.; Sidebottom, H.; Treacy, J. EUROTRAC Symposium, 1994; p 105.
(35) Bethel, H. L.; Atkinson, R.; Arey, J. *Int. J. Chem. Kinet.* **2001**, *33*, 310.
(36) Magneron, I.; Bossoutrot, V.; Mellouki, A.; Laverdet, G.; Le Bras, G. *Environ. Sci. Technol.* **2003**, *37*, 4170.
(37) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.
(38) Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **1994**, *26*, 367.
(39) Langer, S.; Ljungström, E. *J. Phys. Chem.* **1994**, *98*, 5906.
(40) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley & Sons: New York, 1966.
(41) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.
(42) Wallington, T. J.; Liu, R.; Dagaut, P.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 41.
(43) Mellouki, A.; Téton, S.; Le Bras, G. *Int. J. Chem. Kinet.* **1995**, *27*, 791.
(44) Porter, E.; Wenger, J.; Treacy, J.; Sidebottom, H.; Mellouki, A.; Téton, S.; Le Bras, G. *J. Phys. Chem. A* **1997**, *101*, 5770.
(45) Smith, I. W. M.; Ravishankara, A. R. *J. Phys. Chem. A* **2002**, *106*, 4798.
(46) Moriaty, J.; Sidebottom, H.; Wenger, J.; Mellouki, A.; Le Bras, G. *J. Phys. Chem. A* **2003**, *107*, 1499.
(47) Téton, S.; Mellouki, A.; Le Bras, G.; Sidebottom, H. *Int. J. Chem. Kinet.* **1996**, *28*, 291.
(48) Le Calvé, S.; Le Bras, G.; Mellouki, A. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5622.
(49) Jenkin, M. E.; Hayman, G. D.; Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Nielsen, O. J.; Ellermann, T. J. *J. Phys. Chem.* **1993**, *97*, 11723.
(50) Sehested, J.; Mogelberg, T.; Wallington, T. J.; Kaiser, E. W.; Nielsen, O. J. *J. Phys. Chem. A* **1996**, *100*, 17218.
(51) Wallington, T. J.; Japar, S. M. *Environ. Sci. Technol.* **1991**, *25*, 410.
(52) Eberhard, J.; Müller, C.; Stocker, D. W.; Kaiser, E. W. *Int. J. Chem. Kinet.* **1993**, *25*, 639.
(53) Sempeles, J.; Andino, J. M. *Int. J. Chem. Kinet.* **2000**, *32*, 703.
(54) Johnson, D.; Andino, J. M. *Int. J. Chem. Kinet.* **2001**, *33*, 328.

(55) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *31*, 501.
(56) Tuazon, E. C.; Carter, W. P. L.; Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1991**, *23*, 1003.
(57) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1991**, *23*, 907.
(58) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1992**, *24*, 199.
(59) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int. J. Chem. Kinet.* **1995**, *27*, 453.
(60) Wallington, T. J.; Andino, J. M.; Potts, A. R.; Rudy, S. J.; Siegl, W. O. *Environ. Sci. Technol.* **1993**, *27*, 98.
(61) Wenger, J.; Collins, E.; Sidebottom, H.; Le Calvé, S.; Mellouki, A.; Le Bras, G.; Wirtz, K. The US/German Environmental Chamber Workshop, Riverside, CA, 1999.
(62) Langer, S.; Ljungström, E.; Wängberg, I.; Wallington, T. J.; Hurley, M. D.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1996**, *28*, 299.
(63) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Straccia, A. M.; Platz, J.; Christensen, L. K.; Sehested, J.; Nielsen, O. J. *J. Phys. Chem. A* **1997**, *101*, 5302.
(64) Thüner, L. P.; Barnes, I.; Maurer, T.; Sauer, C. G.; Becker, K. H. *Int. J. Chem. Kinet.* **1999**, *31*, 797.
(65) Wenger, J.; Porter, E.; Collins, E.; Treacy, J.; Sidebottom, H. *Chemosphere* **1999**, *38*, 1197.
(66) Geiger, H.; Becker, K. H. *Atmos. Environ.* **1999**, *33*, 2883.
(67) Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 2632.
(68) Dagaut, P.; Liu, R.; Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* **1990**, *94*, 1881.
(69) Platz, J.; Christensen, L. K.; Sehested, J.; Nielsen, O. J.; Wallington, T. J.; Sauer, C. G.; Barnes, I.; Becker, K. H.; Vogt, R. *J. Phys. Chem. A* **1998**, *102*, 4829.
(70) Maurer, T.; Hass, H.; Barnes, I.; Becker, K. H. *J. Phys. Chem. A* **1999**, *103*, 5032.
(71) Moriaty, J. Ph,D, thesis, University College Dublin, 2000.
(72) Sauer, C. G.; Barnes, I.; Becker, K. H.; Geiger, H.; Wallington, T. J.; Christensen, L. K.; Platz, J.; Nielsen, O. J. *J. Phys. Chem. A* **1999**, *103*, 5959.
(73) Cabanas, B.; Martin, P.; Salgado, S.; Ballesteros, B.; Martinez, E. *J. Atmos. Chem.* **2001**, *40*, 23.
(74) Papagni, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2000**, *32*, 79.
(75) D'Anna, B.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3479.
(76) Noda, J.; Holm, C.; Nyman, G.; Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **2003**, *35*, 120.
(77) Moortgat, G. K.; Wirtz, K.; Hjorth, J.; Ljungström, E.; Ruppert, L.; Hayman, G.; Mellouki, A. Evaluation of Radical Sources in Atmospheric Chemistry through Chamber and Laboratory Studies (RADICAL), EU Report, 2002.
(78) Semmes, D. H.; Ravishankara, A. R.; Gump-Perkins, C. A.; Wine, P. H. *Int. J. Chem. Kinet.* **1985**, *17*, 303.
(79) Thévenet, R.; Mellouki, A.; Le Bras, G. *Int. J. Chem. Kinet.* **2000**, *32*, 676.
(80) Tyndall, G. S.; Orlando, J. J.; Wallington, T.; Hurley, M. D.; Goto, M.; Kawasaki, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2189.
(81) Cameron, M.; Sivakumaram, V.; Dillon, T. J.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3628.
(82) Sivakumaram, V.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2003**, *5*, 106.
(83) Vandenberk, S.; Peeters, J. *J. Photochem. Photobiol.* **2003**, *157*, 269.
(84) Dobé, S.; Khachatryan, L. A.; Bérces, T. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 847.
(85) Alvarez-Idaboy, J. R.; Mora-Diez, N.; Boyd, R. J.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2001**, *123*, 2018.
(86) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **2000**, *104*, 3211.
(87) Niki, H.; Maker, P. D.; Savage, C. M.; Hurley, M. D. *J. Phys. Chem.* **1987**, *91*, 2174.
(88) Gierczak, T.; Burkholder, J. B.; Bauerle, S.; Ravishankara, A. R. *Chem. Phys. Lett.* **1998**, *213*, 229.
(89) Notario, A.; Mellouki, A.; Le Bras, G. *Int. J. Chem. Kinet.* **2000**, *32*, 62.
(90) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1982**, *14*, 839.
(91) Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* **1987**, *91*, 5050.
(92) Le Calvé, S.; Hitier, D.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1998**, *102*, 4579.
(93) Atkinson, R.; Aschmann, S. M. *J. Phys. Chem. A* **1988**, *92*, 4008.
(94) Vandenberk, S.; Vereecken, L.; Peeters, J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 461.
(95) Vasvári, V.; Szilagyi, I.; Beucsisra, A.; Dobé, S.; Bercès, T.; Henon, E.; Canneaux, S.; Bohr, F. *Phys. Chem. Chem. Phys.* **2001**, *3*, 551.
(96) Wollenhaupt, M.; Carl, S. A.; Horowitz, A.; Crowley, J. N. *J. Phys. Chem. A* **2000**, *104*, 2695.
(97) Gierczak, T.; Gilles, M. K.; Bauerle, S.; Ravishankara, A. R. *J. Phys. Chem. A* **2003**, *107*, 5014.
(98) Wollenhaupt, M.; Crowley, J. N. *J. Phys. Chem. A* **2000**, *104*, 6429.
(99) Talukdar, R. K.; Gierczak, T.; McCabe, D. C.; Ravishankara, A. R. *J. Phys. Chem. A* **2003**, *107*, 5021.
(100) Orlando, J. J.; Tyndall, G. S.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2000**, *104*, 11578.
(101) Cox, R. A.; Patrick, K. F.; Chant, S. A. *Environ. Sci. Technol.* **1981**, *15*, 587.
(102) Thévenet, R. Ph.D. Thesis, University of Orléans, 2000.
(103) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1995**, *27*, 261.
(104) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 177.
(105) El Boudali, A.; Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem.* **1996**, *100*, 12364.
(106) Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1997**, *101*, 5489.
(107) Christensen, L. K.; Ball, J. C.; Wallington, T. *J. Phys. Chem. A* **2000**, *104*, 345.
(108) O'Donnell, S. M., Ph.D. Thesis, University College Dublin, 1999.
(109) Wallington, T. J.; Hurley, M. D.; Maurer, T.; Barnes, I.; Becker, K. H.; Tyndall, G. S.; Orlando, J. J.; Pimentel, A. S.; Bilde, M. *J. Phys. Chem. A* **2001**, *105*, 5146.
(110) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Carter, W. P. L. *J. Phys. Chem. A* **1998**, *102*, 2316.
(111) Picquet-Varrault, B.; Doussin, J.-F.; Durand-Jolibois, R.; Carlier, P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2595.
(112) Kerr, J. A.; Stocker, D. W. *J. Atmos. Chem.* **1986**, *4*, 263.
(113) Picquet-Varrault, B.; Doussin, J.-F.; Durand-Jolibois, R.; Carlier, P. *J. Phys. Chem. A* **2002**, *106*, 2895.
(114) Veillerot, M.; Foster, P.; Guillermo, R.; Galloo, J. C. *Int. J. Chem. Kinet.* **1996**, *28*, 235.
(115) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Int. J. Chem. Kinet.* **1993**, *25*, 783.
(116) Fantechi, G.; Jensen, N. R.; Hjorth, J.; Peeters, J. *Int. J. Chem. Kinet.* **1998**, *30*, 589.
(117) Papagni, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2001**, *33*, 142.
(118) Le Calvé, S.; Mellouki, A.; Le Bras, G.; Treacy, J.; Wenger, J.; Sidebottom, H. *J. Atmos. Chem.* **2000**, *37*, 161.
(119) Orlando, J. J.; Tyndall, G. S.; Ceazan, N. *J. Phys. Chem. A* **2001**, *105*, 3564.
(120) Gierczak, T.; Burkholder, J. B.; Talukdar, R. K.; Mellouki, A.; Barone, S. B.; Ravishankara, A. R. *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 1.
(121) Thiault, G.; Thévenet, R.; Mellouki, A.; Le Bras, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 613.
(122) Magneron, I.; Thévenet, R.; Mellouki, A.; Le Bras, G.; Moortgat, G. K.; Wirtz, K. *J. Phys. Chem.* **2002**, *106*, 2526.
(123) Perry, R. A.; Atkinson, R.; Pitts, J. N., Jr. *J. Phys. Chem.* **1977**, *81*, 1607.
(124) Thiault, G. Ph.D. thesis, University of Paris 7, 2002.
(125) Orlando, J. J.; Tyndall, G. S. *J. Phys. Chem. A* **2002**, *51*, 12252.
(126) Orlando, J. J.; Tyndall, G. S.; Paulson, S. E. *Geophys. Res. Lett.* **1999**, *26*, 2191.
(127) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1990**, *22*, 591.
(128) Atkinson, R.; Arey, J.; Aschmann, S. M.; Corchnoy, S. B.; Shu, Y. *Int. J. Chem. Kinet.* **1995**, *27*, 941.
(129) Williams, D. C.; O'Rji, L. N.; Stone, D. A. *Int. J. Chem. Kinet.* **1993**, *25*, 539.
(130) Rudich, Y.; Talukdar, R. K.; Fox, R. W.; Ravishankara, A. R. *J. Phys. Chem.* **1996**, *100*, 5374.
(131) Kwok, E. S. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **1996**, *28*, 925.
(132) Atkinson, R. *Int. J. Chem. Kinet.* **1987**, *19*, 799.
(133) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 541.
(134) Wallington, T. J.; Andino, J. M.; Skewes, L. M.; Siegl, W. O.; Japar, S. M. *Int. J. Chem. Kinet.* **1989**, *21*, 993.
(135) Samadeni, M.; Stocker, D. W.; Kerr, J. A. *J. Atmos. Chem.* **1993**, *16*, 79.
(136) Dagaut, P.; Wallington, T. J.; Liu, R.; Kurylo, M. J. *J. Phys. Chem.* **1988**, *92*, 4375.
(137) Wallington, T.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 177.
(138) Le Calvé, S.; Le Bras, G.; Mellouki, A. *Int. J. Chem. Kinet.* **1997**, *29*, 683.
(139) Kerr, J. A.; Sheppard, D. W. *Environ. Sci. Technol.* **1981**, *15*, 960.
(140) Huie, R.; Clifton, C.; Karafi, S. *J. Phys. Chem.* **1991**, *95*, 9336.
(141) Dagaut, P.; Liu, R.; Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* **1989**, *93*, 7838.
(142) Atkinson, R. *Int. J. Chem. Kinet.* **1997**, *29*, 99.
(143) Atkinson, R.; Carter, W. P. L. *J. Atmos. Chem.* **1991**, *13*, 195.
(144) Carter, W. P. L.; Atkinson, R. *J. Atmos. Chem.* **1985**, *3*, 377.
(145) Atkinson, R. *J. Atmos. Chem.* **1990**, *244*, 1.
(146) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Henry, D. G. *J. Phys. Chem.* **1997**, *81*, 22483.
(147) Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1999**, *103*, 1768.

(148) Méreau, R.; Rayez, M. T.; Caralp, F.; Rayez, J. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1919.
(149) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1899.
(150) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1907.
(151) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4319.
(152) Ferenac, M. A.; Davis, A. J.; Holloway, A. S.; Dibble, T. S. *J. Phys. Chem. A* **2003**, *107*, 63.
(153) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1978**, *82*, 135.
(154) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C. J.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.
(155) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1981**, *80*, 499.
(156) Barnes, I.; Becker, K. H.; Ruppert, L. *Chem. Phys. Lett.* **1993**, *203*, 295.
(157) Barnes, I.; Bastian, V.; Becker, K. H.; Tong, Z. *J. Phys. Chem.* **1990**, *94*, 2413.
(158) Hjorth, J.; Lohse, C.; Nielsen, C. J.; Skov, H.; Restelli, G. *J. Phys. Chem.* **1990**, *94*, 7494.
(159) Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1997**, *101*, 9137.
(160) Mellouki, A., personal communication.
(161) Stemmler, K.; Mengon, W.; Kerr, J. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2865.

CR020526X