# Radical Reactivity in the Condensed Phase: Intermolecular versus Intramolecular Reactions of Alkoxy Radicals

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S *Supporting Information*

ABSTRACT: Condensed-phase alkoxy (RO) radicals can undergo unimolecular (e.g., intramolecular H atom abstraction) reactions as well as bimolecular (intermolecular H atom abstraction) reactions, though the competition between these two channels is not well constrained. Here, we examine this branching by generating RO radicals from the photolysis of a large alkyl nitrite ($C_{20}H_{41}ONO$) in hexanes and nebulizing the mixture into an aerosol mass spectrometer for analysis. Product ions associated with unimolecular (isomerization) reactions were observed to increase upon photolysis. However, no formation of the C_{20} alcohol ($C_{20}H_{41}OH$, the expected product from RO + RH reactions) was observed, suggesting that bimolecular reactions are at most a minor channel for this condensed-phase system (involving saturated hydrocarbons). This result, combined with previous studies of liquid-phase RO radicals carried out at higher concentrations, suggests that when 1,5-H atom abstraction reactions are facile (i.e., in which a 1,5-H atom shift from a secondary or tertiary carbon can occur), this channel will dominate over bimolecular reactions.

Unimolecular Product

Bimolecular Product
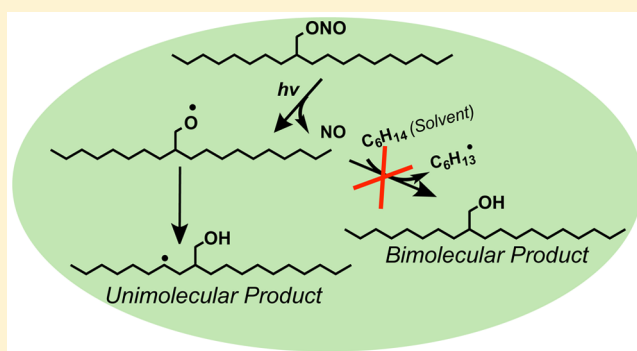
Condensed-phase organic radicals are ubiquitous in both natural and engineered chemical systems and play central roles in key processes such as the degradation of pollutants,[1] weathering of materials,[2] combustion reactions,[3] and the oxidative evolution of atmospheric organic aerosol particles.[4] Such organic radicals, which include alkyl (R), alkoxy (RO), and alkylperoxy (RO_2) species, are highly reactive and often can undergo several different reactions. Most mechanistic studies of radical reactions have focused on the gas phase, which (under most conditions) limits the available reactions to unimolecular processes or bimolecular reactions with major inorganic species (O_2, NO_x, etc.).[3,5,6] However, the condensed phase represents a more complex molecular environment because the high concentrations may facilitate bimolecular reactions with other organic species (molecules or radicals).[7−12] Condensed-phase radicals can therefore exhibit fundamentally different reactivity than gas-phase radicals; however, these generally have received far less study, leading to major uncertainties in the radical chemistry of important multiphase systems (e.g., atmospheric aerosol and cloud droplets).

Here, we utilize a novel approach for studying the reactions of large organic radicals in the condensed phase via nebulization of the reaction mixture into an aerosol mass spectrometer (AMS). This technique, used previously for the study of aqueous-phase oxidation reactions,[13,14] allows for the sensitive, real-time measurement of radical reaction kinetics and products, and avoids many of the analytical challenges associated with collecting aliquots of the mixture for offline analysis. Our specific focus is the chemistry of alkoxy radicals

(RO), key intermediates in the atmospheric oxidation of organic compounds,[15−17] as well as combustion processes.[3] RO radicals can form within the condensed phase (e.g., in atmospheric particles or droplets, fuel mixtures, etc.) by several channels: self- and cross-reactions of RO_2 radicals, the reaction of RO_2 with NO, and the direct photolysis or thermal decomposition of peroxide (ROOH, ROOR) species. In the gas phase, RO radicals react via one of three channels (Scheme 1): (r_1) isomerization, a 1,5-intramolecular H atom abstraction reaction that increases the degree of functionalization; (r_2) reaction with O_2 to form a carbonyl and HO_2; or (r_3) C−C bond scission (fragmentation) to form two smaller species (a carbonyl and an alkyl radical).[18] In the condensed organic phase, an additional channel (r_4) is available: the intermolecular (bimolecular) abstraction of H atoms from other organic species (RO + RH), forming an alcohol (ROH) and an alkyl radical.

Bimolecular reactions of RO (r_4) have been shown to be an important channel for small ($C_1−C_4$) RO radicals in organic solvents[19] and recently have been invoked to explain observations of alcohol formation in heterogeneous oxidation experiments of organic aerosol particles.[8−10,20−22] On the other hand, studies of larger condensed-phase radicals indicate that reaction r_4 becomes less important once RO radicals reach the

Scheme 1. Possible Reactions of Gas- And Condensed-Phase Alkoxy Radicals
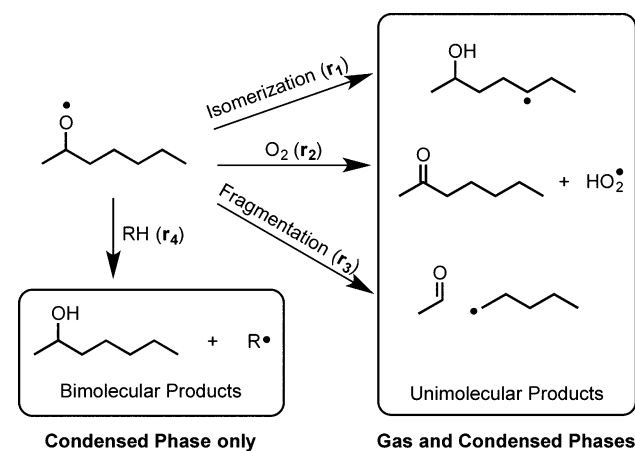
size at which unimolecular isomerization is facile (i.e., in which a 1,5-H atom shift from a secondary or tertiary carbon can occur), with decreases in observed ROH yields and increases in the yields of isomerization products.[23] While such studies suggest the dominance of reaction r_1 over r_4 for large RO radicals, they were carried out under oxygen-free conditions, with high concentrations of radicals, and results may not be representative of radical reactivity in the atmosphere. Thus, the relative importance of unimolecular and bimolecular reactions of large RO radicals is poorly constrained under atmospheric conditions. Indeed, literature recommendations for the relative rates of unimolecular and bimolecular alkoxy radical reactions vary dramatically; for example, one compilation of radical reaction rates indicates a fast rate of bimolecular reaction,[24] whereas structure−activity relationships predict it to be orders of magnitude slower than unimolecular reactions.[25]

In our previous work, we examined the gas-phase unimolecular chemistry of alkoxy radicals, specifically the branching between isomerization (r_1) and fragmentation (r_3), using the photolysis of a series of gas-phase C_{10} alkyl nitrites (RONO) to generate RO radicals.[26] Here, we extend this technique to the study of the chemistry of RO radicals in the condensed phase. Large alkyl nitrites were photolyzed in hexanes (0.01−0.1% v/v) to generate condensed-phase RO radicals, and reaction kinetics and products were monitored via nebulization into a high-resolution AMS.[27] Described here are results for octyl-2-dodecyl-1-nitrite ($C_{20}H_{41}ONO$), which forms an octyl-2-dodecyl-1-oxy ($C_{20}H_{41}O$) radical upon photolysis. Other large alkyl nitrites (eicosanyl-1-nitrite, $C_{20}H_{41}ONO$, hexacosanyl-2-nitrite, $C_{26}H_{53}ONO$, and octacosanyl-10-nitrite, $C_{28}H_{57}ONO$) were also studied; results were similar to those of octyl-2-dodecyl-1-nitrite and thus are shown only in the Supporting Information.

Upon UV irradiation of the RONO mixture, there is a dramatic change in the chemical composition of the solution mixture. The output of the atomizer (aerosol loading as measured by the AMS) increased by as much as a factor of 10 over the course of 1 h. While the reason for this remains unclear, this growth likely reflects changes in the behavior of the atomized solution over the course of the experiment. In a blank experiment involving the irradiation of $C_{20}H_{41}OH$ (the synthetic precursor of the nitrite, as described in the Experimental Section), no chemical changes were observed,

confirming that the observed chemistry arises from RONO photolysis.

Figure 1 shows the aerosol mass spectra (m/z 260−320) for a 0.025% $C_{20}H_{41}ONO$/hexane mixture before and after irradiation. The major ion associated with the precursor $C_{20}H_{41}ONO$ is $C_{19}H_{39}^+$ $[M−CH_2ONO]^+$ at m/z 267.305; as expected, the intensity of this ion drops dramatically with irradiation. A second tracer ion for RONO might be $C_{20}H_{40}^+$ $[M−HONO]^+$ at m/z 280.313. However, this is also a major ion ($[M−H_2O]^+$) in the mass spectrum of the corresponding alcohol, ROH ($C_{20}H_{41}OH$) (Figure S2, Supporting Information). ROH may be formed photochemically (r_4, Scheme 1), or it may instead simply be an unreacted precursor from RONO synthesis; these two possibilities are discussed below.

Several large C_{20} oxygen-containing ions increase upon irradiation, indicating that they are reaction products. The three most intense ones are $C_{20}H_{38}O^+$, $C_{20}H_{39}O^+$, and $C_{20}H_{39}O_2^+$; similar product ions have been previously observed in studies of gas-phase alkane oxidation by Lim and Ziemann[16] and in our earlier work on SOA from photolysis of gas-phase RONO species.[26] On the basis of that work, these ions correspond to the hydroxycarbonyl ($C_{20}H_{38}O^+$, $[M−H_2O]^+$), its cyclization product the cyclic hemiacetal ($C_{20}H_{39}O^+$, $[M−OH]^+$), and acetal or hemiacetal dimers ($C_{20}H_{39}O_2^+$, $[M−C_{20}H_{41}O_2]^+$), respectively, all first-generation products of alkane oxidation. The source of a fourth major product ion, a N-containing fragment at m/z 277.276 ($C_{19}H_{35}N^+$), is unknown; it may result from fragmentation of a nitrate species on the heater or during ionization, but further study is needed.

Typical time series of the key ions in the mass spectrum, normalized to the total organic signal to account for changes in atomizer output, are shown in Figure 2. Repeat experiments gave similar results, though with some differences (up to 50%) in the relative abundances of the large oxygen-containing ions ($C_{20}H_{38}O^+$ and $C_{20}H_{39}O^+$); these may be due to small variations in the AMS vaporizer temperature, and do not affect the overall conclusions of this work. Also shown are the traces for NO^+ and NO_2^+, fragments of the RONO reactant, as well as organic nitrate ($RONO_2$) products. Upon initiation of photolysis, the abundance of $C_{19}H_{39}^+$ decays exponentially ($k_{phot} = 3.6 \times 10^{-4}$ s^{-1}), as expected for the nitrite reactant. By contrast, $C_{20}H_{40}^+$ drops slightly and then remains fairly constant; the difference between these two traces suggests contributions by ROH, which is discussed in detail below. The
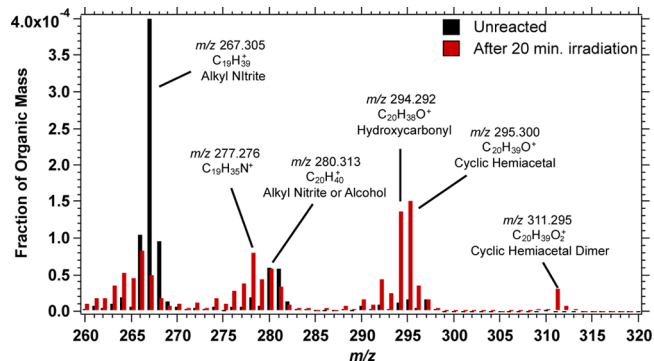

Figure 1. Unit−mass resolution AMS spectrum (m/z 260−320) of $C_{20}H_{41}ONO$ in hexanes in the dark (black) and after 20 min of irradiation (red, positive x-axis offset). Ion formulas were identified by high-resolution analysis, and molecular assignments are based on Lim and Ziemann.[16]
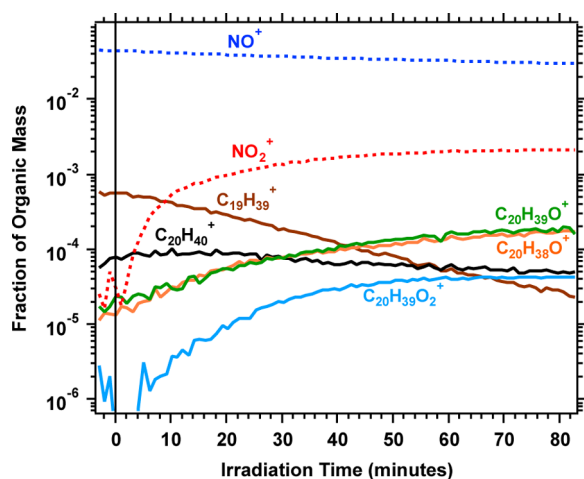
Figure 2. Ion time series for a typical $C_{20}H_{41}ONO$ photolysis experiment in hexanes. All ions are normalized to total organic loading to account for changes in the atomizer output. UV lights were turned on at $t = 0$ (vertical black line), after which point there was a decrease in the abundance of NO^+ and the major RONO ion ($C_{19}H_{39}^+$) and an increase in NO_2^+ and oxygenated ions ($C_{20}H_{38}O^+$, $C_{20}H_{39}O^+$, and $C_{20}H_{39}O_2^+$).

NO^+ ion (a minor fragment in the RONO spectrum) also decreases, though not as rapidly as the RONO marker peak ($C_{19}H_{39}^+$), whereas the NO_2^+ ion rapidly increases. After 60 min, the NO^+/NO_2^+ ratio levels off at ~15, suggesting the formation of organic nitrates.[28−30]

A mechanism consistent with the above observations is given in Scheme 2. Following formation, the RO radical will either fragment (r_3) to two smaller molecules or isomerize (r_1) followed by O_2 addition to form an RO_2 radical (the reaction with O_2, r_2, is expected to be negligible based on analogous gas-phase observations).[18] Products from fragmentation reactions will include species with ≤19 carbon atoms; these may be too volatile to remain in the aerosol phase for analysis and/or difficult to distinguish from the C_{20} fragments within the AMS, and therefore cannot be easily identified. RO_2 can react with either NO or another RO_2 to form an additional RO radical. The newly formed RO radical will "back-isomerize" and form the hydroxycarbonyl, the cyclic hemiacetal, and acetal or hemiacetal dimers.[31] Ions corresponding to products from "forward isomerization" reactions (i.e., dihydroxycarbonyls and hydroxycyclic hemiacetals) were not observed, consistent with our previous studies of gas-phase β-substituted RO radicals.[26] The observation of ions corresponding to the expected products of RO isomerization—nitrates, hydroxycarbonyls, and (cyclic) hemiacetals—provides strong evidence that unimolecular (intramolecular H atom abstraction) reactions are important reaction pathways for condensed-phase $C_{20}H_{41}O$ radicals.

The evidence for bimolecular reactions (intermolecular H atom abstraction reactions) with hexane solvent molecules (r_4) is less clear. This reaction yields ROH and a C_6 species; however, only ROH is likely to be of low enough volatility to be measured by the AMS. AMS measurements of a pure ROH standard (Figure S2, Supporting Information) confirm that the dominant high molecular weight ion is $C_{20}H_{40}^+$ ($[M-H_2O]^+$), formed from dehydration on the vaporizer or within the ionization region. This ion is present prior to photolysis, suggesting that it is also a tracer ion for RONO and/or that some residual ROH from the RONO synthesis was present in the reaction mixture. Its abundance decreases more slowly than that of $C_{19}H_{39}^+$ (the major RONO tracer ion), indicating at least some contribution by ROH, though this still leaves open the possibility of ROH formation from r_4 (which counterbalances the decrease from loss of RONO). In order to investigate the role of r_4 as a source of ROH, the experiment was repeated using CCl_4 instead of hexanes, precluding any

Scheme 2. Mechanism, Reaction Products, And Ion Assignments for a Single C_{20} Alkoxy Radical in the Condensed Phase
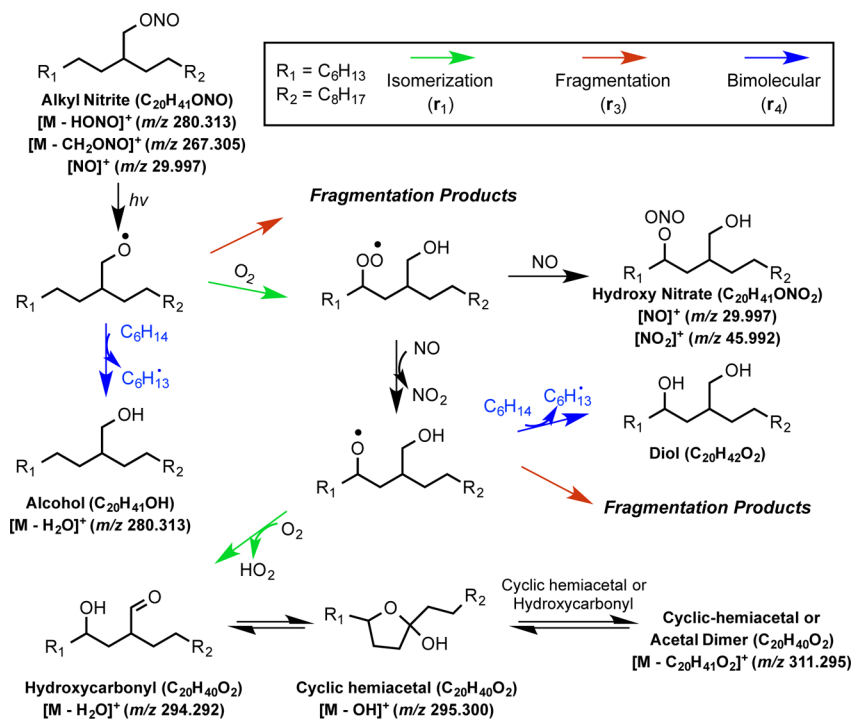
possible bimolecular RO + RH reactions. Results were similar to those using hexane solvent (Figure S3, Supporting Information), with only a slight drop in $C_{20}H_{40}^+$ ion signal upon photolysis, implying little influence of r_4 in either solvent. Furthermore, GC-MS analysis of derivatized aliquots of the irradiated RONO/hexane system (see the Supporting Information, Figures S4 and S5) showed no increase in the total abundance of the alcohol. Both results strongly suggest that any ROH present in the reaction mixture was an artifact from RONO synthesis rather than a product of bimolecular reactions (r_4). The lack of formation of the ROH in these experiments indicates that bimolecular H atom abstraction reactions (RO + RH) are not competitive with the available unimolecular isomerization pathways in this system.

The present results are consistent with previous studies by Kabasakalian and co-workers of the chemistry of condensed-phase long-chain alkoxy radicals, which, as discussed above, found products of unimolecular 1,5-H-abstraction reactions to dominate over those from bimolecular RO + RH reactions.[23,32] Studies that instead showed the dominance of bimolecular reactions focused almost entirely on small (C_1–C_4) radicals,[19] for which the 1,5-isomerization cannot occur and for which fragmentation is known to be slow. Further, most previous studies were conducted under high concentrations (1–10%) of radical precursors, which may promote alkoxy disproportionation (RO + RO) reactions that form ROH and carbonyl species. Such reactions likely explain the roughly equal yields of carbonyls and ketones from such studies,[23] which are not expected from the RO + RH reaction. While some evidence for ROH formation and minor reaction products from H atom abstraction from solvent molecules was also reported,[32] their formation may have been influenced by the reaction conditions (i.e., the oxygen-free conditions and high radical concentrations in that study). The results from this work thus suggest that, under more atmospherically relevant conditions (low radical concentrations, the presence of O_2, and room temperature), isomerization will dominate over bimolecular reactions, at least when saturated hydrocarbon molecules are present. This result is also consistent with the high entropic penalties associated with bimolecular reactions because they involve the loss of translational rather than vibrational degrees of freedom.[33] This inferred dominance of unimolecular abstraction reactions over bimolecular ones likely holds for RO_2 autoxidation chemistry as well, recently suggested as a potentially important oxidation channel within organic aerosol.[34]

We note that this work focuses on only one chemical system, the reactions of unfunctionalized RO radicals within a simple liquid alkane solvent, and thus our results do not necessarily imply that condensed-phase bimolecular H atom abstraction reactions cannot compete with unimolecular reactions in all cases. In particular, when diffusion is slow (e.g., in solid matrixes or "glassy" organic aerosol)[9] or when the surrounding molecules have readily abstractable hydrogen atoms (e.g., oxygenates), bimolecular H atom abstractions may be of increased importance. This is an important area of future research, and may help explain why recent laboratory studies have observed the formation of alcohols.[8–10,20–22] However, alcohol species can also be formed by reactions other than RO + RH, such as RO_2 + RO_2 and RO + RO disproportionation reactions. Moreover, in many cases (such as in most atmospheric organic aerosol), a given condensed-phase radical will likely be chemically similar to its surrounding molecules. There, any enhancement in bimolecular rates (for example,

from more readily abstractable H atoms) will also involve a coincident enhancement in unimolecular rates. In such systems, the reactivity of alkoxy radicals in the condensed (liquid) phase is likely to be dominated by unimolecular chemistry, similar to alkoxy radical reactivity in the gas phase.

■ EXPERIMENTAL SECTION

RONO species were prepared in the laboratory via O-nitrosation of the corresponding alcohols[35] using the same protocol used in our previous study[26] but with slight modifications to the synthesis protocol for solid-phase alcohol precursors (see the Supporting Information). RONO photolysis experiments were conducted by adding 0.01–0.1% (v/v) $C_{20}H_{41}ONO$ in hexanes (Sigma-Aldrich, 99% anhydrous) or CCl_4 (Sigma-Aldrich, 99%) to a borosilicate bottle attached to a constant output atomizer (TSI, Inc.). The output from the atomizer was passed through a charcoal denuder to remove hexane solvent, resulting in particles of average volume-weighted diameter of ∼250 nm; the flow was split to a scanning mobility particle sizer (TSI, Inc.) to measure the particle size and an Aerodyne high-resolution aerosol mass spectrometer (AMS) to measure the particle composition.[27] The AMS was run in high-resolution "W-mode" for exact mass confirmation, and time series for individual ions were constructed using the lower-resolution "V-mode" for greater sensitivity to high molecular weight ions. After ∼10 min of atomization of the unreacted mixture in the dark, a single 40 W blacklight (centered at 350 nm), positioned 2–3 cm adjacent to the reactor, was illuminated. Irradiation continued until the major high molecular weight signals stopped changing (typically within 1 h). For several experiments, perfluorohepta-cosane (PFH, $C_{27}F_{56}$) particles were added for improved mass calibration at at $m/z > 250$. PFH particles were generated by passing air over a heated (∼80 °C) PFH reservoir and then into a cooling area, forming pure PFH particles that were then added to the atomizer aerosol stream and sent into the AMS.

■ ASSOCIATED CONTENT

⑤ Supporting Information

High-mass AMS spectrum of the alcohol, ion time series for octyl-2-dodecyl-nitrite photolysis in CCl_4 and eicosanyl-1-nitrite, hexacosanyl-2-nitrite, and octacosanyl-10-nitrite photolysis in hexanes, the protocol for RONO preparation, and the method and results from GC-MS analysis of the reaction mixture are given. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00913.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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