

# Crossed beam reaction of the phenyl radical, ( $C_6H_5$ , $X^2A'$ ) with molecular oxygen ( $O_2$ , $X^3\Sigma_g^-$ ): Observation of the phenoxy radical, ( $C_6H_5O$ , $X^2A'$ )

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## Abstract

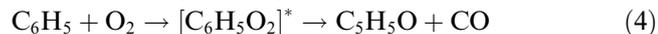
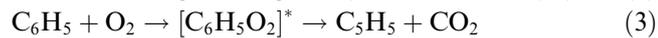
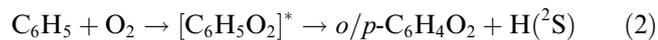
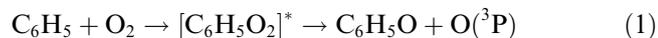
The chemical dynamics of the combustion-relevant reaction of phenyl radicals with molecular oxygen were investigated in a crossed beam reaction at a collision energy of  $107 \text{ kJ mol}^{-1}$ . Under these conditions, the formation of the phenoxy radical ( $C_6H_5O$ ) plus ground state atomic oxygen was observed; no atomic hydrogen exchange pathway was opened. The reaction dynamics of the phenoxy radical channel were found to be direct, involved a stripping-like reaction mechanism, and were initiated by a radical–radical recombination of phenyl plus molecular oxygen forming a short lived phenylperoxy radical ( $C_6H_5O_2$ ). The latter decomposed to the phenoxy radical plus atomic oxygen; the overall reaction was exoergic by about  $38 \pm 15 \text{ kJ mol}^{-1}$ .  
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## 1. Introduction

In recent years, the reaction of phenyl radicals ( $C_6H_5$ ) with molecular oxygen ( $O_2$ ) has received considerable attention both from the experimental and theoretical viewpoints due to its importance of incipient soot formation and also in the combustion processes of aromatic hydrocarbons. Here, chemical reaction networks, which model the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion flames, [1,2] suggest that the phenyl radical in its  $^2A_1$  electronic ground state presents one of the most important transient species to initiate the formation of PAHs. These studies have reached a consent that phenyl radical reactions with unsaturated hydrocarbon molecules such as acetylene trigger the PAH synthesis via an addition of the radical center of the phenyl radical to the  $\pi$  electronic system of the unsaturated co-reactant forming doublet radical intermediates [3]. However, at higher temperatures in combustion flames, the phenyl radicals can be also oxidized

by molecular oxygen [4]. Under combustion conditions, both processes – the growth and oxidation – are competing; consequently, the effective yield of soot formation depends dramatically on the significance of the elementary reactions inducing PAH growths versus an oxidation of the phenyl radical. At temperatures higher than 1000 K, the reaction of phenyl with molecular oxygen is thought to proceed via an initial addition process to form a ro-vibrationally excited phenylperoxy radical [ $C_6H_5O_2$ ]\* intermediate which decomposes primarily via ground state atomic oxygen loss (reaction (1)) [5,6]. A minor channel was suggested to involve atomic hydrogen elimination to *ortho*- and *para*-benzoquinone (reaction (2)). Further, electronic structure calculations predicted two additional pathways: cyclopentadienyl ( $C_5H_5$ ) plus carbon dioxide ( $CO_2$ ) (reaction (3)) and pyranil ( $C_5H_5O$ ) plus carbon monoxide (CO) (reaction (4)) [5]. However, experimental data on the reaction products obtained in a collision-free environment are lacking. Due to the importance of this reaction, we present in this communication data on the crossed molecular beam reaction of ground state phenyl radicals ( $C_6H_5$ ) with molecular oxygen ( $O_2$ ).

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## 2. Experiment and data processing

The experiments were conducted under single collision conditions in a crossed molecular beam machine at The University of Hawai'i [7]. Briefly, a pulsed supersonic beam of phenyl radicals was generated by flash pyrolysis of a helium-seeded nitroso benzene precursor ( $\text{C}_6\text{H}_5\text{NO}$ , Aldrich) at seeding fractions of less than 0.1% in the primary source chamber employing a modified Chen source; this unit was coupled to a piezoelectric pulsed valve operated at 200 Hz. At these conditions, the decomposition of the nitrosobenzene molecule to form nitrogen monoxide and the phenyl radical was quantitative. After passing a skimmer, a four-slot chopper wheel selected a part of the phenyl radical beam with a peak velocity,  $v_p$ , of  $2947 \pm 83 \text{ ms}^{-1}$  and a speed ratio,  $S$ , of  $6.0 \pm 1.0$ . This part of the phenyl radical beam intersected a neat molecular oxygen beam ( $v_p = 883 \pm 10 \text{ ms}^{-1}$ ;  $S = 7.0 \pm 1.0$ ) released by a second pulsed valve at a pressure of 550 torr perpendicularly in the scattering chamber at a collision energy

of  $107 \pm 6 \text{ kJ mol}^{-1}$ . The reactively scattered products were probed using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron impact ionization of the molecules operated at electron energies of 90 eV and an emission current of 2 mA. The detector could be rotated within the plane defined by the primary and the secondary reactant beams to take angular resolved TOF spectra. By integrating the TOF spectra at various laboratory angles, the laboratory angular distribution (LAB), which depicted the integrated signal intensity of an ion of distinct  $m/z$  versus the laboratory angle, could be obtained. Information on the chemical dynamics was gained by fitting these TOF spectra and the angular distribution in the laboratory frame (LAB) using a forward-convolution routine [8]. This approach initially assumed an angular distribution  $T(\theta)$  and a translational energy distribution  $P(E_T)$  in the center-of-mass reference frame (CM). This fitting route accounts for the transformation Jacobian and averages over the apparatus and beam functions such as the velocity distribution as expressed via the speed ratio and the angular divergence. The final result is the generation of a product flux contour map which states the differential cross section,  $I(\theta, u) \sim T(\theta) \times P(u)$ , of the product as the intensity as a function of angle  $\theta$  and product center-of-mass velocity  $u$ . This map serves as an image of the scattering process.

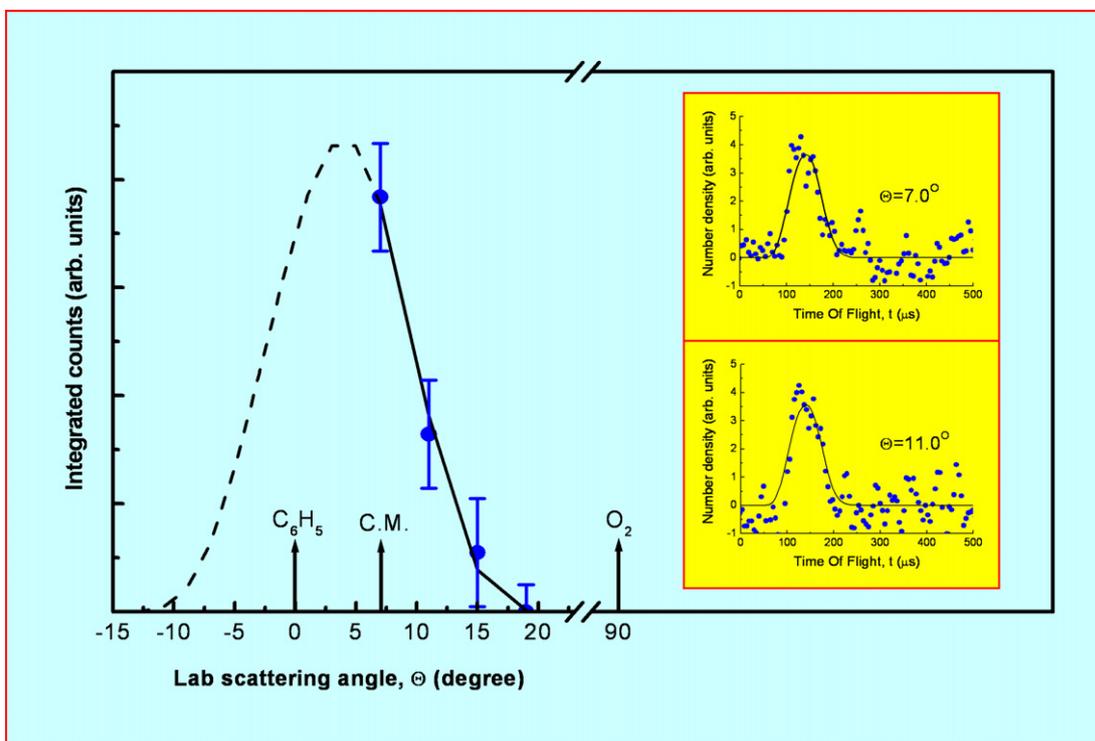


Fig. 1. Laboratory angular distribution of the phenoxy radical product ( $\text{C}_6\text{H}_5\text{O}$ ) at  $m/z = 93$  recorded. Shown is the intensity plotted versus the laboratory angle,  $\theta$ , in degrees. Dots and  $1\sigma$  error bars indicate experimental data, the solid lines the calculated distribution, and CM the center-of-mass angle. The dashed line presents the simulated part of the LAB distribution based on the best fit center-of-mass functions (Fig. 2). Also shown are time-of-flight data at selected laboratory angles; the flight time,  $t$ , is shown in microseconds and plotted against the counts. Dots represent experimental data, the solid line the fit.

### 3. Results

First, we investigated the kinematically most favorable reaction pathway, i.e. the atomic hydrogen loss channel (reaction (2)), and attempted to monitor reactive scattering signal at mass-to-charge  $m/z = 108$  ( $C_6H_4O_2^+$ ) and potential fragments of the nascent product formed during the dissociative ionization of  $C_6H_4O_2$  in the electron impact ionizer of the detector. However, we were unable to detect any reactive scattering signal within the mass-to-charge ratios of 108 to 104. Hereafter, we tuned the mass filter to  $m/z = 93$  to monitor the atomic oxygen loss pathway and the inherent synthesis of the phenoxy radical. Here, signal was observed at  $m/z = 93$  ( $C_6H_5O^+$ ). The time-of-flight (TOF) spectra for two laboratory angles were accumulated over 15 million scans and are shown together with the laboratory angular distribution (LAB) in Fig. 1. It should be noted that the center-of-mass of the reaction was at  $7.3^\circ$ , i.e. very close to the primary beam. An attempt to collect data closer to the beam failed since the background pressure in the detector increased significantly by two to three orders of magnitude; compare to the study of the phenyl–acetylene system, [3] we had to increase the bath temperature of the nitrosobenzene precursor and also the helium backing pressure. We were able to fit the TOF and LAB distribution of these data with a single channel and a mass combination of  $C_6H_5O$  (93 amu.) and O (16 amu.). The center-of-mass translational energy distribution peaks well away from zero between 60 and 80  $\text{kJ mol}^{-1}$ . This Gaussian-like, almost symmetric profile suggests that the fraction of energy released into the translational degrees of the products is expected to be rather large. Also, best fits of the LAB distribution and TOF spectra were obtained with  $P(E_T)$ s extending to 130–160  $\text{kJ mol}^{-1}$  (Fig. 2). Correcting for the relative collision energy of 107  $\text{kJ mol}^{-1}$ , this reveals an exoergicity of reaction (1) to form phenoxy radicals plus ground state oxygen atoms of  $38 \pm 15 \text{ kJ mol}^{-1}$ . This data compares nicely with a value of  $-36 \pm 14 \text{ kJ mol}^{-1}$  as obtained from thermodynamical databases [9] and also from a previous theoretical investigation of this pathway ( $-38 \pm 5 \text{ kJ mol}^{-1}$ ) [5]. Based on the  $P(E_T)$ s, we calculated that  $76 \pm 5 \text{ kJ mol}^{-1}$  on average is released into translational motion of the reactants, i.e. a large fraction of  $53 \pm 9\%$ . This order of magnitude suggests that rather direct nature of the reaction to form phenoxy plus atomic oxygen. Based on these considerations, we can conclude that channel (1) is certainly open. Attempts to detect reactive scattering signal of pathway (4) failed; no signal of the  $C_5H_5O + CO$  channel at  $m/z = 81$  was monitored. Accounting for the kinematics and data accumulation times, we determined that reaction (1) and (4) hold upper limit of 1% and 5% at the most. We acknowledge that due to the dissociative ionization of the phenyl radical to, for instance,  $C_5H_5^+$ , we could not investigate the role of pathway (3) experimentally. Finally, the corresponding center-of-mass angular flux distribution,  $T(\theta)$ , is strongly forward-scattered and shows no intensity

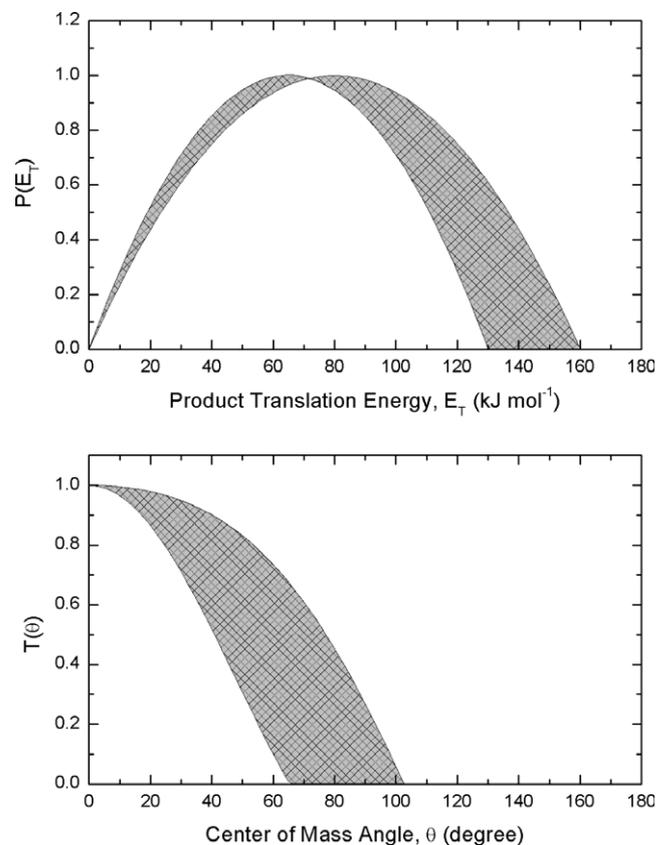


Fig. 2. Center-of-mass angular flux distributions ( $T(\theta)$ ) (lower) and translational energy flux distributions ( $P(E_T)$ ) (upper) for the reaction of phenyl radicals with molecular oxygen; the hatched areas limit the fits obtained within the error limits.

in the range of  $100^\circ$ – $180^\circ$ . This finding as also visualized in the flux contour map of the phenoxy radical (Fig. 3)

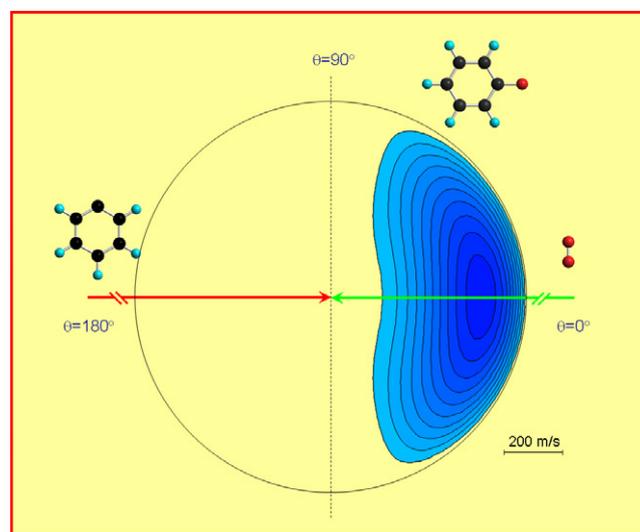


Fig. 3. Flux contour map of the phenoxy radical ( $C_6H_5O$ ) formed in the reaction of phenyl radicals with molecular oxygen. The carbon, hydrogen, and oxygen atoms are denoted in black, blue, and red. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

indicates that the chemical dynamics are rather direct. Also, this significant polarization results from a strong poor coupling between the initial and final orbital angular momentum. It should be stressed that although we could not obtain TOF data at angles closer to the phenyl radical beam, it was crucial to fit the TOF spectra and experimentally derived points of the LAB distribution with a strongly forward-scattered center-of-mass angular distribution. No fit could be obtained by imposing, for instance, forward-backward symmetric or backward-peaked profiles of the  $T(\theta)$ .

#### 4. Discussion and summary

Based on the TOF and LAB distributions and derived center-of-mass functions, we were able to elucidate experimentally the chemical dynamics of the phenoxy plus ground state atomic oxygen channel,  $C_6H_5O + O(^3P)$  (reaction (1)). Both the strongly forward peaked center-of-mass angular distribution and the large fraction of energy channeling in the translational degrees of the phenoxy plus atomic oxygen products of  $53 \pm 9\%$  indicate that the reaction dynamics are rather direct via an extremely short lived phenylperoxy radical holding life times of less than 0.01 ps [10]. Therefore, the phenyl radical likely picks up an oxygen atom from the oxygen molecule, and the phenoxy radical travels in the forward direction with respect to the phenyl radical beam (stripping dynamics). A previous theoretical study of this channel suggested that the phenylperoxy radical is formed without barrier and resides in a shallow potential energy well of only  $194 \text{ kJ mol}^{-1}$  with respect to the separated reactants. Considering the derived center-of-mass functions and flux contour map, the intermediate is highly ro-vibrationally excited and decomposes on a very short time scale. This is likely due to the effect of the high collision energy utilized in the present crossed beam study. Similar ‘direct’ dynamics involving the existence of short lived reaction intermediates have been also observed in the reactions of, for instance, excited state carbon atoms,  $C(^1D)$ , with ethylene, propylene, [11] and acetylene [12]. It should be recalled that we were unable to observe the kinematically most favorable atomic hydrogen loss pathway (reaction (2)). Mebel et al. suggested that this channel has to involve at least two isomerization processes of the initially formed phenylperoxy radical via a tight transition states located

only  $20 \text{ kJ mol}^{-1}$  below the separated reactants. Based on the failed observation of channel (2), we may conclude that the life time-of  $[C_6H_5O_2]^*$  is too short to allow these isomerization steps to take place. Likewise, the formation of  $C_5H_5O$  via reaction (4), which was not observed experimentally either, requires at least three isomerization steps from the initial adduct. Therefore, we can also suggest that the life time-of  $[C_6H_5O_2]^*$  is insufficient to allow this isomerization sequence to be competitive with the atomic oxygen loss. Summarized, the initial addition of the phenyl radical to molecular oxygen leads to a very short-lived, ro-vibrationally excited phenylperoxy radical formed under single collision conditions at a collision energy of  $107 \text{ kJ mol}^{-1}$ . Here, rather direct reaction dynamics dictate the formation of the phenoxy radical plus ground state oxygen atoms.

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