

Product studies of gas-phase reactions of organic compounds

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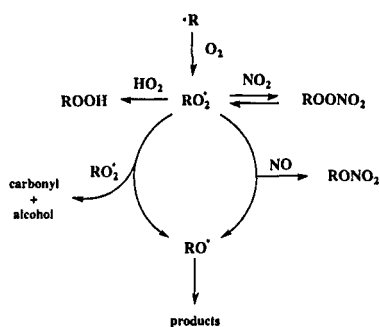
Abstract: Large quantities of volatile non-methane organic compounds (NMOCs) are emitted into the atmosphere from anthropogenic and biogenic sources. In the troposphere, these NMOCs can undergo photolysis, reaction with the hydroxyl (OH) radical, reaction with the nitrate (NO₃) radical, and reaction with ozone (O₃). While the kinetics of the initial OH radical, NO₃ radical and O₃ reactions are reasonably well known or can often be estimated with some degree of reliability, the subsequent reaction mechanisms and the products formed under tropospheric conditions are generally much less well understood. The various methods of generation of OH radicals, NO₃ radicals and O₃ for laboratory product studies, together with methods of analysis and potential complications due to other reactions, are discussed.

INTRODUCTION

Large quantities of volatile non-methane organic compounds (NMOCs) are emitted into the atmosphere from anthropogenic and biogenic sources, with the world-wide emissions being estimated to be 100 million tons per year from anthropogenic sources (ref. 1) and 1150 million tons per year from biogenic sources (ref. 2). In the troposphere in the gas phase, these NMOCs can undergo photolysis at wavelengths >290 nm, react with the hydroxyl (OH) radical, react with the nitrate (NO₃) radical (primarily during nighttime hours), and react with ozone (O₃) (ref. 3,4). In addition, at certain times and locations reaction with the Cl atom can be important (ref. 5) and certain basic nitrogen-containing NMOCs (for example, amines) can react with gaseous nitric acid to form the corresponding nitrate salts (see, for example, ref. 6). As a result of some three decades of research, rate constants for the gas-phase reactions of a large number of NMOCs with OH radicals, NO₃ radicals and O₃ have been measured (ref. 3,7-10), and methods (of varying reliability depending on the structure of the NMOC) are available for the estimation of rate constants for NMOCs for which experimental data have not been obtained (ref. 7,9,11,12).

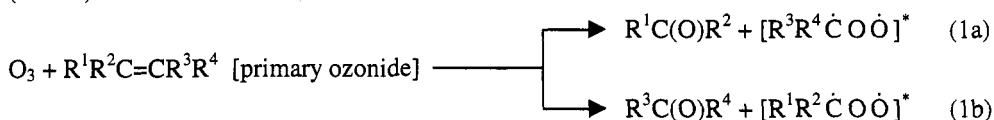
However, while the kinetics and mechanisms of the initial reactions of OH radicals, NO₃ radicals and O₃ with many NMOC are understood, the products and mechanisms of the subsequent reactions of the initially-formed radicals are much less well understood. A knowledge of the products and mechanisms of the tropospheric degradation reactions of NMOC is necessary to understand the impact of emissions of NMOC on the Earth's ecosystem, through effects such as deposition of NMOC reaction products (including of acidic species), *in situ* tropospheric formation of toxic air contaminants, the formation of photochemical air pollution on urban and regional scales, depletion of stratospheric ozone, and the potential for global warming.

The OH radical- and NO₃ radical-initiated reactions of alkanes, alkenes and many other NMOCs lead to the formation of an alkyl or substituted alkyl radical (R), which then reacts as shown schematically below (ref. 3,10)

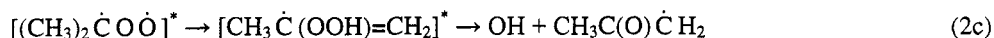
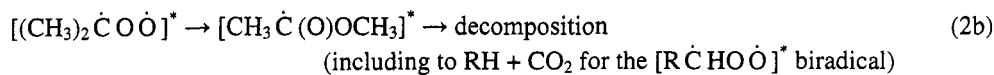


Reaction Scheme 1

The reactions of O_3 with alkenes and NMOC containing $>C=C<$ bond(s) proceed by initial addition to form a primary ozonide, which then decomposes to a carbonyl plus a biradical (ref. 10):

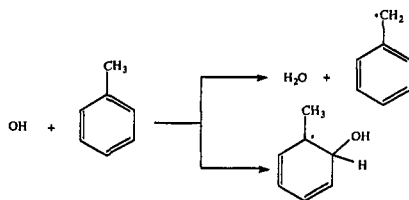


The initially energy-rich biradicals are then collisionally stabilized or react via decomposition/rearrangement pathways (ref. 10), as shown for the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical,



followed by reactions of the stabilized biradicals and the other radical species formed from the decomposition/rearrangement reactions (these radicals often being alkyl or substituted alkyl radicals whose subsequent reactions are as shown in Reaction Scheme 1 above).

The other reaction system which differs from Reaction Scheme 1 concerns reaction of the OH radical with aromatic hydrocarbons, where a fraction (including all) of the reaction proceeds by initial OH radical addition to the carbon atoms of the aromatic ring to form a hydroxycyclohexadienyl radical [OH-aromatic adduct] (ref. 3,8). OH-aromatic adducts then react with O_2 and NO_2 , with the O_2 reaction dominating for tropospheric conditions for the OH-benzene, OH-toluene and OH-xylene adducts, but possibly not for OH-polycyclic aromatic hydrocarbon (OH-PAH) adducts (ref. 3,13,14).



Reaction Scheme 2

There are two general approaches to studying the products of NMOC atmospheric reactions; one being to study the products and mechanisms of individual reactions involved in the NMOC atmospheric degradations; and the second to study the products of the OH radical, NO_3 radical and O_3 reactions of the NMOC of interest. A large amount of work has been

carried out to investigate individual reactions involved in NMOC tropospheric degradations, examples being product studies of the self-reactions of $\text{R}\dot{\text{O}}_2$ radicals and of $\text{R}\dot{\text{O}}_2$ radicals with the HO_2 radical, and studies of CH_3S and CH_3SO radical reactions. As may be expected, extremely useful data are obtained from such studies and our knowledge of the mechanisms and products of $\text{R}\dot{\text{O}}_2 + \text{R}\dot{\text{O}}_2$, $\text{R}\dot{\text{O}}_2 + \text{HO}_2$, CH_3S and CH_3SO radical reactions arises from these studies (see ref. 15,16). The results of this type of study are evident in the NASA (ref. 17) and IUPAC (ref. 15,16) reviews and evaluations, as well as in the reviews and evaluations of NMOC chemistry of Atkinson (ref. 3,7-10). In fact, this is the best way to have a complete understanding of the elementary reactions involved in the tropospheric chemistry of an NMOC; however, the number of reactions to be studied, even for a single NMOC, is enormous and there are great difficulties in generating the intermediate radical species for such studies. Moreover, many of the studies of individual reactions are carried out at pressures and O_2 concentrations very different from those encountered in the troposphere, and in some cases pressure and O_2 dependencies are important, an example being the initial reaction of the OH radical with CH_3SCH_3 (ref. 16).

Despite the long-term advantages of studying individual elementary reactions, there is a place for studies of the products formed from the tropospheric oxidations of NMOCs, in which the first-generation products are identified and quantified and the reaction mechanism deduced from the product distribution. Such studies are the focus of this article (noting that many of the methods of OH radical and NO_3 radical generation and product detection methods are also applicable to kinetic, product and mechanistic studies of elementary reactions). Only studies carried out at atmospheric pressure of air and at around room temperature are discussed.

GENERATION OF OH RADICALS

There are a number of methods used to generate OH radicals, with one of the criteria being the presence or absence of NO (which determines whether $\text{R}\dot{\text{O}}_2$ radicals react with NO or with HO_2 and $\text{R}\dot{\text{O}}_2$ radicals). The goal is to have a clean source of OH radicals with minimal complications caused by other reactive species such as NO_3 radicals and O_3 and by photolysis, and to have a sufficiently high concentration of OH radicals for sufficiently long that relatively low-reactivity NMOC can undergo appreciable reaction (*i.e.* $\int [\text{OH}]t \geq 1 \times 10^{12}$ molecule cm^{-3} s). Not included here is the use of irradiated NO_x -NMOC-air mixtures (ref. 18,19); these systems are not a clean source of OH radicals, with NO_3 radicals and O_3 typically being present at appreciable concentrations. Furthermore, the OH radical concentrations in irradiated NO_x -NMOC-air mixtures are typically around 10^6 molecule cm^{-3} , and photolysis of the NMOC and/or of the reaction products can a complication.

Photolysis of HONO. Nitrous acid (HONO) photolyzes in the wavelength region 300-400 nm to form OH radicals (ref. 15),



and OH radical concentrations of $\sim 5 \times 10^7$ molecule cm^{-3} can be readily obtained (ref. 20). In theory, the photolysis of HONO is an excellent source of OH radicals in the presence of NO, because the overall reaction produces only OH radicals and NO. However, HONO must be synthesized prior to use and it is difficult to generate pure in the absence of significant quantities of NO and NO_2 (ref. 20), which compete with the NMOC for OH radicals. This difficulty in reproducibly synthesizing pure HONO has been a factor in the relatively infrequent use of HONO as an OH radical precursor in product studies. The recently published preparation method of Febo *et al.* (ref. 21), involving the reaction of gaseous HCl with solid sodium nitrite,

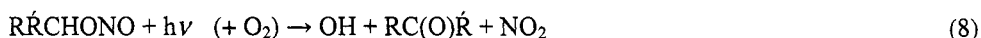


to produce >95% pure HONO should make HONO attractive as an OH radical precursor.

Photolysis of Alkyl Nitrites, RONO. The photolysis of alkyl nitrites of structure $\text{R}\dot{\text{R}}\text{CHONO}$ ($\text{R}, \dot{\text{R}} = \text{H}$ or alkyl) in the wavelength region 300-400 nm leads to the production of OH radicals through the reaction sequence.



Using methyl nitrite photolysis, OH radical concentrations of $\sim 1 \times 10^8$ molecule cm^{-3} can be readily obtained for time-scales of 10 min or more (the time being limited by the photolytic lifetime of methyl nitrite) (ref. 22). The advantage of alkyl nitrites as an OH radical precursor is that the alkyl nitrites are easy to synthesize in pure form and can be readily stored for indefinite periods of time. The disadvantage is that the overall reaction



leads to the co-production of NO_2 , which is both a sink for OH radicals (through its reaction to form nitric acid) and a source of O_3 and hence NO_3 radicals, through the reactions.

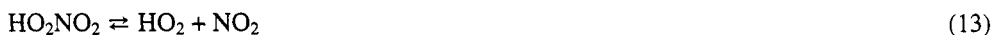


Furthermore, the formation of a carbonyl (HCHO from methyl nitrite, CH_3CHO from ethyl nitrite, acetone from isopropyl nitrite and 2-butanone from 2-butyl nitrite) can interfere with the analysis of products from the NMOC being studied (for example, the use of methyl nitrite precludes the analysis of HCHO as a product of the NMOC being studied). Precautions need to be taken to minimize or avoid, or take into account, the possible reactions of the organic being studied with $\text{O}({}^3\text{P})$ atoms [from photolysis of NO_2 ; reaction (9)], O_3 , and NO_3 radicals. Inclusion of NO in the reactant mixtures (*i.e.*, RONO-NO-NMOC-air mixtures) is generally used to suppress the formation of O_3 and hence of NO_3 radicals by the reaction

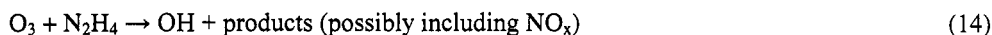


The photolysis of alkyl nitrites has been widely used to generate OH radicals in kinetic and product studies, with examples in product studies being the use of methyl nitrite (ref. 23), ethyl nitrite (ref. 24,25), isopropyl nitrite (ref. 26) and 2-butyl nitrite (ref. 24).

Other OH Radical Sources (in the Presence of NO_x). Other sources of OH radicals in the presence of NO_x have been utilized for kinetic studies (ref. 8), these being the dark reaction of HO_2NO_2 (pernitric acid) with NO (ref. 27),



the dark reaction of hydrazine and O_3 (ref. 28),



and the dark, heterogeneous reaction of hydrogen peroxide with NO_2 (ref. 29). The use of dark reactions to generate OH radicals has the advantage of avoiding the possibility of photolysis of the NMOC reactant and/or reaction products. However, the presence of O_3 in the $\text{O}_3 + \text{N}_2\text{H}_4$ system precludes studies of NMOC which react with O_3 , and the $\text{O}_3 + \text{N}_2\text{H}_4$ and the $\text{H}_2\text{O}_2 + \text{NO}_2$ reaction systems are complex and incompletely understood, and are presently probably not appropriate for use in product studies.

A few methods of generation of OH radicals in the absence of NO_x have been used for product studies, as noted below.

Photolysis of H_2O_2 . The photolysis of H_2O_2 at wavelengths <300 nm (for example, at 254 nm) leads to the formation of OH radicals (ref. 15).



Obviously, the photolysis of H_2O_2 -NO-NMOC-air mixtures will lead to the generation of OH radicals in the presence of NO. H_2O_2 is a "sticky" compound, with a strong potential for loss to reaction vessel walls where it may participate in heterogeneous reactions. Furthermore, the necessity to use wavelengths <300 nm also leads to the potential for photolysis of the NMOC and/or reaction products.

Dark Reaction of O_3 with Alkenes. The observations that the gas-phase reactions of O_3 with alkenes and other NMOC containing $>\text{C}=\text{C}<$ bonds lead to the production of OH radicals [reaction (2c)], often in close to unit yield (ref. 30-33), has led to the use of this reaction system as a dark source of OH radicals in the absence of NO (ref. 13,34,35). This source of OH radicals has decided limitations; to NMOCs which do not react with O_3 (ref. 13,34) or to the alkene or NMOC containing a $>\text{C}=\text{C}<$ bond whose reaction with O_3 is being used as the OH radical source (ref. 35). Furthermore, the competition between the NMOC being studied and the alkene (or compound containing the $>\text{C}=\text{C}<$ bond) for OH radicals limits the amount of reaction of the NMOC being studied. Atkinson and Aschmann (ref. 13), using part-per-million mixing ratios of alkene and aromatic hydrocarbon (the NMOC being studied), obtained up to ~30% reaction for an NMOC with a relatively high OH radical reaction rate constant of $\sim 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

GENERATION OF NO_3 RADICALS.

Two methods have been used to generate NO_3 radicals in product studies carried out at atmospheric pressure, as discussed below.

Thermal Decomposition of N_2O_5 . The thermal decomposition of N_2O_5 (ref. 15)



leads to the generation of NO_3 radicals, and this radical generation method has been extensively used for product studies (ref. 36,37). N_2O_5 is readily synthesized from the reaction of NO_2 with O_3 [reaction (11)] followed by,



with N_2O_5 being collected in a trap cooled to 196 K. N_2O_5 can be stored indefinitely at 77 K under vacuum.

In Situ Generation of NO_3 Radicals (and N_2O_5). Reaction of O_3 with NO_2 leading to NO_3 radical formation [reaction (11)], followed by reactions (16) and (-16) has been used to generate NO_3 radicals *in situ* in the reaction vessel for product studies (ref. 37).

GENERATION OF O₃

O₃ is readily produced by either a corona discharge in O₂ using commercial ozone generators, or by photolysis of O₂ or air at 184.9 nm using commercial low-pressure mercury arcs with a quartz envelope, and no further discussion is given here.

REACTION VESSELS

A variety of reaction vessels have been used for product studies, with static reaction vessels ranging in volume from <1 to ~150,000 liter (ref. 38,39). In static [or slow-flow systems which are effectively continuous stirred-flow reaction vessels (ref. 40)], NMOC reactants are exposed to OH radicals, NO₃ radicals or O₃, and products are analyzed by whatever analytical method is appropriate (and works). High pressure flow systems have been used in a few studies: Berndt and Böge (ref. 41) have used a flow system capable of operation over the pressure range ~5-1000 mbar to study NO₃ radical reactions, producing NO₃ radicals by the thermal decomposition of N₂O₅ and analyzing the reactants and reaction products by gas chromatographic methods; and Donahue *et al.* (ref. 42) have used a high pressure flow system with a modulated OH radical source to investigate the products of the reaction of the OH radical with CF₃CF=CF₂ in the presence of NO, with analysis by *in situ* Fourier transform infrared (FTIR) absorption spectroscopy.

ANALYTICAL TECHNIQUES

As expected, a number of analytical methods have been used for the identification and quantification of reactants and reaction products. These include *in situ* FTIR absorption spectroscopy, *in situ* mass spectrometry (MS), *in situ* atmospheric pressure ionization tandem mass spectrometry (API-MS/MS), and (generally off-line) analyses by gas chromatography with flame ionization detection (GC-FID), gas chromatography with FTIR detection (GC-FTIR), combined gas chromatography-mass spectrometry (GC-MS and GC-MS/MS), and various derivatization-chromatography methods (including high performance liquid chromatography with various detectors). All of these analytical methods have their advantages and disadvantages, and the various analytical techniques tend to be complementary. For example, many hydroxycarbonyl compounds do not gas chromatograph without derivatization (which is also neither simple nor necessarily quantitative), and FTIR absorption spectroscopy often loses many of its advantages when dealing with relatively large (>C₅) oxygenated organic compounds because of the similarity of group absorptions irrespective of the isomeric structure of the compound (and hence the potential for overlapping absorption bands and non-specificity in compound identification). API-MS/MS has proven useful for the identification of multifunctional oxygenated products species such as hydroxycarbonyls, hydroxyhydroperoxides, carbonyl-hydroperoxides, nitrooxycarbonyls and nitrooxyhydroperoxides (ref. 43,44), although to date the identifications have not been isomer specific. GC techniques have good sensitivity and when coupled with MS and, to a lesser extent, FTIR detectors, provide good identification capabilities. However, the requirement to be able to chromatograph a compound can cause difficulties (for example, for many hydroxycarbonyls and hydroperoxides). The use of gas sampling loops and injection valves lead to problems for >C₁₀ hydrocarbons and oxygenated compounds with less carbon atoms; these problems can be circumvented by sample collection onto solid adsorbents with subsequent thermal desorption directly (with cryofocusing) onto a GC column (ref. 31,35). FTIR spectroscopy is generally less sensitive than GC analyses, therefore requiring higher initial reactant concentrations which can conflict with a desire to use low initial reactant concentrations for low volatility NMOC (to minimize wall adsorption/desorption problems on the reaction vessel walls). Combined with a general lack of compound identification

specificity for larger NMOC, FTIR spectroscopy is best suited to the analyses of products formed from relatively small ($\leq C_6$) NMOC [a prime example being for the products of the tropospheric degradation reactions of hydrofluorocarbons and hydrochlorofluorocarbons (ref. 45,46)].

Various experimental methods used in product studies of the reactions of OH radicals, NO_3 radicals and O_3 with NMOC are described in ref. 35,39,43,44,47-51 and these publications should be consulted for further details. In particular, the use of several analytical techniques to study the same reaction system allows for a more comprehensive product identification and quantification, with data for certain products being obtained by more than one analysis method.

POSSIBLE EXPERIMENTAL COMPLICATIONS

Besides the need to be aware of the potential for reactions of the NMOC with $O(^3P)$ atoms, O_3 , and NO_3 radicals when using the photolysis of nitrous acid or alkyl nitrites as a source of OH radicals (see, for example, ref. 52), there are other complications for certain NMOC, as noted below.

Reactions of NMOC with NO_2 . A number of alkenes (mainly conjugated dienes) react with NO_2 in the gas phase (ref. 10 and references therein). A partial listing of the alkenes which react with NO_2 and their room temperature rate constants is given in ref. 10, and the rate constants for those NMOC which are observed to react with NO_2 range up to $1.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For an NO_2 concentration of $1 \times 10^{13} \text{ molecule cm}^{-3}$ (a mixing ratio of ~ 400 ppb), this results in up to $0.8\% \text{ min}^{-1}$ reaction of the NMOC, a complication which cannot be ignored in laboratory studies. Moreover, in the presence of NO in air, the products of the NO_2 reaction lead to the formation of OH radicals (ref. 10), and the dark losses of the NMOC are then due to reaction with NO_2 and OH radicals and the consumption rate of the NMOC is around twice as fast as expected from the NO_2 reaction alone. Indeed, for NMOC such as -phellandrene and -terpinene, dark NO- NO_2 -alkene-air mixtures can be used to study the products of the OH radical reactions (after taking into account the products formed from the NO_2 reaction).

Formation of OH Radicals from the O_3 Reactions with NMOC. The finding that OH radicals are formed, often in close to unit yield, from the reactions of O_3 with alkenes and other NMOC containing $>C=C<$ bonds (ref. 30-33) means that unless the OH radicals are scavenged the reaction being studied involves both OH radical and O_3 reactions and the products observed and quantified are not solely from the O_3 reaction. Product studies of O_3 reactions over the past 8 years have used sufficient concentrations of an alkane (for example, cyclohexane) to scavenge $>90\text{-}95\%$ of the OH radicals formed from the O_3 reaction (ref. 47,50,53).

Formation of Cl Atoms from Chlorine-Containing NMOC. The reactions of OH radicals, NO_3 radicals and O_3 with chlorine-containing NMOCs have the potential to lead to the formation of Cl atoms, which are highly reactive towards most NMOC and can initiate chain reactions (ref. 54). Again, a sufficient concentration of an alkane can be added to the reactant mixture to scavenge the majority of any Cl atoms formed. Ethane has often been used as the alkane because it rapidly with Cl atoms but is of low reactivity towards both OH radicals and NO_3 radicals (ref. 16).

Reactions of NMOC with Gaseous Nitric Acid. A number of amines and other nitrogen-containing NMOC react with gaseous nitric acid to form the nitrate salts.



Because nitric acid is formed when generating OH radicals in the presence of NO (from the OH + NO₂ reaction) and from wall losses of N₂O₅, studies of the OH radical and NO₃ radical reactions with certain nitrogen-containing NMOC can be complicated by additional losses of the NMOC due to reaction with gaseous nitric acid generated during the reactions. Tuazon *et al.* (ref. 55) circumvented this problem by scavenging nitric acid during the OH radical-initiated reaction of 2-vinylpyridine, by adding excess pyridine to the reactant mixtures.

CONCLUSIONS

While much progress has been made during the past few years (see, for example, ref. 47-51), product studies are still limited by the need for better analytical techniques for the identification and quantification of oxygenated product species, and by the general lack of commercially available standards for identification and quantification purposes.

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