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Formation of Highly Oxidized Radicals and Multifunctional Products from the Atmospheric Oxidation of Alkylbenzenes

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ABSTRACT Aromatic hydrocarbons contribute significantly to tropospheric ozone and secondary organic aerosols (SOA). Despite large efforts in elucidating the formation mechanism of aromatic-derived SOA, current models still substantially underestimate the SOA yields when comparing to field measurements. Here we present a new, up to now undiscovered pathway for the formation of highly oxidized products from the OH-initiated oxidation of alkyl benzenes based on theoretical and experimental investigations. We propose that unimolecular H-migration followed by O₂-addition, a so-called autooxidation step, can take place in bicyclic peroxy radicals (BPRs), which are important intermediates of the OH-initiated oxidation of aromatic compounds. These autooxidation steps lead to the formation of highly oxidized multifunctional compounds (HOMs), which are able to form SOA. Our theoretical calculations suggest that the intramolecular H-migration in BPRs of substituted benzenes could be fast enough to compete with bimolecular reactions with HO₂ radicals or NO under atmospheric conditions. The theoretical findings are experimentally supported by flow tube studies using chemical ionization mass spectrometry to detect the highly oxidized peroxy radical intermediates and closed-shell products. This new unimolecular BPR route to form HOMs in the gas phase enhances our understanding of the aromatic oxidation mechanism, and contributes significantly to a better understanding of aromatic-derived SOA in urban areas.

KEYWORDS: Highly Oxidized Multifunctional Products; Bicyclic Peroxy Radicals; Unimolecular Hydrogen Migration; Mass Spectrometry

37 TOC GRAPHICS

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Introduction

Aromatic compounds represent an important fraction of the total volatile organic compounds in the urban atmosphere and play an important role in the formation of both tropospheric ozone and secondary organic aerosols (SOAs).¹⁻⁵ Typical anthropogenic sources of aromatic compounds include on-road vehicles, solvent usage, and industrial emissions. In industrialized regions of developing countries like China, serious pollutions from BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) were observed in winter due to coal combustion, e.g., BTEX concentrations were usually $\sim 30 \mu\text{g m}^{-3}$ ($1 \mu\text{g m}^{-3} \sim 7.5 \times 10^9 \text{ molecules cm}^{-3} \sim 0.3 \text{ ppbv}$) or higher in non-haze days and could easily exceed $100 \mu\text{g m}^{-3}$ in haze days in northern China^{6, 7} and other regions.^{8, 9}

In the troposphere, oxidation of aromatic compounds is initiated by their reactions with OH radicals *via* H-abstraction from the alkyl groups and, more importantly, *via* OH addition to the aromatic ring, followed by further reactions to form bicyclic peroxy radicals (BPRs) (**Scheme 1**).^{1, 10, 11} Based on the current mechanistic understanding, BPRs react with HO₂ radicals forming bicyclic hydroxyhydroperoxides (ROOH) as the main product under low-NO_x conditions. The reaction with NO yields bicyclic organic nitrates (RONO₂) as well as the corresponding bicyclic oxy radicals that finally form carbonylic products, such as (methyl) glyoxal, and other SOA precursors.¹²⁻¹⁴ As a result of a smog chamber study on the oxidation of benzene, toluene, and xylene, it was found that SOA yields under low-NO_x conditions were higher than those obtained under high-NO_x conditions, presumably due to the formation of high yields of ROOHs from the reactions of BPRs with HO₂ radicals.¹⁵ The bimolecular reactions of BPRs with HO₂ and NO have been incorporated into SOA formation models,¹⁶⁻¹⁸ which, however, still underestimated the

SOA formation from xylene and toluene under both high- NO_x and low- NO_x conditions.^{17, 18} The discrepancy between field measurements and modeling studies might suggest an alternative pathway of SOA formation from BPRs without the participation of HO_2 or NO .

SCHEME 1. Main oxidation routes of benzene

Here we suggest an alternative reaction pathway of BPRs that starts with an unimolecular isomerization step of BPRs being competitive with the bimolecular BPR reaction, e.g. at $0.1 - 10 \text{ s}^{-1}$ with NO in the range of $0.4 - 40 \text{ ppbv}$ or at $\sim 0.01 \text{ s}^{-1}$ with HO_2 of 40 pptv and the bimolecular rate coefficients of $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁹ Our recent theoretical study on the oxidation of benzyl alcohol showed that the intramolecular H-migrations of the corresponding BPRs proceed with rate coefficients of $\sim 10 \text{ s}^{-1}$ at 298 K .²⁰ Fast H-migrations under atmospheric conditions were also found for peroxy radicals formed in the oxidation of a series of important organic precursor compounds,²¹⁻²⁹ resulting in the formation of highly oxidized multifunctional compounds (HOMs). Particularly, fast H-migration might partially account for the recently observed HOMs with an $\text{O}:\text{C}$ ratio up to 1.09 in the OH -initiated oxidation of benzenes.³⁰ Given the importance of alkylbenzenes in the urban atmosphere, we investigated here the role of H-migrations of BPRs from the oxidation of aromatic compounds using toluene (**T**), ethylbenzene (**EB**), and isopropylbenzene (**IB**) as the model substances.

80

81 **Theoretical and Experimental Methods**

82 **Theoretical Methods** All molecular structures were optimized at DFT-M06-2X/6-
83 311++G(2df, 2p) level which has been assessed to be suitable for thermokinetic studies.³¹ The
84 optimized structures were submitted to electronic energies using restricted open-shell complete
85 basis set model chemistry (ROCBS-QB3)³² which uses the spin-restricted wave functions to
86 eliminate the need for empirical correction for spin contamination in UCBS-QB3. Values of the
87 T1 diagnostic in ROCCSD/6-31+G(d') calculations were used to check the multireference
88 characteristic of the wavefunctions. Generally, a T1 diagnostic larger than 0.02 suggests a
89 multireference nature of the wavefunction,^{33, 34} but Olivella et al. also found that RCCSD(T)
90 agreed well with the multireference method CASPT2 in the calculations of benzene oxidation
91 when the T1 diagnostic is less than 0.044.³⁵ In this work, we found that the T1 diagnostics were
92 all less than 0.03 for the transition states of critical steps, indicating the reliability of our
93 calculations. All the quantum chemical calculations were carried out using the Gaussian 09
94 package.³⁶

95 The reaction rate coefficients of the unimolecular reactions were calculated using the
96 unimolecular rate theory coupled with the energy-grained master equation for collisional energy
97 transfer (RRKM-ME),^{37, 38} and the rate coefficients of bimolecular reactions were determined
98 using traditional transition state theory.^{39, 40} The RRKM-ME calculations were carried out using
99 the Mesmer code.⁴¹ A single exponential-down model was used to approximate the collisional
100 energy transfer with $\langle \Delta E \rangle_{\text{down}}$ of 200 cm⁻¹. The collisional parameters were estimated using the
101 method of Gilbert and Smith,⁴² and the asymmetric Eckart model was used for the tunneling
102 correction factors.⁴³ With the uncertainty in barrier heights (~4 kJ/mol by ROCBS-QB3) and in

tunneling correction factors, we estimate an uncertainty of about one order of magnitude for the unimolecular rates at 298 K.

Experimental Methods The experimental studies were performed in a free-jet flow system at a temperature of 295 ± 2 K, a pressure of 1 bar air and a reaction time of 7.9 s.^{44, 45} The detection of highly oxidized peroxy radicals and closed-shell products was carried out by means of CI-API-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometry (Airmodus, ToFwerk, resolving power >3000 Th/Th) at atmospheric pressure using acetate as the reagent ion.⁴⁴⁻⁴⁷ The stated concentrations represent estimated lower end values assuming efficient clustering of acetate ions with the highly oxidized products with a rate coefficient at the collision limit.^{44, 45} This experimental approach allows following the early, highly oxidized products, including peroxy radicals, with a detection limit as low as 10^4 molecules cm^{-3} . OH radicals were generated via ozonolysis of tetramethylethylene. Calculated steady-state OH concentrations were in the range $(2.4 - 53) \times 10^4$ molecules cm^{-3} . More experimental information is given in Supporting Information.

Results and Discussion

OH addition to **T**, **EB**, and **IB** forms four different adducts, denoted as R1-R4 for additions to *ipso*-, *ortho*-, *meta*-, and *para*-positions, respectively, resulting after two subsequent O₂ additions in the formation of the corresponding BPRs in alkyl benzenes.^{11, 20, 48-51} Calculations showed that the first O₂ adds to the aromatic ring from the same direction as the OH radical (*syn*), while the second O₂ adds from the opposite direction relative to OH group (*anti*). BPRs are therefore denoted as R_{*n*}-*ij*OO-*s*-*k*OO-*a*, in which *n* is the site of OH addition, *i* and *j* are the sites connecting the -OO- unit, and *k* is the site of the second O₂ addition, and *a/s* is *anti/syn* (*see*

Scheme 1 for the numbering of sites). Additions of OH to *meta*-position are usually ignored because of their small branching ratios. The radicals R1-26OO-*s*-3OO-*a*, R2-13OO-*s*-6OO-*a* and R4-35OO-*s*-2OO-*a* can possibly undergo intramolecular H-migrations as shown in **Scheme 2**, resulting in another set of peroxy radicals O₂QOOH (HO-Ar-(O₂)₃, denoted as R1-QP, R2-QPH2 and R4-QP1/R4-QP2) after the third O₂ addition. H-migration channel is not available to R2-13OO-*s*-4OO-*a*, which could also be formed from R2 channel.

Scheme 2. H-migrations in bicyclic peroxy radicals (*a/s* = *anti/syn* represents the direction of –OO– or –OO relative to –OH group)

Theoretical Results In order to probe the feasibility of the proposed H-migrations, we first estimated their rate coefficients using quantum chemistry calculations and the unimolecular rate theory (RRKM-ME). The results are listed in Table 1. All H-migrations in R1-BPRs and R2-

BPRs are endothermic and therefore highly reversible. H-migrations in R4-BPRs are about thermal neutral due to the conjugated π -bond in the radical products and fast recombination of R4-QOOH with O_2 , and are therefore virtually irreversible. Barrier heights for H-migrations are reduced by 9 - 20 kJ/mol upon successive methyl substitution from **T** to **EB** and to **IB**, and barrier heights in R4-BPRs are much lower than those in R1- and R2-BPRs. The lower barriers and irreversibility for R4-BPRs imply the importance or even the dominance of H-migration under atmospheric conditions for these radicals. For O_2 addition to R4-QOOH, calculations show that radicals R4-QP1 and R4-QP2 are formed with branching ratios of 0.67 and 0.33 for **T**, 0.19 and 0.81 for **EB**, and 0.56 and 0.44 for **IB**, respectively, at 298 K.

Each bicyclic peroxy radical has multiple conformers due to internal rotations, of which the internal rotations of the alkyl groups and the $-OO$ group are frozen in transition states for H-migrations. Therefore, we have paid special attention to identify the lowest energy conformer for each bicyclic peroxy radical by rotating all the rotatable bonds. In the kinetics calculations, we have also treated the two internal rotations as two uncoupled hindered rotors, and have obtained their potential energy profiles by fixing the corresponding dihedral angles while relaxing all other coordinates in optimization. The potential energy profiles are shown in Figures S1-S3 in the Supporting Information. The unimolecular rate coefficients obtained are listed in Table 1. Discussions below were based on rates predicted with consideration of internal rotations.

Assuming steady state conditions for QOOH led to the effective rate coefficients $k_{b, \text{Eff}}$ (in s^{-1}) from BPRs to QPs *via* H-migration as

$$k_{b, \text{Eff}} = \frac{k_F k_b [O_2]}{k_R + k_b [O_2]}$$

Table 1. Reaction energies and barrier heights (ΔE_{0K} and $\Delta E_{0K}^\ddagger$, in kJ/mol) at ROCBS-QB3 level, the rates at 298 K and T -dependence rate coefficients (k_F , k_R , and $k_{b,eff}$, all in s^{-1}) for the intramolecular H-migrations in BPRs

BPRs	ΔE_{0K}	$\Delta E_{0K}^\ddagger$	$k_F^{(a)}$	$k_R^{(a)}$	$k_{b,eff}^{(a)}$	$k_F^{(b)}$	$k_R^{(b)}$	$k_{b,eff}^{(b)}$
T-R1-	65.2	110.1				5.2×10^{-6}	1.9×10^6	5.1×10^{-6}
						$\ln k_{b,eff}(T) = 18.77 - 9.11 \times 10^3/T$		
T-R2-	67.8	101.8				5.2×10^{-5}	2.8×10^8	8.0×10^{-6}
						$\ln k_{b,eff}(T) = 16.37 - 8.37 \times 10^3/T$		
T-R4-	12.5	93.2				2.6×10^{-2}	2.6×10^1	2.6×10^{-2}
						$\ln k_{b,eff}(T) = 9.67 - 3.92 \times 10^3/T$		
EB-R1-	52.2	92.1	1.3×10^{-2}	5.1×10^6	1.2×10^{-2}			
	52.2	94.2	1.0×10^{-2}	3.7×10^6	9.4×10^{-3}			
			$\ln k_{b,eff}(T) = 23.54 - 7.37 \times 10^3/T$					
EB-R2-	53.3	85.8	1.0×10^{-2}	3.7×10^6	1.6×10^{-2}	1.2×10^{-2}	2.0×10^8	2.5×10^{-3}
			$\ln k_{b,eff}(T) = 18.32 - 6.69 \times 10^3/T$			$\ln k_{b,eff}(T) = 16.24 - 6.63 \times 10^3/T$		
EB-R4-	-3.9	76.8	4.2×10^1	8.9×10^0	4.2×10^1	7.0	8.9	7.0
			$\ln k_{b,eff}(T) = 13.00 - 2.71 \times 10^3/T$			$\ln k_{b,eff}(T) = 10.167 - 2.40 \times 10^3/T$		
IB-R1-	51.3	81.3	4.5×10^{-1}	6.1×10^7	2.0×10^{-1}			
			$\ln k_{b,eff}(T) = 21.17 - 6.78 \times 10^3/T$					
IB-R2-	31.3	70.2	6.7×10^1	6.6×10^6	5.9×10^1	21	6.7×10^6	8.8
			$\ln k_{b,eff}(T) = 21.29 - 5.11 \times 10^3/T$			$\ln k_{b,eff}(T) = 17.34 - 4.51 \times 10^3/T$		
IB-R4-	-7.7	67.6	4.7×10^2	3.2×10^1	4.7×10^2	14	33	14
			$\ln k_{b,eff}(T) = 14.65 - 2.49 \times 10^3/T$			$\ln k_{b,eff}(T) = 11.32 - 2.53 \times 10^3/T$		
T-R1-QP		149.2						$< 10^{-8}$ (298 K)
		132.0						$< 10^{-8}$ (298 K)
T-R2-QP		93.3						1.1×10^{-2} (298 K)
T-R4-QP		84.0						~ 8 (298 K)
EB-R4-QP2-s		83.0						~ 0.6 (298 K)
IB-R4-QP2-s		79.4						~ 16 (298 K)

^(a) Treating internal rotations as hindered rotors; ^(b) Treating internal rotation as harmonic oscillators

Scheme 3. H-migrations in R1-QP, R2-QPH2, and R4-QP1/-QP2

where k_F , k_R , and $k_b[\text{O}_2]$ are defined in **Scheme 2**. We have estimated $k_{b,\text{eff}}$ using our calculated values for k_F and k_R (see Table 1) and $k_b = 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for a temperature range of 243 - 333 K⁵² and $[\text{O}_2] = 5 \times 10^{18} \text{ molecules cm}^{-3}$. The results are also included in Table 1. The results clearly showed that H-migration in BPRs could be important under typical atmospheric

conditions except for **T**-R1- and **T**-R2-BPR. The estimated $k_{b,\text{Eff},298\text{K}}$'s of $\sim 7\text{ s}^{-1}$, $\sim 9\text{ s}^{-1}$, and $\sim 14\text{ s}^{-1}$ in **EB**-R4-, **IB**-R2-, and **IB**-R4-BPRs, respectively, are higher than or comparable to the possible pseudo first-order rate coefficients of $0.1 - 10^{-1}\text{ s}$ for the bimolecular removals with NO of $0.4 - 40\text{ ppbv}$ or $\sim 0.01\text{ s}^{-1}$ with HO_2 radicals of 40 pptv in the atmosphere, suggesting the importance of H-migration in BPRs even in the highly polluted atmosphere. H-migration in **T**-R4-BPR with $k_{b,\text{Eff},298\text{K}}$ of $\sim 0.02\text{ s}^{-1}$ could be comparable to the bimolecular removals when NO/ HO_2 concentrations are low in remote areas and even in the urban atmosphere in the afternoon (NO concentrations $< 1\text{ ppbv}$).⁵³ Expectedly, the H-migration becomes faster at high temperatures and slower at low temperatures. It should be still important even in the cold winter with $k_{b,\text{Eff},263\text{K}}$ of $\sim 2.5\text{ s}^{-1}$, 1.2 s^{-1} , and 4.7 s^{-1} for **EB**-R4-, **IB**-R2-, and **IB**-R4-BPRs.

The R2-QPH2 and R4-QP1 radicals formed from H-migration of BPRs might undergo another H-migration (**Scheme 3**). We have obtained barriers of 93.3 and 84.0 kJ/mol for H-migrations in **T**-R2-QPH2 and **T**-R4-QP1 and estimated rate coefficients of $\sim 1.1 \times 10^{-2}$ and $\sim 8\text{ s}^{-1}$ at 298 K. The H-migrations in **T**-R1-QP would be too slow because of high barriers of $> 130\text{ kJ/mol}$. For **EB** and **IB**, the R4-QP2 radicals could undergo a different H-migration from the methyl group with barriers of only 83.0 kJ/mol and 79.4 kJ/mol. Radicals R4-QP2-OO as HO-Ar-(O₂)₄ are followed by the addition of the fourth O₂. A third H-migration in R4-QP2-OO is also possible in analogy to that in R4-BPRs (**Scheme 3**). It should be noted here that the barrier heights might be over-estimated because the T1 diagnostics in ROCCSD calculations of these transition states were higher than 0.05. Similar effective rate coefficients for **EB**- and **IB**-QPs are expected because methyl substitution would have a small effect on the barrier height (might be slightly smaller due to the increased size of the radicals). HOMs are formed as Ar(O₂)₃ isomers

from both R2-QPH2 and R4-QP1s and Ar(O₂)₄ from R4-QP2, all with a recycling of OH radicals.

The theoretical results here suggested potential formation pathways for highly oxygenated HO-Ar-(O₂)₃ radicals as R4-QP1 and R4-QP2 in **T** and as all possible QPs in **EB** and **IB** via the first H-migration in BPRs (**Scheme 2**), as well as the formation of the corresponding closed-shell HOMs as Ar-(O₂)₃ (from R2-QPs and R4-QP1) after a second H-migration (**Scheme 3**). In the atmosphere, radicals HO-Ar-(O₂)₃ would also react with NO and HO₂ radicals forming organic nitrates, hydroperoxide moiety-containing HOMs, and others.⁵²

Figure 1. Mass spectra recorded from the reaction of OH radicals with isopropylbenzene, **IB**. The red spectrum represents the background measured in absence of isopropylbenzene. Products are detected as adduct with acetate. The spectrum depicted in part A was measured in absence of NO and that in part B with a NO concentration of 5×10^{10} molecules cm⁻³. Reactant concentrations (unit: molecules cm⁻³): [O₃] = 6.6×10^{11} , [TME] = 1.0×10^{11} and [isopropylbenzene] = 1.64×10^{13} .

Experimental Results

The predicted formation of highly oxidized radicals and closed-shell products having undergone multiple H-migration steps was further investigated in a flow tube reactor. At the low radical concentrations and short reaction times (7.9 s) used, bimolecular reactions between radicals are negligible and any detected highly oxidized RO₂ radicals should arise dominantly from unimolecular pathways. Low radical concentrations suggest negligible reactions between BPRs and between BPRs and other peroxy radicals or HO₂ radicals.

Figure 1A shows a measured mass spectrum during an experiment where **IB** was oxidized by OH radicals. Signals at nominal mass-to-charge ratios 260, 292 and 324 Th were attributed to the acetate adducts of RO₂ radicals with chemical formula HO-C₉H₁₂-(O₂)_x with x = 2, 3 and 4, respectively. The radicals with x = 2 would thus correspond to BPRs, those with x = 3 to R2-QPH2 and R4-QP1/QP2, and those with x = 4 to R4-QP2-OO in **Schemes 2 and 3**. Signals at 275 and 307 Th can correspond to the closed-shell products arising from the RO₂ radicals with x = 3 and 4, respectively, after formal loss of one -OH group (-17 Th). The signals at 275 Th and 307 Th are consistent with the products Ar-(O₂)₃ and Ar-(O₂)₄, i.e. C₉H₁₂-(O₂)₃ and C₉H₁₂-(O₂)₄ in **IB** in **Scheme 3**.

Experiments in the presence of NO were carried out in order to test for the functionality of the supposed RO₂ radicals by measuring the corresponding organic nitrates formed via RO₂ + NO → RONO₂. Figure 1B clearly illustrates the occurrence of the expected nitrates from the RO₂ radicals with x = 2 and 3 for [NO] of 5 × 10¹⁰ molecules cm⁻³, strongly supporting the identification of highly oxidized RO₂ radicals. Moreover, H/D exchange experiments with D₂O have been performed to identify the number of acidic H atoms in the products, i.e. the total number of HO- and HOO-groups.⁵⁴ Figures S4a and S4b show mass spectra from the reaction of

OH radicals with **IB** recorded in absence and presence of D₂O, respectively. According to that, the RO₂ radical HO-C₉H₁₂(O₂)_x with x = 2 (BPRs) contains only one acidic H-atom, very likely the HO-group from the attacking OH radical on the aromatic ring, being in line with the assumed BPR structure in **Scheme 2**. Two acidic H-atoms were found for the RO₂ radical with x = 3 and its corresponding closed-shell product formed after elimination of one OH group, consistent with the expected RO₂ radicals R2-QPH2 and R4-QP1/QP2 and closed-shell Ar-(O₂)₃, respectively, which either contain one HO- and one HOO-group or two HOO-groups (**Scheme 3**). Similarly, three acidic H-atoms were found for the RO₂ radical with x = 4 and closed-shell compounds after eliminating one OH group, consisting with the expected R4-QP2-OO and Ar-(O₂)₄ in **Scheme 3**. It should also be noted that the HO-Ar-(O₂)_x intensities for x = 2 are most likely underestimated due to the presence of only one HO-group and the associated relatively low acetate-cluster stability, and better detection sensitivity is expected for the radicals with x = 3 and 4 as well as for the closed-shell products with x = 3 -17 Th due to the presence of a second functional group that enhances the cluster stability.⁵⁵

Figure 2 shows a comparison of the detected RO₂ radicals and closed-shell HOMs from the OH radical reactions of benzene (part A) and **IB** (part B). The almost linear increase of the RO₂ radical concentrations with rising precursor conversion indicates the absence of significant bimolecular reactions with other RO₂ or HO₂ radicals. Low HO-C₆H₆(O₂)_x with x = 3 and 4 from benzene is consistent with the extremely high barriers of more than 120 kJ/mol for H-migrations in BPR of benzene (Figure S5). The detection of the corresponding nitrates from HO-C₆H₆(O₂)_x with x = 3 and 4 in benzene was impossible due to insufficient signal intensities. Results for toluene and ethylbenzene are given in Figures S6 and S7.

Figure 2. Signals attributed to RO₂ radical HO-aromatic(O₂)_x for x = 2, 3 and 4 as a function of reacted benzene (part A) and isopropylbenzene (part B). The closed-shell product formed from the RO₂ radical with x = 3 (x = 3 -17 Th) is given in B as well. Reactant concentrations (unit: molecules cm⁻³): [O₃] = (3.4 – 75) × 10¹⁰, [TME] = 1.0 × 10¹¹, [benzene] = 1.0 × 10¹⁴ and [isopropylbenzene] = 1.64 × 10¹³. Organic nitrate detection for RO₂ radicals shown with a dashed line was not successful caused by low signal intensity.

Figure 3. RO₂ radical concentrations HO-Ar-(O₂)_x with x = 3 normalized by the RO₂ concentration for x = 2 observed from the reaction of OH radicals with benzene, toluene, ethylbenzene and isopropylbenzene. The given ratio for the benzene system represents an upper limit because of the large uncertainty of the HO-(C₆H₆)(O₂)₃ concentration.

The importance of alkyl substitution for the formation of highly oxidized RO₂ radicals becomes obvious from the comparison of the experimental results for the four aromatic compounds investigated (Figure 3). The ratio HO-Ar-(O₂)₃/HO-Ar-(O₂)₂ is independent of the amount of converted aromatic compound for all four reaction systems, being in line with the almost linear signal increase with rising precursor conversion as given in Figures 2, S5 and S6. The observed trend of the ratios is in accordance with the predicted overall rates of $\sim(8.8 - 14)$, ~ 7.0 , and $\sim 2.6 \times 10^{-2} \text{ s}^{-1}$ from BPRs ($x = 2$) to HO-Ar-(O₂)₃ for **IB**, **EB**, and **T**. Note that some HO-Ar-(O₂)₂ radicals have no H-migration channel, such as the R2-13OO-s-4OO-a, because no neighboring hydrogen is available in these structures.

Atmospheric Implication We have predicted theoretically and confirmed experimentally the occurrence of intramolecular H-migrations in BPRs formed in the atmospheric oxidation of **T**, **EB**, and **IB** and the subsequent formation of HOMs in gas phase. These HOMs should contribute significantly to the formation of SOA in urban areas. Earlier studies have shown the importance of HOMs in the OH-initiated oxidation of biogenic VOCs,⁴⁴ and we have now found that similar HOM formation pathways exist also for alkylbenzenes in the atmosphere. The recycling of OH radicals along with the gas-phase formation of Ar-(O₂)₃ from R2/R4-BPRs suggests a certain degree of autoxidation without the involvement of HO₂/NO. The role of H-migration might be more important in *m*-xylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene than in toluene because of the higher branching ratios of $\sim 13\%$, $\sim 27\%$, and $>90\%$ for R4 radicals than that of $\sim 5\%$ in toluene amongst the OH addition channels.^{11, 48, 49}

ASSOCIATED CONTENT

Supporting Information. Details of theoretical and experimental methods, potential energy profiles for internal rotations, mass spectra, and potential energy diagram for Benzene-BPR. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interests.

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