Rate coefficients and product branching ratios for the oxidation of phenyl and naphthyl radicals: A theoretical RRKM-ME study

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Abstract. Theoretical VRC-TST/RRKM-ME calculations were performed to evaluate total rate coefficients and product branching ratios for the oxidation of phenyl and 1- and 2-naphthyl radicals with O₂ at temperatures relevant to combustion (1500, 2000, and 2500 K) and pressures of 0.01, 0.1, 1.0, and 10 atm. The results give the rate coefficients in the range of $3.0\text{--}5.5\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ with slightly positive temperature dependence, activation energies varying within 2.3–3.3 kcal/mol, and pre-exponential factors of $7\text{--}10\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The dominant reaction channel in all three cases is elimination of the oxygen atom from peroxy complexes formed at the initial O₂ addition step and leading to the phenoxy and naphthoxy radical products. The contribution of this channel increases with temperature. Chemically-activated phenoxy and naphthoxy radicals either decompose to the cyclopentadienyl+CO and indenyl+CO products, respectively, or undergo thermal equilibration. The relative yields of the decomposition/equilibration products strongly depend on temperature and pressure in the way that a temperature growth favors decomposition, whereas an increase in pressure favors equilibration. At the lowest temperature considered, 1500 K, the reactions also yield significant amounts of pyranil+CO (phenyl+O₂) or 1-benzopyranil+CO (1-naphthyl+O₂). A comparison of the phenyl+O₂ and naphthyl+O₂ reactions reveals that although the general trends in the oxidation kinetics of phenyl and naphthyl radicals are similar, the size and especially the position of the radical site in the aromatic moiety may affect the details of the mechanism and relative product yields.

Keywords: Oxidation, Reaction mechanisms, PAH, Soot

1. Introduction

The reactions of aromatic radicals with molecular oxygen play an important role in combustion of hydrocarbon fuels. The oxidation reactions on one hand compete with the formation of polycyclic aromatic hydrocarbons (PAH) in combustion flames but on the other hand, produce smaller species. Some of them contain five-member rings, such as cyclopentadienyl and indenyl, which in turn, propagate further PAH synthesis and thus contribute to the formation of a large variety of cyclopentafused PAH. In addition, oxidation generates energy for further growth processes [1].

Phenyl and naphthyl are prototypes of single and multi-ring aromatic radicals. A detailed theoretical analysis of the mechanism and kinetics of their reactions with O_2 is sought to better understand how larger PAH radicals are oxidized in flames. The mechanism and kinetics of the $C_6H_5+O_2$ reaction has received considerable attention by the combustion community in the last two decades [2-17].

Previously, Mebel and co-workers reported an extensive *ab initio* G2M study of the $C_6H_5O_2$ potential energy surface (PES) to map out the detailed mechanism of the phenyl radical oxidation [12]. According to their study, the most energetically favorable reaction channels are those leading to the formation of cyclopentadienyl radicals $c-C_5H_5$ together with $CO+O$ or CO_2 , followed by the channels producing pyranil+CO and o-benzoquinone+H. Noteworthy, the calculations showed that cyclic peroxides with five- or six-membered rings do not exist as stable local minima on the PES [7,12]. However, the PES by itself is not sufficient to predict reaction rate coefficients and product branching ratios at temperatures and pressures relevant to combustion.

Experimentally, rate coefficients for the $C_6H_5+O_2$ reaction have been measured in two overlapping temperature ranges, 297–473 K ($p = 20\text{--}80$ Torr) [5] and 418–815 K ($p = 0.7$ mbar) [14], which are considerably lower than typical combustion temperatures. The canonical variational transition state theory (CVTST) calculations based on a density functional O3LYP/6-31G(d) potential reported by Silva and Bozzelli [13] reproduced the experimental rate coefficients for the $C_6H_5+O_2$ association channel at temperatures close to 400 K, but failed to describe the observed temperature dependence. A question of

which reaction products can be formed under combustion conditions also remains open. Whereas at low temperatures the $\text{C}_6\text{H}_5+\text{O}_2$ reaction has been shown to proceed via the addition-stabilization mechanism leading to the phenyl peroxy radical $\text{C}_6\text{H}_5\text{OO}$ [5], at $T \geq 1000$ K the reaction is believed to produce $\text{C}_6\text{H}_5\text{O}+\text{O}$ with further fragmentation of phenoxy radical yielding the $\text{C}_5\text{H}_5+\text{CO}$ products [5,6]. Additionally, the minor reaction channels producing *o*- and *p*-benzoquinone, *o/p*- $\text{C}_6\text{H}_4\text{O}_2$, plus H atoms were also suggested [7]. However, the only products observed in the recent crossed molecular beam experiments at collision energies of 5-26 kcal mol⁻¹ [15-17], which correspond to high combustion temperatures and beyond, were $\text{C}_6\text{H}_5\text{O}+\text{O}$.

The oxidation of the smallest all-six-member-ring PAH radical, naphthyl, is less studied. Marinov et al. [18] estimated the rate coefficient of the $1\text{-C}_{10}\text{H}_7+\text{O}_2$ reaction producing $\text{C}_{10}\text{H}_7\text{O}+\text{O}$ in their kinetic modeling of a laminar premixed *n*-butane flame. Lin and co-workers have measured thermal rate coefficients for the 2-naphthyl+ O_2 system at temperatures of 299–444 K using cavity ring-down spectroscopy [19]. They also used G2MS//B3LYP/6-31+G(d,p) and CVTST calculations to compute the rate coefficients and reported a good agreement of their theoretical results with the experimental values. In terms of the reaction products, Lin and co-workers [19] proposed that at low temperatures the reaction proceeds via the association–stabilization mechanism forming the naphthyl peroxy radical $\text{C}_{10}\text{H}_7\text{OO}$ which then may lose the terminal oxygen atom yielding the naphthoxy radical, $\text{C}_{10}\text{H}_7\text{O}$. Mebel and co-workers [20] recently reported a detailed ab initio study for the reaction of 1- and 2-naphthyl radicals with O_2 augmented with a qualitative kinetic analysis. They computed rate coefficients for individual reaction steps at the high-pressure limit and product branching ratios in a steady-state regime. The simplified kinetic analysis revealed that some other products, such as indenyl+ CO_2 , 1,2-naphthoquinone+H, and 1- and 2-benzopyrans+CO may appear under combustion conditions. However, neither experimental nor theoretical data are available on pressure and temperature dependent product branching ratios.

The goal of the present study is to theoretically predict thermal rate coefficients and product branching ratios for the phenyl+O₂ and naphthyl+O₂ reaction systems at the conditions relevant to combustion, which can be integrated into kinetic simulations of hydrocarbon flames. Our approach in achieving this goal is to apply current theoretical models for kinetic calculations, such as the variable reaction coordinate-transition state theory (VRC-TST) to treat the barrierless entrance channels and RRKM-Master Equation (RRKM-ME) simulations to compute product branching ratios in the overall reaction mechanism.

2. Calculation Methods

2.1. Entrance channel reaction rate coefficients

The VRC-TST calculations of thermal rate coefficients for barrierless phenyl+O₂ and naphthyl+O₂ association channels were carried out using the VARIFLEX code developed by Klippenstein and co-workers [21,22]. Briefly, the VRC-TST approach separates the transition state's degrees of freedom into "conserved" and "transitional" modes. The conserved modes marginally change over the reaction process and are treated as rigid rotors or harmonic oscillators by directly computing the corresponding sums of states. The transitional modes are treated classically through a phase-space integral. Then, the partition function of a transition state is calculated through a convolution of these two types of modes, by varying the distance along the reaction coordinate and recalculating the contribution of the transitional modes to the partition function until a minimum reaction rate is found [21].

To compute the potential along the minimal energy reaction path (MEP), i.e., the stretching potential, for the addition of O₂ to C₆H₅, we scanned the PES by fixing the reaction coordinate, i.e., the C₆H₅—O₂ bond distance $r(\text{C}_6\text{H}_5\text{—O}_2)$, while fully optimizing all other geometric parameters. $r(\text{C}_6\text{H}_5\text{—O}_2)$ was varied within the 1.4-4.0 Å range with a step size of 0.05 Å and C_s symmetry constraints were imposed with the O₂ and C₆H₅ fragments lying in the same plane. The MEP potential was computed at two levels of theory, single-reference B3LYP/6-311++G** and multi-reference complete-active-space self-

consistent-field CASSCF(9,9)/aug-cc-pVDZ. The potential obtained by the PES scan at the CASSCF(9,9)/aug-cc-pVDZ level was further refined by single point energy calculations at the higher multi-reference second-order perturbation-theory CASPT2(19,14)/aug-cc-pVDZ level (further details of MEP calculations can be found in the Supplemental Material).

For the larger naphthyl+O₂ system, we used the CASPT2(19,14) stretching potential computed for the phenyl+O₂ system scaled to reproduce the accurate C₁₀H₇—O₂ bond dissociation energies in the 1- and 2-naphthyl peroxy radicals computed at the G3(MP2,CC) level [20]. All density functional and ab initio calculations were carried out using the GAUSSIAN 98 [23], MOLPRO 2002 [24], and DALTON 2.0 [25] program packages.

The computed stretching potentials for VARIFLEX calculations were provided in a tabulated form and then interpolated by the VARIFLEX built-in procedure. The anisotropy of the potential was taken into account by specifying the OOC and OCC angles corresponding to the equilibrium structures of phenylperoxy and naphthylperoxy radicals. The geometries, frequencies, and moments of inertia required for VRC-TST calculations were taken from the previous quantum mechanical studies [12,20]. The energy grain size and maximum energy value utilized in VARIFLEX calculations were identical to those values used in RRKM-ME simulations described in the following section.

The O atom loss from the C₆H₅OO intermediate **1** (Figure S1) and C₁₀H₇OO intermediates **a1** (Figure S2) and **b1** (Figure S6) occurs via distinct transition states followed by weakly bound van der Waals complexes **2**, **a2**, and **b2**, respectively. However, at high temperatures considered in the present study, the tight transition states, such as that between **1** and the C₆H₅O...O complex **2** and its analogs in the naphthyl+O₂ system, represent kinetic bottlenecks for the dissociation (O loss) processes and the complexes do not play any kinetic role. Therefore, the rate coefficients for the oxygen atom loss from **1**, **a1**, and **b1** were computed using the distinct transition states leading to the van der Waals complexes.

2.2. RRKM-ME calculations of product branching ratios

The rate coefficients of the chemically-activated reaction systems were computed using the MultiWell 2012.2 code [26-28] for the phenyl+O₂ and naphthyl+O₂ reaction mechanisms from the PESs published earlier and shown in the Supplemental Material (see Figures S1-S9). MultiWell solves the one-dimensional time-dependent energy-transfer master equations for a multi-well and multi-channel unimolecular reaction system using the Monte Carlo stochastic method. Microcanonical rate coefficients for all elementary reactions involved were computed with MultiWell at the RRKM level.

Key parameters required for MultiWell simulations, such as reaction barriers, frequencies, and moments of inertia, were taken from the previous calculations [12,20]. Following Gilbert and Smith [29], vibrational frequencies were examined by graphically visualizing the associated normal mode vibrations to identify internal rotational modes and, accordingly, all internal rotors were treated as 1-D hindered rotors. The microcanonical rate constants for the barrierless entrance reactions (computed by VARIFLEX as described in the previous section) were read into MultiWell and directly incorporated into the ME simulation.

Reaction rates were computed at three different temperatures of 1500, 2000, and 2500 K and pressures of 0.01, 0.1, 1.0, and 10 atm. In the future, we plan to continue our study to give comprehensive rate coefficients (including lower temperatures and higher pressures) to all channels. Argon was chosen as the bath gas collider. The exponential-down model with $\langle\Delta E\rangle_{\text{down}} = 260 \text{ cm}^{-1}$ was used to describe the collisional energy transfer [30]. Lennard-Jones parameters were estimated from an empirical correlation [31]. The exact count, with an energy grain size of 10 cm^{-1} for the first segment of the double array and a maximum energy of $500,000 \text{ cm}^{-1}$, was employed to determine the density of states. For each set of initial conditions, the number of trials was varied to keep statistical error below 5 %.

The chemical-activated rate coefficients were derived from the accumulated species fractions of the products, as we have done previously [32]. The accumulated species fractions were found by running a MultiWell simulation started with a chemical-activated initial energy distribution. The species fractions were found after the average energy of the initial adduct converges, indicating the end of the chemically-

activated simulation. Simulation times ranged from 10^{-8} s ($T=2500$ K, $p=10$ atm) to 8×10^{-5} s for ($T=1500$ K, $p=0.01$ atm). Product formation rates were obtained by multiplying the species fractions of the products by the high-pressure reaction rate coefficient of the adduct formation reaction. Our solution is independent of time. The evolving populations as a sum of the direct and indirect routes is also a description of a real kinetic system, and similar tools, as described here and in [32], are used to extract phenomenological rate constants.

3. Results and Discussion

3.1. Overall thermal rate coefficients

It is imperative to compare the computed overall phenyl+O₂ → products rate coefficients with the available experimental data. Since our goal is to generate reliable rate coefficients for combustion temperatures, we focus our comparison on the higher-temperature data set reported by Schaugg and co-workers for the 418–815 K temperature range and $p = 0.7$ mbar measured using a fast flow reactor technique [14]. As seen in Figure 1, the VRC-TST/RRKM-ME calculations closely reproduce Schaugg’s experiment. The difference between the calculated and measured rate coefficients is within a factor of 1.4–2.0 at higher temperatures (656–815 K) and slightly increases to a factor of 3.0 at 418 K. The calculated rate coefficients show positive temperature dependence, which is consistent with the experiment; the fitted Arrhenius expression gives the activation energy of 1.9 kcal/mol, only slightly higher than the apparent activation energy of 0.6 kcal/mol observed in experiment. The agreement between the theoretical and experimental activation energies is even better within the higher temperature 724–815 K range, where the measured rate coefficients exhibit strong Arrhenius-like behavior with $E_a = 2.2$ kcal/mol.

One can expect that our theoretical rate coefficients calculated at temperatures relevant to combustion should be accurate within 40% or better as the agreement between experiment and theoretical predictions improves with temperature. Meanwhile, the larger deviation observed at low temperatures (T

= 418 K) may be attributed to the fact that computed rate coefficients are much more sensitive to inaccuracies in the stretching potential and in the theoretical approach in general, the factors which affect theoretical rate coefficients more significantly at lower temperatures than at high temperatures. Interestingly, the low-temperature kinetic measurements reported by Yu and Lin [5] for the 297–473 K temperature range and pressures of 20–80 Torr show a negative activation energy of -0.32 kcal/mol, although in the temperature range where the two experimental data sets overlap, 418–473 K, the rate coefficients obtained by Yu and Lin are in close agreement with those measured by Schaugg et al.

The available experimental data suggest that the rate coefficient has a minimum at around 400 K. Such a behavior can be explained by the fact that the bimolecular rate coefficient is proportional to $\exp(\Delta S^\ddagger/R) \times T^2 \times \exp(-\Delta H^\ddagger/RT)$ and even though the reaction is barrierless and thus has a negative $\Delta H^\ddagger$, as the temperature rises, the decrease of $\exp(-\Delta H^\ddagger/RT)$ appears to be slower than the increase of T^2 in the pre-exponential factor. A physical reason for the rate coefficient to pass through the minimum could be the role played by two (entrance and exit) transition states. At low temperatures the loose, barrierless association TS is dominant and the rate constant decreases with increasing temperature. At high temperatures the tight TS separating intermediate **1** from van der Waals complex **2** dominates and the reaction behaves qualitatively like it has a single TS with essentially no barrier - the rate coefficient increases with increasing temperature. Noteworthy is that our calculations correctly reproduced the positive temperature dependence of the rate coefficient at higher temperatures, whereas the earlier calculations by Silva and Bozzelli [13] did not.

Rate coefficients for the phenyl+O₂ and 1- and 2-naphthyl+O₂ reactions computed at combustion-relevant temperatures of 1500–2500 K are collected in Table 1. Since the total rate coefficients are practically pressure-independent, only the values computed at 1 atm are presented in Table 1, whereas the data for the other pressures (0.01, 0.1, and 10 atm) are given in the Supplemental Material (Tables S1-S15). The results demonstrate that $k_{\text{total}}(\text{phenyl}+\text{O}_2)$ and $k_{\text{total}}(1\text{-naphthyl}+\text{O}_2)$ are in the range of 3.0-4.2×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ and are close to each other at the same temperatures, with differences not

exceeding 10%. In contrast, $k_{\text{total}}(2\text{-naphthyl}+\text{O}_2)$ is computed to be 15–32 % higher, in the range of $3.5\text{--}5.5\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A simple Arrhenius fit of the computed rate coefficients gives the A factors of 6.68×10^{-11} , 6.77×10^{-11} , and $1.05\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the phenyl+O₂, 1-naphthyl+O₂, and 2-naphthyl+O₂ reactions, respectively, with the corresponding activation energies being 2.47, 2.33, and 3.27 kcal/mol, respectively.

3.2. Product branching ratios and individual rate coefficients for product formation

Considering the phenyl + O₂ system, the reaction products include phenoxy radical C₆H₅O + O, pyranlyl C₅OH₅ + CO, C₅H₅+CO₂, and 1,2-benzoquinone C₆H₄O₂ + H [12]. Phenoxy radical, due to its chemical activation, can further dissociate to cyclopentadienyl C₅H₅ + CO. For the 1-(2-)naphthyl + O₂ systems, the predicted reaction products include 1-(2-)naphthoxy 1-(2-)C₁₀H₇O + O, 1-(2-)benzopyranlyl 1-(2-)C₉OH₇ + CO, and 1,2-naphthoquinone 1,2-C₁₀H₆O₂ + H [20]. Chemically-activated naphthoxy radicals can further decompose to indenyl C₉H₇ + CO.

An important finding of our RRKM-ME simulation is the fact that collisionally stabilized intermediates were practically not detected as products in the temperature range of 1500–2500 K and at all studied pressures. The fact that there is no stabilization of the initial adduct was verified based on the output of MultiWell calculations, which provides an average energy of each potential well at each time. Using this, we tracked the energy of the initial adduct and confirmed that it is in an excited state even after the species fractions has dropped to insignificant levels (less than 10⁻⁴). This allowed us to conclude that no stabilization followed by thermal decomposition has occurred. The MultiWell calculations performed at four different pressures revealed that the combined yield of phenoxy radical and its decomposition product C₅H₅+CO as well as the combined yields of 1- or 2-naphthoxy radicals and their decomposition product indenyl+CO, are pressure-independent. The same is true for the branching ratios of all other reaction products. Hence, Figure 2 shows plots of the branching ratios only as functions of temperature.

The oxygen atom elimination, leading to phenoxy+O and eventually to C_5H_5+CO+O , is the dominant reaction channel for the phenyl+O₂ system, with its branching ratio increasing from 0.83 at 1500 K to 0.97 at 2500 K. The second significant channel is pyranlyl+CO with the highest yield of 0.10 observed at the lowest temperature of 1500 K. For all other products, including $C_5H_5+CO_2$ and $1,2-C_6H_4O_2+H$, the branching ratios do not exceed 0.05. The product yields are similar for the 2-naphthyl+O₂ reaction, where the combined branching ratio of the 2-naphthoxy+O/indenyl+CO products increases from 0.81 at 1500 K to 0.95 at 2500 K. The only slight difference from the phenyl+O₂ system is that the relative yields of the other products are nearly equally distributed at 0.06-0.07 (1500 K), 0.03-0.04 (2000 K), and 0.01-0.02 (2500 K).

The 1-naphthyl+O₂ reaction displays a somewhat distinct behavior. The O atom elimination channel leading to 1-naphthoxy and then to indenyl+CO is still the major channel, with its branching ratio increasing from 0.51 to 0.77 with temperature. However, the contributions of the other channels are more significant than those for the phenyl+O₂ and 2-naphthyl+O₂ reactions; for instance, the branching ratios of 1-benzopyranlyl+CO, $1,2-C_{10}H_6O_2+H$, and indenyl+CO₂ range from 0.24, 0.14, and 0.11 at 1500 K to 0.13, 0.07, and 0.03 at 2500 K, respectively. The higher yields of these other products formed after an O atom insertion into the aromatic ring in the 1-naphthyl+O₂ reaction correlates well with the relative energy of the transition state for this insertion, -25.5 kcal/mol with respect to the initial reactants, that is substantially lower than the corresponding values for the phenyl+O₂ and 2-naphthyl+O₂ reactions, -18.9 and -20.0 kcal/mol, respectively [12,20].

The phenoxy and naphthoxy radicals formed after elimination of an O atom from the initial phenyl peroxy and naphthyl peroxy radical complexes can further dissociate to C_5H_5+CO or indenyl+CO due to their chemical activation or, alternatively, can be thermally equilibrated by collisions. The equilibrated species may then undergo thermal decomposition but we do not consider this secondary reaction mechanism in the present study and count the equilibrated C_6H_5O and $1-/2-C_{10}H_7O$ radicals as final products of the primary reactions.

The MultiWell calculations reveal that the branching ratios of $\text{C}_6\text{H}_5\text{O}+\text{O}$ vs. $\text{C}_5\text{H}_5+\text{CO}+\text{O}$ and of $1\text{-C}_{10}\text{H}_7\text{O}+\text{O}$ vs. indenyl+CO+O strongly depend both on temperature and pressure. Figure 3 shows rate coefficients for the formation of these individual products at different pressures and temperatures, which are computed by multiplying the total rate coefficients with the product branching ratios. In the phenyl+O₂ reaction, at the lowest pressure of 0.01 atm and a temperature of 1500 K, a large fraction of phenoxy radicals equilibrate rather than dissociate and the computed rate coefficients for the formation of the $\text{C}_6\text{H}_5\text{O}+\text{O}$ and $\text{C}_5\text{H}_5+\text{CO}+\text{O}$ products are 1.74×10^{-11} and 7.06×10^{-12} cm³ molecule⁻¹ s⁻¹, with their respective branching ratios being 0.59 and 0.24, respectively. However, dissociation becomes more favorable than equilibration with a further temperature increase, and the rate coefficient to produce $\text{C}_5\text{H}_5+\text{CO}+\text{O}$ and its branching ratio rise to 3.90×10^{-11} cm³ molecule⁻¹ s⁻¹ and 0.94, respectively. The rate coefficient and branching ratio for the reaction channel leading to $\text{C}_6\text{H}_5\text{O}+\text{O}$ drop to 1.33×10^{-12} cm³ molecule⁻¹ s⁻¹ and 0.03, respectively. The increase in pressure at constant temperature increases the yield of equilibrated $\text{C}_6\text{H}_5\text{O}$ and accordingly the rate coefficient to form this product. Since the combined branching ratio of the two products is pressure-independent, the pressure increase also reduces the yield and the rate coefficient for $\text{C}_5\text{H}_5+\text{CO}+\text{O}$. Nevertheless, even at the highest pressure of 10 atm and temperature of 2500 K most of phenoxy radicals dissociate and the branching ratio of $\text{C}_5\text{H}_5+\text{CO}+\text{O}$ is still 0.61 vs. 0.36 for equilibrated $\text{C}_6\text{H}_5\text{O}+\text{O}$.

The 1-naphthyl+O₂ reaction shows similar trends but with two caveats. First, the combined branching ratios of $1\text{-C}_{10}\text{H}_7\text{O}+\text{O}$ /indenyl+CO+O are lower than the respective values for $\text{C}_6\text{H}_5\text{O}+\text{O}$ / $\text{C}_5\text{H}_5+\text{CO}+\text{O}$ and hence, the individual rate coefficients of both 1-naphthoxy and indenyl product channels are lower as compared to those for phenoxy and cyclopentadienyl. Second, the decomposition of chemically-activated 1-naphthoxy radicals to indenyl+CO from the 1-naphthyl+O₂ reaction is generally less favorable than the decomposition of chemically-activated phenoxy radicals from phenyl+O₂. As a result, at the high pressure of 10 atm, which strongly favors the equilibration process, the computed branching

ratio of indenyl+CO+O, 0.34, remains lower than the respective value of 0.43 for 1-naphthoxy+O even at the highest temperature of 2500 K.

The 2-naphthyl+O₂ reaction exhibits similar trends: the relative yield for the indenyl+CO+O decomposition products and the respective rate coefficient increase with temperature and decrease with pressure, whereas the opposite behavior is observed for the equilibrated 2-naphthoxy product. However, the decomposition process in this system appears to be significantly more favorable. At the lowest pressure of 0.01 atm, least conducive for equilibration, the branching ratio of indenyl+CO+O ranges from 0.66 at 1500 K to 0.95 at 2500 K, with that for equilibrated 2-naphthoxy+O being 0.15 and 0.00, respectively.

The 2-naphthoxy+O product becomes more favorable than indenyl only at the higher pressures of 1 and 10 atm and only at our lowest temperature of 1500 K, whereas at higher temperatures, especially at 2500 K, indenyl remains the dominant product. Again, the differences in the branching ratios of the C₅H₅+CO+O and indenyl+CO+O decomposition products can be traced back to the PESs for the fragmentation of phenoxy and 1- and 2-naphthoxy radicals. The critical barriers on their dissociation pathways were computed to be 53.8, 58.2, and 48.3 kcal/mol, respectively [12,20], clearly indicating that the decomposition process is most favorable for 2-naphthoxy and least favorable for 1-naphthoxy, in line with the observed trends in the branching ratios. In turn, the difference in the barrier heights for the phenoxy and naphthoxy radicals can be attributed to the difference in the relative stability of the bi(tri)cyclic intermediates **4** (phenoxy), **a4** (1-naphthoxy), and **b4** (2-naphthoxy) [12,20], where **a4** is destabilized as compared to **4** due to the rigidity introduced by the presence of the additional C₆ ring next to the rearrangement site, but **b4** in contrast is stabilized by extra electronic delocalization owing to the presence of the additional ring away from the rearrangement site.

4. Conclusions

Theoretical VRC-TST/RRKM-ME calculations show that total rate coefficients for the oxidation reactions of aromatic phenyl and naphthyl radicals with O₂ at combustion-relevant temperatures of 1500–2500 K and pressures of 0.01–10 atm are in the range of $3.0\text{--}5.5\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ and exhibit positive temperature dependence with activation energies of 2.3–3.3 kcal/mol and pre-exponential factors of $7\text{--}10\times10^{-11}$ cm³ molecule⁻¹ s⁻¹. The phenyl+O₂ and 1-naphthyl+O₂ rate coefficients are similar to each other, whereas those for 2-naphthyl+O₂ are 15–30% higher. The dominant channel for all three oxidation reactions is elimination of the oxygen atom from peroxy complexes formed at the initial O₂ addition step and leading to phenoxy and naphthoxy radical products. The contribution of this channel increases with temperature. For phenyl+O₂, a small but significant yield of pyranil+CO, 0.10, is observed at the lowest temperature of 1500 K. For 1-naphthyl+O₂, the branching ratio of 1-benzopyranil+CO at 1500 K is somewhat higher, 0.24, and those for 1,2-naphthobenzoquinone+H and indenyl+CO₂ also slightly exceed 0.10. In contrast, the relative yields of 2-benzopyranil, indenyl, and 1,2-naphthobenzoquinone are found to be minor for the 2-naphthyl+O₂ reaction over the entire 1500–2500 K temperature range. Also, the relative yields of products formed after O insertion into an aromatic ring are independent of pressure.

Chemically-activated phenoxy and naphthoxy radicals can further decompose to cyclopentadienyl+CO and indenyl+CO, respectively, or undergo thermal equilibration. The branching of decomposition/equilibration products strongly depends on temperature and pressure, in the way that an increase in temperature favors decomposition and an increase in pressure favors equilibration. The decomposition process is found to be most favorable for 2-naphthoxy radical and least favorable for 1-naphthoxy, with phenoxy radical being intermediate.

Our study shows that although the general trends in the oxidation kinetics of phenyl and naphthyl radicals are similar (similar rate coefficients, dominance of the O₂ addition/O elimination channel, small but still significant yields of pyranil-like products at lower temperatures), they may differ in details. The differences are attributed not only to the size of the aromatic species but also to the position of the

radical site in the aromatic moiety. Further studies of the PESs and kinetics of larger polycyclic aromatic radicals, such as acenaphthyl, phenathryl, and anthracyl would be informative to generalize the new insights into the oxidation mechanisms of larger PAH. Although one the primary motivations for this study was to provide reaction rate data for larger PAHs and soot, a direct comparison between small PAH rate coefficient values, such as those computed in the present work, and experimental soot oxidation rates is not fully appropriate. A truly meaningful comparison requires considering a fuller set of reactions, not just oxidation of an “open” aromatic radical with O₂, but also creation of such radical sites and competing reactions for those sites. More importantly, not all radical sites will undergo such oxidation; for example, as was established in a recent study [33], a radical site on a zigzag edge does not undergo oxidation. This is clearly a subject for future studies. The present rates are sufficiently fast (as compared to the values presently used in soot models) to allow for slower overall oxidation rates due to competing reactions or surface site unavailability.

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Table 1. Total bimolecular rate coefficients of product formation (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) calculated at different temperatures and $p = 1 \text{ atm}$.

$T, \text{ K}$	phenyl+O ₂	1-naphthyl+O ₂	2-naphthyl+O ₂
1500	2.96×10^{-11}	3.08×10^{-11}	3.53×10^{-11}
2000	3.46×10^{-11}	3.81×10^{-11}	4.58×10^{-11}
2500	4.16×10^{-11}	4.20×10^{-11}	5.49×10^{-11}

Figure Captions

Figure 1. Comparison of the calculated total rate coefficients of the phenyl+O₂ reaction with the experimental data at $T = 418\text{-}815 \text{ K}$ (from [14]).

Figure 2. Temperature dependence of product branching ratios of the phenyl+O₂ (a), 1-naphthyl+O₂ (b), and 2-naphthyl+O₂ (c) reactions. Combined branching ratios are shown for the C₆H₅O+O/C₅H₅+CO+O, 1-C₁₀H₇O+O/indenyl+CO+O, and 1-C₁₀H₇O+O/indenyl+CO+O products.

Figure 3. Rate coefficients for the formation of the C₆H₅O+O and C₅H₅+CO+O products in the phenyl+O₂ reaction (a), 1-C₁₀H₇O+O and indenyl+CO+O in the 1-naphthyl+O₂ reaction (b), and 2-C₁₀H₇O+O and indenyl+CO+O in the 2-naphthyl+O₂ reaction (c) calculated at different temperatures and pressures.

Figure 1

Figure 2

Figure 3

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