

Gas-phase degradation of organic compounds in the troposphere

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Abstract: The present status of knowledge of the gas-phase reactions of selected classes of volatile non-methane organic compounds (NMOCs) [alkanes, alkenes, aromatic hydrocarbons, oxygen-containing NMOCs and nitrogen-containing NMOCs] and their degradation products in the troposphere is briefly discussed. In the troposphere, NMOCs can undergo photolysis, reaction with the hydroxyl (OH) radical during daylight hours, reaction with the nitrate (NO₃) radical (primarily during nighttime), reaction with ozone (O₃), and, in certain situations, reaction with the chlorine (Cl) atom. The kinetics and mechanisms of the initial OH radical, NO₃ radical and O₃ reactions are reasonably well understood. However, the subsequent reactions of the organic radicals formed after the initial OH radical, NO₃ radical and O₃ reactions are in many cases much less well understood, and photolysis of NMOCs under tropospheric conditions is in general a poorly understood area. In the tropospheric degradations of NMOCs, the important intermediate radicals are alkyl or substituted alkyl radicals (\dot{R}), alkyl peroxy or substituted alkyl peroxy radicals ($R\dot{O}_2$), and alkoxy or substituted alkoxy radicals ($R\dot{O}$). While much progress has been made in elucidating the reactions of organic peroxy and alkoxy radicals, the mechanisms of the gas-phase reactions of O₃ with alkenes, and the mechanisms and products of the OH radical-initiated reactions of aromatic hydrocarbons, there are still areas of uncertainty which impact the ability to accurately model the tropospheric degradations of NMOCs and to predict the products formed. These will be discussed.

INTRODUCTION

Large quantities of non-methane organic compounds (NMOC), including isoprene (2-methyl-1,3-butadiene), a series of C₁₀H₁₆ monoterpenes, C₁₅H₂₄ sesquiterpenes, and oxygenated NMOCs (including methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, and linalool) are emitted into the troposphere from vegetation (ref. 1). NMOC are also emitted into the troposphere from a variety of anthropogenic sources, including combustion sources (vehicle and fossil-fueled power plant emissions), fuel storage and transport, solvent usage, emissions from industrial operations, landfills, and hazardous waste facilities. Literature estimates of the U.S.A. and world-wide emissions of NMOC are 20 and 60-140 million tons per year, respectively, from anthropogenic sources and 30 and 1150 million tons per year, respectively, from biogenic sources (ref. 1-4).

Organic compounds present in the atmosphere are partitioned between the gas and particle phases (ref. 5,6), and the phase in which a chemical exists in the atmosphere can significantly influence its dominant tropospheric removal process(es) and lifetime (ref. 6). Gas/particle partitioning depends on the liquid-phase (or sub-cooled liquid-phase) vapor pressure, P_L , at the ambient atmospheric temperature, the surface area of the particles per unit volume of air, θ , and the nature of the particles and of the chemical being adsorbed. The

fraction of the chemical present in the particle phase, ϕ , depends on these parameters as shown in Equation (I) (ref. 5,6),

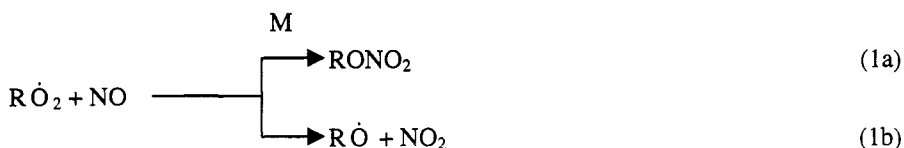
$$\phi = c6/(c6 + P_L) \quad (I)$$

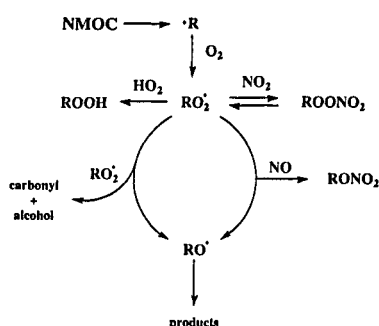
where c is a parameter which depends on the chemical being adsorbed and on the nature of the particle. To a first approximation, chemical compounds with liquid-phase vapor pressures of $P_L < 10^{-6}$ Pa at the ambient atmospheric temperature are present in the particle phase, and those with values of $P_L > 1$ Pa at the ambient atmospheric temperature exist essentially totally in the gas-phase (ref. 6). Chemicals with intermediate values of P_L are present in both the gas and particle phases.

In the troposphere, NMOCs (and their reaction products) are removed by the physical processes of wet and dry deposition (which are not discussed here), and are degraded by the chemical processes of photolysis, reaction with hydroxyl (OH) radicals, reaction with nitrate (NO₃) radicals and reaction with O₃ (ref. 2,7,8). Additionally, reactions of Cl atoms with alkanes and other NMOCs have been observed in the lower Arctic troposphere during springtime (ref. 9,10), and it is possible that similar occurrences occur in other localities (ref. 11). Assessments of the impact of Cl atom-initiated removal of organic compounds in the global troposphere (ref. 12,13) and in the global marine boundary layer (ref. 14) indicate that Cl atom chemistry plays, at most, a minor role and hence Cl atom reactions are not discussed here.

PRODUCTS AND MECHANISMS OF THE TROPOSPHERIC REACTIONS OF NMOCs

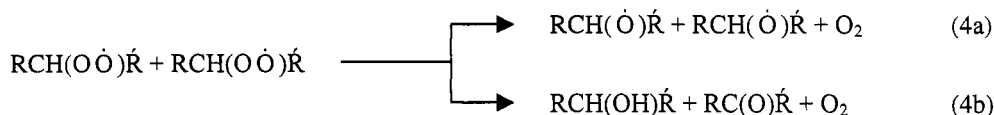
The atmospheric chemistry of the various classes of NMOCs were discussed by the National Research Council (ref. 2) and recent reviews and evaluations of various aspects of NMOC tropospheric chemistry have been published within the past few years (ref. 7,8,15,16). Photolysis and the initial reactions of many NMOCs with OH radicals and NO₃ radicals lead to the formation of alkyl or substituted alkyl (\dot{R}) radicals, and the reactions of O₃ with alkenes and other NMOCs containing $>C=C<$ bonds lead to the formation of organic peroxy ($R\dot{O}_2$) radicals. The degradation/transformation reactions of NMOCs which occur in the troposphere can therefore to a first approximation be represented by Reaction Scheme 1, with the important intermediate radicals being alkyl or substituted alkyl radicals (\dot{R}), alkyl peroxy or substituted alkyl peroxy radicals ($R\dot{O}_2$), and alkoxy or substituted alkoxy radicals ($R\dot{O}$). However, there are reactions which lead to product species whose subsequent reactions are unique and differ from those of \dot{R} , $R\dot{O}_2$ and $R\dot{O}$ radicals formed from alkanes, alkenes and other NMOCs. These include the formation of biradicals from the O₃ reactions with alkenes, and the formation of hydroxycyclohexadienyl or substituted hydroxycyclohexadienyl radicals from the OH radical reactions with aromatic hydrocarbons, and these are discussed below. As evident from Reaction Scheme 1, the tropospheric reactions of NMOCs share many reaction sequences in common, and certain areas of uncertainty which affect the products formed are also common to almost all NMOCs. These areas of uncertainty include those involving the reactions of $R\dot{O}_2$ and $R\dot{O}$ radicals, as discussed below.





Reaction Scheme 1

Reactions of Organic Peroxy Radicals. As shown in Reaction Scheme 1, organic peroxy radicals react with NO, NO₂, HO₂ radicals and organic peroxy radicals.



Alkyl peroxy nitrates thermally decompose rapidly back to reactants at around room temperature (ref. 15,16), and hence the $\text{RO}_2 + \text{NO}_2$ reaction is unimportant in the lower troposphere for $\text{R} = \text{alkyl}$ or substituted alkyl (but not for $\text{R} = \text{acyl}$). In the troposphere, important reactions of RO_2 radicals are with NO and HO₂ radicals, and the competition between these reactions determines whether net O₃ formation or net O₃ destruction occurs. Kinetic and product data for RO_2 radical reactions with NO and with the HO₂ radical are available mainly for alkyl peroxy radicals formed from alkanes (ref. 15,17), and kinetic and product data for the reactions of a wide variety of organic peroxy radicals with NO and HO₂ radicals are needed. Organic peroxy radicals also react with NO₃ radicals (ref. 16), and this reaction pathway can be important during nighttime (ref. 18).

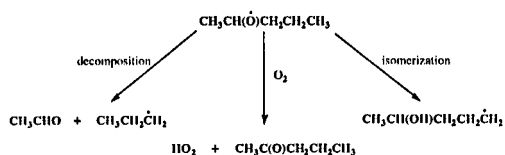


It should be noted that for the reactions of NMOC with the NO₃ radical, NO will be at low concentrations (due to the rapid reaction of NO with the NO₃ radical and with O₃). Nitrooxyalkyl peroxy radicals are therefore expected to react primarily with NO₂, to form thermally unstable peroxy nitrates such as $\text{CH}_3\text{CH}(\text{OONO}_2)\text{CH}_2\text{ONO}_2$, and HO₂ and NO₃ radicals, with self-reactions of nitrooxyalkyl peroxy radicals or combination reactions with other peroxy radicals being important in laboratory studies.

Organic Nitrate Formation. Organic nitrates (RONO₂) are formed in one channel [reaction (1a)] of the reaction of organic peroxy radicals with NO. Accurate knowledge of the formation yields of organic nitrates from the $\text{RO}_2 + \text{NO}$ reactions is crucial for accurate predictions of ozone formation in "smog" chambers as well as in the ambient atmosphere. The formation yields of organic nitrates are significantly temperature and pressure dependent, decreasing with increasing temperature and with decreasing pressure (ref. 7,15,17). To date, experimentally measured organic nitrate formation yield data are available only for secondary alkyl peroxy radicals formed from the NO_x-air photooxidations of C₂-C₈ *n*-alkanes and for a few other alkyl and β-hydroxyalkyl peroxy radicals formed from alkanes and alkenes (ref.

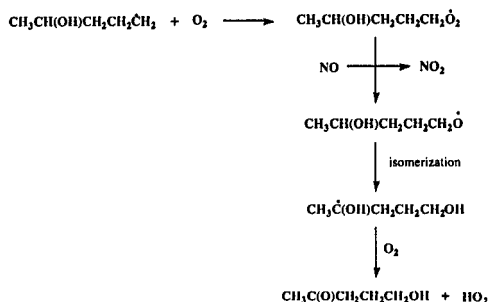
7,15,17). Additional yield data are needed for organic nitrates formed from the wide variety of organic compounds observed in ambient air.

Reactions of Alkoxy Radicals. As shown in Reaction Scheme 1, alkoxy radicals are formed as intermediates during the tropospheric degradations of NMOCs. The subsequent reactions of alkoxy radicals determine the products formed (and, in the presence of NO, the amounts of O₃ formed). In the troposphere, alkoxy radicals can react with O₂, unimolecularly decompose by C-C bond scission, or isomerize by a 1,5-H shift through a 6-membered transition state (ref. 15,19). Taking the 2-pentoxy radical formed from the OH radical reaction with *n*-pentane in the presence of NO as an example, these reactions are shown in Reaction Scheme 2.



Reaction Scheme 2

The alkyl and δ -hydroxyalkyl radicals formed from the decomposition and isomerization pathways, respectively, react further by reaction schemes analogous to those shown in Reaction Scheme 1. For example, the subsequent reactions of the CH₃CH(OH)CH₂CH₂H₂ radical formed by isomerization of the 2-pentoxy radical (Reaction Scheme 2) in the presence of NO lead to formation of 5-hydroxy-2-pentanone, as shown in Reaction Scheme 3.

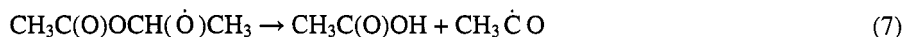


Reaction Scheme 3

Reactions of α -hydroxyalkyl radicals such as CH₃Ċ(OH)CH₂CH₂CH₂OH (which are also formed by H-atom abstraction from the C-H bonds of >CHOH and -CH₂OH groups in alcohols) with O₂ lead to the carbonyl plus the HO₂ radical (ref. 7,15).

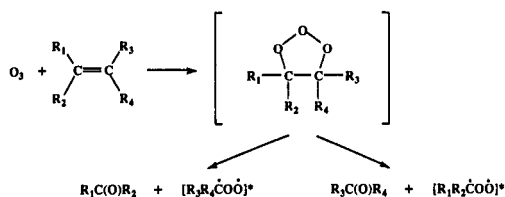


In addition, Tuazon *et al.* (ref. 20) have shown that alkoxy radicals of structure RC(O)OCH($\dot{\text{O}}$)R formed from the OH radical-initiated reactions of certain esters react via a novel rearrangement proceeding through a 5-membered transition state. For example:



The products formed from alkoxy radicals therefore depend on the reaction pathway occurring. There is now a semi-quantitative (or better) understanding of the tropospheric reactions of alkoxy radicals formed from alkanes and of β -hydroxyalkoxy radicals formed from the OH radical-initiated reactions of alkenes (ref. 15,19), and this understanding appears to hold for substituted alkoxy radicals formed from certain other classes of NMOCs (ref. 21,22). However, we do not have such a quantitative or even semi-quantitative understanding

of the reactions of alkoxy radicals of structure $>C(\dot{O})OR$ ($R = \text{alkyl}$) formed from ethers and glycol ethers, nor do we have a quantitative or semi-quantitative understanding of the reactions of alkoxy radicals of structure $-C(O)CH(\dot{O})R$ ($R = \text{alkyl}$) formed from esters. This may also be the case for alkoxy radicals containing other structural features.



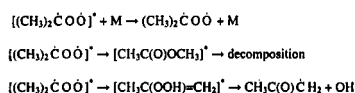
Reaction Scheme 4

In addition to reaction with O_2 , decomposition by C-C bond scission and isomerization through a 6-membered transition state, halogenated alkoxy radicals formed from haloalkanes and haloalkenes can also decompose by elimination of a Cl or Br atom (ref. 4). For example, for the $CH_3CH_2CH_2CH(\dot{O})Br$ radical formed after H-atom abstraction from the 1-position of 1-bromobutane.



The above generalized reactions hold for alkanes, for the OH and NO_3 radical-initiated reactions of alkenes and of certain NMOC containing $>C=C<$ bonds, and for the OH radical-initiated reactions of many oxygenated NMOC. However, as noted above, the reaction mechanisms of the reactions of O_3 with alkenes and NMOC containing $>C=C<$ bonds and of the OH radical with aromatic hydrocarbons are significantly different (ref. 7,15), and these reaction systems are briefly discussed below.

Reactions of Alkenes and NMOC containing $>C=C<$ bonds with O_3 . O_3 initially adds to the $>C=C<$ bond to form an energy-rich primary ozonide, which rapidly decomposes as shown in Reaction Scheme 4 to form two sets of (carbonyl + biradical), where $[]^*$ denotes an energy-rich species (ref. 15). Recent studies have shown that the relative importance of the two decomposition pathways of the primary ozone to form the two (carbonyl plus biradical) products depends on the structure of the alkene (ref. 15). The fate of the initially energy-rich biradicals is presently not well understood. The biradicals can be collisionally stabilized or decompose by a number of pathways, as shown in Reaction Scheme 5 for the $[(CH_3)_2\dot{C}OO]^*$ biradical.

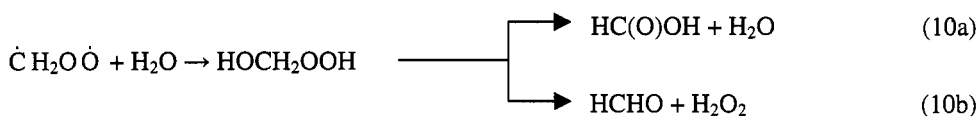


Reaction Scheme 5

The isomerization/decomposition reactions of the "energy-rich" biradicals include the "ester channel" and the "hydroperoxide" channel, as shown in Reaction Scheme 5. $O(^3P)$ atom elimination has not been observed for alkenes at room temperature and atmospheric pressure of air (ref. 15) and the evidence for the occurrence of the "ester" channel involves the elimination of CO_2 and the formation of an RH product from biradicals of the structure $[R\dot{C}HO]^*$. However, OH radicals are formed from the reactions of O_3 with alkenes, often in unit or close to unit yield (ref. 15,23). For acyclic alkenes and cycloalkenes not containing terminal $=CH_2$ groups, OH radical formation generally increases with the number of alkyl substituent groups or, equivalently, with the number of alkyl substituents on the biradicals.

This formation of OH radicals from the reactions of O₃ with alkenes leads to secondary reactions of the OH radical with the alkene and, unless the OH radicals are scavenged, the O₃ reaction involves OH radical reactions and hence the products observed and their yields may not be those for the O₃ reactions. The formation of OH radicals is postulated to occur via the "hydroperoxide" channel (ref. 15,24), as shown in Reaction Scheme 5. Assuming that the OH radicals observed to be formed in these reactions arise via the hydroperoxide channel, then the organic co-product radicals [for example, the CH₃C(O)ĊH₂ radical formed together with the OH radical from the [(CH₃)₂ĊOO]^{*} biradical in reaction (10)] will react as described in Reaction Scheme 1, leading to a variety of carbonyl, hydroxycarbonyl and hydroperoxycarbonyl products (ref. 15,24). To date, these reactions have not been quantitatively elucidated for any biradical. While there have been significant (and largely qualitative or semi-quantitative) advances in our knowledge of the isomerization and/or decomposition reactions of the energy-rich biradicals over the past few years, there is still a need to quantitatively elucidate these reactions.

The other important aspect of the reactions of O₃ with alkenes concerns the reactions of the thermalized biradicals in the troposphere. The thermalized biradicals are known to react with aldehydes, SO₂, CO, H₂O and NO₂ (ref. 15,16), and it is expected that they will also react with NO. Based on the available data for the reactions of the ĊH₂OĊ biradical with these reactants, it appears that the reaction of the thermalized ĊH₂OĊ biradical with water vapor will be its dominant loss process under tropospheric conditions, and it may be assumed to be the case for biradicals in general. The reaction of the ĊH₂OĊ biradical with water vapor proceeds by initial formation of hydroxymethyl hydroperoxide [HOCH₂OOH], which can decompose (probably heterogeneously) to either HC(O)OH + H₂O or, less likely, to HCHO + H₂O₂ (ref. 25).



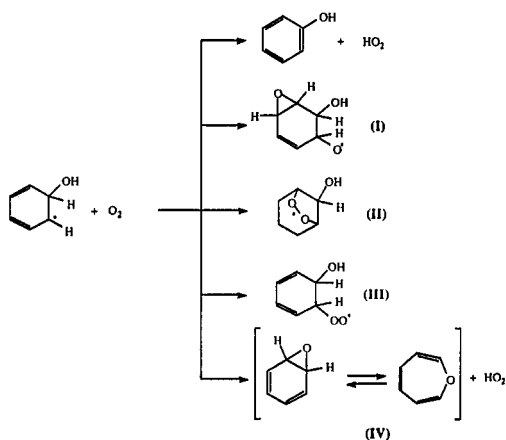
The reactions of biradicals of structure RĊHOĊ and RRĊOOĊ with water vapor have not been directly studied to date, and it is possible that the formation of the carbonyl plus H₂O₂ is important, or even dominant, for mono- and di-substituted biradicals (ref. 26). In laboratory systems, other reaction pathways of the thermalized biradicals can be important and may need to be considered (ref. 15,24,27-29).

Aromatic Hydrocarbons. Benzene and the alkyl-substituted benzenes such as toluene, ethylbenzene, the xylenes, and the trimethylbenzenes react with OH radicals and NO₃ radicals (ref. 7,30,31), with the OH radical reactions dominating as the tropospheric removal process. The OH radical reactions proceed by H-atom abstraction from the C-H bonds of the alkyl substituent groups (or from the C-H bonds of the aromatic ring in the case of benzene), and by OH radical addition to the aromatic ring to form a hydroxycyclohexadienyl or alkyl-substituted hydroxycyclohexadienyl radical (OH-aromatic adduct) (ref. 7,30). The H-atom abstraction pathway accounts for ≤ 10 % of the overall OH radical reactions with benzene and the methyl-substituted benzenes at room temperature and atmospheric pressure (ref. 7). The tropospheric reactions of the benzyl and alkyl-substituted benzyl radicals formed from the pathway involving H-atom abstraction from the alkyl-substituent groups are analogous to those for alkyl radicals discussed above (ref. 7).

The major reaction pathway involves the formation of the OH-aromatic adduct(s). The reactions of the OH-benzene, OH-toluene and OH-xylene adducts with NO, NO₂, and O₂ have been studied by several groups (ref. 7,32-34). Reactions with NO have not been observed (ref. 32,35). However, reactions of the OH-benzene, OH-toluene and OH-xylene adducts with O₂ and NO₂ are observed (ref. 7,32,35), and the kinetic data show that in the lower troposphere, including polluted urban airmasses, the dominant reaction of OH-aromatic adducts is with O₂. The uncertainty in the tropospheric degradation mechanism of aromatic

hydrocarbons concerns the products and mechanisms of the reactions of the OH-aromatic adducts with NO_2 and, especially, O_2 . Reaction Scheme 6 shows postulated reactions of the OH-benzene adduct with O_2 , leading to phenol, an epoxide-alkoxy radical (I), a bicycloalkyl radical (II), a peroxy radical (III), and benzene oxide/oxepin (IV) (ref. 36-38).

The potential subsequent reactions of the species (I) through (IV) lead to the formation of ring-opened unsaturated carbonyls, dicarbonyls and epoxy-carbonyls. Product studies carried out to date under simulated atmospheric conditions for benzene, toluene, and the xylenes generally account for only ~30-50 % of the reaction products (ref. 7), which



Reaction Scheme 6

include phenolic compounds and ring-opened dicarbonyls (ref. 7,39). 3-Hexene-2,5-dione, the expected co-product to the α -dicarbonyl glyoxal, has been reported as a product of the OH radical-initiated reactions of *p*-xylene and 1,2,4-trimethylbenzene (ref. 7,39,40). The formation of other ring-opened unsaturated carbonyls have been reported (ref. 7,39-42), although no quantitative yield data have been published to date. The unsaturated 1,4-dicarbonyls and di-unsaturated 1,6-dicarbonyls formed from aromatic hydrocarbons are highly reactive (ref. 7,39,43,44). Mechanistic and product data (and especially quantitative data for the formation yields of the various potential unsaturated dicarbonyls and unsaturated epoxy-carbonyls) are needed to elucidate the reactions of the OH-aromatic adducts with O_2 and NO_2 , and to determine the first-generation products whose tropospheric chemistry then need to be studied.

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