

# Crossed-Beams and Theoretical Studies of the O(<sup>3</sup>P, <sup>1</sup>D) + Benzene Reactions: Primary Products, Branching Fractions, and Role of Intersystem Crossing

Gianmarco Vanuzzo, Adriana Caracciolo, Timothy K. Minton<sup>§, #</sup>, Nadia Balucani\*,  
Piergiorgio Casavecchia\*

*Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123  
Perugia, Italy*

Carlo de Falco

*MOX – Modellistica e Calcolo Scientifico, Dipartimento di Matematica, Politecnico di Milano,  
20133 Milano, Italy*

Alberto Baggioli, Carlo Cavallotti\*

*Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, 20131 Milano,  
Italy*

**ABSTRACT:** Reliable modeling of hydrocarbon oxidation relies critically on knowledge of the branching fractions (BFs) as a function of temperature ( $T$ ) and pressure ( $p$ ) for the products of the hydrocarbon reaction with atomic oxygen in its ground state, O(<sup>3</sup>P). During the past decade, we have investigated in depth reactions of O(<sup>3</sup>P) with a variety of small unsaturated hydrocarbons using the crossed molecular beam (CMB) technique with *universal* mass-spectrometric (MS) detection and time-of-flight (TOF) analysis, combined with synergistic theoretical calculations of the relevant potential energy surfaces (PESs) and statistical computations of product branching fractions (BFs) including intersystem crossing (ISC). This allowed us to determine the primary products, their BFs, and extent of ISC, to ultimately provide theoretically channel-specific rate constants as a function of  $T$  and  $p$ . In this work, we have extended this approach to the oxidation of one of the most important species involved in the combustion of aromatics: the benzene (C<sub>6</sub>H<sub>6</sub>) molecule. Despite extensive experimental and theoretical studies on the kinetics and dynamics of the O(<sup>3</sup>P)+C<sub>6</sub>H<sub>6</sub> reaction, the relative importance of the C<sub>6</sub>H<sub>5</sub>O(phenoxy)+H open-shell products and of the spin-forbidden C<sub>5</sub>H<sub>6</sub>(cyclopentadiene)+CO and phenol adduct closed-shell products is still an open question, which has hampered the development of reliable benzene combustion models. We have investigated with the CMB technique the reaction dynamics of O(<sup>3</sup>P)+benzene at the collision energy ( $E_c$ ), of 8.2 kcal/mol, focusing on the occurrence of the phenoxy+H and spin-forbidden C<sub>5</sub>H<sub>6</sub>+CO and phenol channels in order to shed further light on the dynamics, including the role of ISC, of this complex and important reaction. Concurrently, we have also investigated the reaction dynamics of

O(<sup>1</sup>D)+benzene at the same E<sub>c</sub>. Synergistic, high-level electronic structure calculations of the underlying triplet/singlet PESs, including nonadiabatic couplings, have been performed to complement and assist the interpretation of the experimental results. Statistical (RRKM)/Master Equation (ME) computations on these PESs, with inclusion of ISC, of the product distribution, and BFs, have been performed and compared to experiment. In the light of the reasonable agreement between the CMB experiment, literature kinetic experimental results, and theoretical predictions for the O(<sup>3</sup>P)+benzene reaction, the so validated computational methodology is used to predict (i) the BF between C<sub>6</sub>H<sub>5</sub>O+H and C<sub>5</sub>H<sub>6</sub>+CO channels as a function of collision energy and also temperature (at 0.1 and 1 bar) finding that their increase progressively favors radical (phenoxy+H) over molecule (C<sub>5</sub>H<sub>6</sub>+CO and phenol stabilization) forming channels, and (ii) channel-specific rate constants as a function of *T* and *p*, expected to be useful for improved combustion models.

§Visiting Professor from: Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA

#Current address: [Ann and H.J. Smead Aerospace Engineering Sciences](#), University of Colorado at Boulder, 3775 Discovery Drive, Boulder, CO 80303-0429, USA E-mail: [tminton@colorado.edu](mailto:tminton@colorado.edu)

## 1. INTRODUCTION

Since the early pioneering work of Cvetanovic in the 1950s,<sup>1-3</sup> the reactions of ground state atomic oxygen, O(<sup>3</sup>P), with unsaturated hydrocarbons (UHs) (alkynes, alkenes, dienes, and aromatics) have received a great deal of attention because of their importance in atmospheric chemistry<sup>4</sup> and especially combustion chemistry.<sup>5-8</sup> Initially, the effort has been mainly devoted to kinetics<sup>3</sup>, but starting from the early 1980s, also dynamic work, under single-collision conditions, was undertaken using a variety of techniques, from crossed molecular beam (CMB) methods with mass spectrometric (MS) detection<sup>9-14</sup> to laser-based spectroscopic techniques in a cell or flow system.<sup>15,16</sup> However, the characterization of the detailed reaction mechanism, in particular the determination of the relative importance of the various competing reaction channels, has always been a challenge. As a consequence, results have been often fraught with uncertainty and controversy (see, for instance, Table 2 in ref. 17). It is worth recalling that the reactions of O(<sup>3</sup>P) with UHs are multichannel nonadiabatic reactions, in which intersystem crossing (ISC) from the entrance triplet potential energy surface (PES) to the underlying singlet PES plays a central role,<sup>10-12,17-19</sup> and this makes the detailed characterization of the reaction dynamics quite taxing. In fact, a detailed comprehension of the mechanism of the combustion relevant, multichannel reactions of O(<sup>3</sup>P) with UHs requires the identification of all primary reaction products, the determination of their branching fractions (BFs), and an assessment of the role of ISC. This can be achieved by combining CMB experiments (using universal, soft electron ionization, MS detection and time-of-flight (TOF) analysis) with high-level *ab initio* electronic structure calculations of the triplet/singlet PESs and their couplings, and RRKM/ME (Rice-Ramsperger-Kassel-Marcus/Master Equation) computations of product branching fractions (BFs) including ISC.<sup>19-23</sup> We emphasize that reliable information on product BFs as a function of temperature and then predictions of channel-specific rate constants as a function of temperature and pressure are crucially needed for improving current combustion models.<sup>19-24</sup>

Over the past several years we have investigated in combined CMB/theoretical studies the dynamics of a variety of  $O(^3P)$  reactions with UHs (alkynes, alkenes and dienes) involving two, three, and four carbon atoms, such as acetylene,<sup>25</sup> ethylene,<sup>17,26-28</sup> propyne,<sup>21,29</sup> propene,<sup>20,30</sup> allene (propadiene),<sup>31</sup> 1-butene,<sup>22</sup> 1,2-butadiene,<sup>32</sup> and 1,3-butadiene.<sup>33</sup> In particular, exploiting *soft* electron ionization, we have been able to identify for the first time all primary reaction product channels (up to six or seven for some of the above systems) and determine their BFs. The experimental BFs have usually been compared with RRKM/ME statistical predictions on state-of-the-art triplet/singlet PESs with inclusion of ISC. Once the statistical predictions were validated by experiment, theory was used to predict BFs and extent of ISC as a function of temperature and pressure<sup>22,23</sup> for inclusion, ultimately, in combustion models.

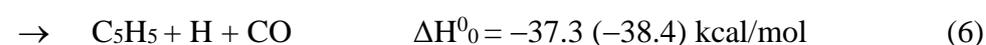
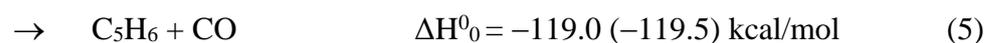
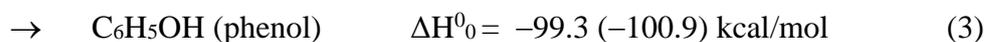
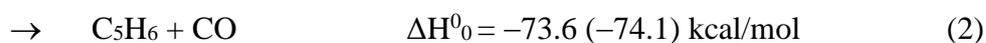
Very recently, we have extended our CMB investigations of  $O(^3P)$  reactions with UHs also to aromatic hydrocarbons (AHs), such as benzene, toluene, as well as the prototypical hetero-aromatic pyridine. Preliminary results on the reaction of  $O(^3P)$  with the exemplary aromatic molecule benzene have just been reported in the form of a Letter.<sup>34</sup> As in most of our recent studies, the CMB investigation was accompanied by synergistic theoretical calculations of the triplet/singlet PES as well as statistical calculations of BFs, with inclusion of ISC effects, for deriving channel-specific rate constants as a function of temperature and pressure for inclusion in improved combustion models of the important  $O(^3P) + \text{benzene}$  system. Here, we report a full account of this study.

Among the AHs, benzene certainly plays a crucial role because it is a large component of fuels, being also commonly formed in combustion of aliphatics, and generates polycyclic aromatic hydrocarbons (PAHs) and soot<sup>6</sup> that affect significantly the atmospheric chemistry, the environment, and also our health.<sup>4,35,36</sup> For these reasons, during the past decades, benzene oxidation was studied in detail in order to reach a global understanding of hydrocarbon combustion processes.<sup>2,10,14,24,,34,37-48</sup> However, up to the present days, the detailed dynamics (primary products and BFs) of the  $O(^3P) + \text{benzene}$  reaction were still not well understood, which has hampered the development of detailed, reliable chemical kinetic combustion models.<sup>7,49,50</sup> In fact, although many

kinetic models have been proposed for benzene oxidation, their validity as well as that of models of other one-ring aromatics combustion such as toluene and xylenes, are to a great extent subject to uncertainties in the product identity and BFs of the reaction between benzene and O(<sup>3</sup>P).

Although numerous studies were in fact carried out on the O(<sup>3</sup>P) + benzene reaction from both theoretical and experimental points of view, the extent of formation of the spin-forbidden CO + C<sub>5</sub>H<sub>6</sub> (cyclopentadiene) products from this reaction, which implies an ISC process from the triplet to the underlying singlet PES, is still an open question. For a detailed review of previous studies, see Supporting Information (SI). To shed further light on, and with the aim to clarify the overall dynamics of the O(<sup>3</sup>P) + benzene system including the role of ISC, we have investigated this reaction at E<sub>c</sub> = 8.2 kcal/mol under single collision conditions, using the CMB technique with universal MS detection and TOF analysis. Notably, because we use a supersonic beam of atomic oxygen containing mainly ground state O(<sup>3</sup>P), but also a significant fraction of excited O(<sup>1</sup>D) (see section 2), the detailed dynamics of the O(<sup>1</sup>D) + benzene reaction was also characterized at the same E<sub>c</sub> and compared with that of O(<sup>3</sup>P), as well as with previous CMB results<sup>51</sup> on O(<sup>1</sup>D) + C<sub>6</sub>H<sub>6</sub>.

On the basis of the theoretical part of the present work,<sup>34</sup> which supersedes previous theoretical studies,<sup>24,48</sup> the energetically available reactive channels for the O(<sup>3</sup>P, <sup>1</sup>D) + benzene reactions are the following:



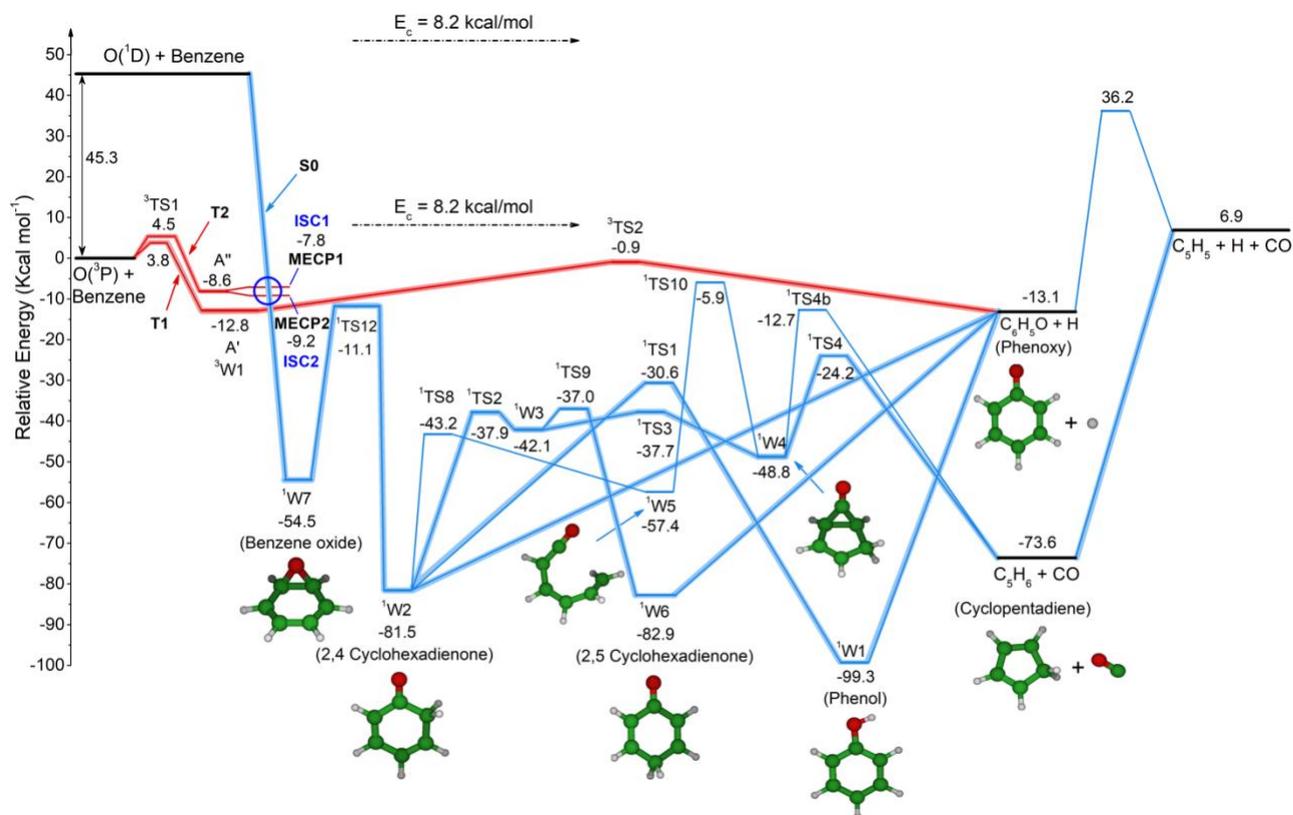
Above, the reported enthalpies of reaction at 0 K are those calculated in this work (in parenthesis experimental values from recommended  $\Delta\text{H}^0_0$ );<sup>52</sup> C<sub>5</sub>H<sub>6</sub> stands for 1,3-cyclopentadiene, while C<sub>5</sub>H<sub>5</sub>

for the cyclopentadienyl radical. Note that the H abstraction channel leading to OH + C<sub>6</sub>H<sub>5</sub> (phenyl) is endoergic by about 10 kcal/mol for O(<sup>3</sup>P) and exhibits a high energy barrier (of about 12 kcal/mol);<sup>48</sup> therefore it is expected to contribute negligibly to the O(<sup>3</sup>P) reaction, and to be minor also for the O(<sup>1</sup>D) reaction<sup>51</sup> (see Supplementary Information, SI).

The reactivity that follows O(<sup>3</sup>P) addition to benzene is well described by the C<sub>6</sub>H<sub>6</sub>O potential energy surface shown in Figure 1 (see section 2.2, and ref. 34), which represents a very significant improvement with respect to previous PESs.<sup>24,48</sup> In fact, as discussed in ref. 34 and below, besides the multireference character of some important aspects of the triplet and singlet PES, which required the appropriate high-level of quantum treatment for more accurate energies, it is the detailed treatment of ISC that was lacking for this system until the present study (see section 2.2).<sup>34</sup> This turned out to be crucial for treating reliably the reaction kinetics and dynamics. In Figure 1 we have highlighted in red the adiabatic triplet pathways leading to phenoxy + H products and to the minimum energy crossing points (MECPs) where ISC from the triplet to the singlet PES takes place, while in blue the singlet pathways leading to cyclopentadiene + CO, to phenoxy + H, and to the 3-body channel C<sub>5</sub>H<sub>5</sub>(cyclopentadienyl) + H + CO. The schematic triplet/singlet PES depicted in Figure 1, first reported (in a somewhat different version) in our recent Letter,<sup>34</sup> will be used to discuss and rationalize the findings from the present CMB experiments and to understand the detailed mechanism of the O(<sup>3</sup>P, <sup>1</sup>D) + C<sub>6</sub>H<sub>6</sub> reactions.

We note that the formation of phenol (channel (3)) or cyclopentadiene + CO (channel (2)) leads to free-radical chain termination during benzene oxidation at high temperatures; in contrast, the production of phenoxy radical + H (channel (1)) provides secondary chain branching. We can therefore expect significant effects of the product BFs on models of benzene oxidation. Notably, there appears to be a significant disagreement between the BFs derived from previous CMB studies<sup>10,34</sup> and those recently obtained from kinetic investigations with synchrotron radiation.<sup>24</sup>

The paper is organized as follows. In Section 2 the experimental and theoretical methods are illustrated. Experimental results with their analysis and theoretical results are presented in Sections 3 and 4, respectively. Discussion follows in Section 5, while Section 6 summarizes the conclusions.



**Figure 1.** Triplet (T1, T2) (red lines) and singlet (S0) (blue lines) potential energy surfaces for the  $O(^3P) + C_6H_6$  reaction (kcal/mol) (see also ref. 34). Intersystem crossing (ISC) structures determined at the  $\omega B97X-D/6-311+G(d,p)$  level, using unrestricted (ISC1) and restricted (ISC2) wavefunctions. The reactants and the main observed products (phenoxy + H, cyclopentadiene + CO, and cyclopentadienyl + H + CO), are indicated in black. The abstraction channel leading to OH +  $C_6H_5$  (phenyl), which is endothermic for  $O(^3P)$  by about 12 kcal/mol (see ref. 48), while exothermic for  $O(^1D)$  by about 36 kcal/mol (see ref. 51 and SI), the pathway from  $^3W1(A'')$  to phenoxy + H, which has a high transition state of about 16 kcal/mol with respect to reactants (see ref. 48), and the pathway to  $C_6H_4$ (benzyne) +  $H_2O$  products ( $\Delta H^0 = -26.5$  kcal/mol (see ref. 34)), which have a very low probability of formation, are not represented.

## 2. METHODS

**2.1. Experiment.** The title reactions have been investigated using the CMB scattering technique with MS detection and TOF analysis.<sup>53-57</sup> Briefly, two supersonic beams of the reactants are crossed at  $90^\circ$  under single-collision conditions in a large scattering chamber kept at about

$2 \times 10^{-6}$  mbar in operating conditions ( $2 \times 10^{-7}$  mbar base pressure). The angular and velocity distributions of the reaction products are recorded by a triply differentially pumped, ultra-high-vacuum (UHV) ( $10^{-11}$  mbar) detector equipped with a tunable electron impact ionizer followed by a quadrupole mass filter and a Daly<sup>58</sup> type ion detector. The whole detector unit can be rotated in the plane of the two beams around their intersection axis ( $\Theta=0^\circ$  represents the direction of the atomic oxygen beam). The velocity of reactants and products is derived using single-shot and pseudo-random, respectively, TOF analysis. Product angular distributions were recorded by modulating the benzene beam at 160 Hz for background subtraction. In the TOF measurements of reaction products, high-time resolution was achieved by spinning the pseudorandom TOF disk (provided with four 127-bit pseudorandom sequences), located at the entrance of the detector, at 328.1 Hz (corresponding to a dwell time of 6  $\mu$ s/channel). The flight length was 24.3 cm.

The supersonic beam of O atoms was produced by a radio-frequency (RF) discharge source<sup>59,60</sup> operating at a RF power of 300 Watt and a gas pressure of 85 mbar of a dilute (5%) mixture of O<sub>2</sub> in He carrier, through a 0.48 mm diameter, water cooled quartz nozzle, followed by a 0.8 mm diameter boron nitride skimmer and a further collimating aperture. In this manner, the atomic oxygen beam mainly contains O(<sup>3</sup>P) and some amount of O(<sup>1</sup>D) ( $\leq 10\%$ ).<sup>60</sup> Peak velocity and speed ratio were 2206 m/s and 4.5, respectively. The supersonic beam of benzene was generated by expanding through a 0.1 mm diameter stainless-steel nozzle, kept at room temperature, 103 mbar of neat benzene maintained in a bath at 290 K to avoid vapour pressure fluctuations. Beam peak velocity and speed ratio were 521 m/s and 4.2, respectively. The resulting collision energy ( $E_c$ ) was 8.2 kcal/mol. The small percentage of O(<sup>1</sup>D) present in the atomic oxygen beam is expected to contribute significantly to the measured product distributions because the reaction cross section of O(<sup>3</sup>P) with benzene is considerably lower than that of O(<sup>1</sup>D), as the O(<sup>3</sup>P) + C<sub>6</sub>H<sub>6</sub> reaction is characterized by a very significant entrance energy barrier of about 4 kcal/mol,<sup>34</sup> while the O(<sup>1</sup>D) reaction is barrierless.<sup>51</sup>

From laboratory (LAB) angular and TOF distributions at different mass-to-charge ( $m/z$ ) ratios, product angular,  $T(\theta)$ , and translational energy,  $P(E'_T)$ , distributions in the center-of-mass (CM) system have been derived for all channels (1-6) of the  $O(^3P)$  and  $O(^1D)$  reactions. For the physical and quantitative interpretation of the scattering data it is necessary to perform a coordinate transformation and move from the LAB frame to the CM reference frame.<sup>53-56</sup> For reactions with multiple channels, as it is the case in the present work, if more than one product channel contributes to the signal at a given  $m/z$  ratio, a weighted total CM differential cross section reflecting the various possible contributions is used in the data analysis of the LAB angular and TOF distributions for a specific  $m/z$ , that is:  $I_{CM}(\theta, E'_T)_{total} = \sum_i w_i \times [T(\theta) \times P(E'_T)]_i$  with the parameter  $w_i$ , representing the relative contribution of the integral cross section of the  $i^{th}$  channel, being a best-fit parameter.<sup>18,19,56</sup> The  $T(\theta)$  and  $P(E'_T)$  functions contain all the information about the reaction dynamics. The best-fit of the LAB product angular,  $N(\Theta)$ , and TOF,  $N(\Theta, t)$ , distributions is done by forward convoluting tentative CM distributions over the experimental conditions. Specifically, the CM angular and translational energy distributions are assumed, averaged and then transformed to the LAB frame for comparison with the experimental distributions, and the procedure is repeated until a satisfactory fit of the experimental distributions is obtained.

**2.2. Theory.** The approach used to investigate the title reaction has been described in our previous studies,<sup>34,61</sup> and will therefore only be briefly summarized here. Structures and vibrational frequencies of all stationary points were determined at the unrestricted  $\omega$ B97X-D/6-311+G(d,p) level. Energies were then calculated at the CCSD(T)/aug-cc-pVTZ level, using DF-MP2/aug-cc-pVQZ – DF-MP2/aug-cc-pVTZ level corrections for basis set size effects. For saddle points with significant multireference character and for barrierless reactions, energies were determined at the CASPT2/aug-cc-pVTZ level. Specifically, the energy barriers of all transition states on the triplet PES and of  $^1W4$  decomposition to CO and  $C_5H_6$  ( $^1TS4$ ) and  $^1TS12$  were computed at the CASPT2 level. A 0.25 IPEA shift was used for all CASPT2 calculations. Details on the adopted active spaces

are collected in our previous study.<sup>34</sup> Structures, frequencies, and energies of all the calculated stationary points are the same as in our previous study,<sup>34</sup> made exception for the H beta-scission on the triplet PES, <sup>3</sup>TS2, whose barrier was re-evaluated using a larger (12e,11o) active space composed of the oxygen (4e,3o) p orbitals and electrons, of the (6e,6o)  $\pi$  and  $\pi^*$  electrons and orbitals of benzene, and of the (2e,2o)  $\sigma$  and  $\sigma^*$  electrons and orbitals of the reacting C-H bond. The barrier so calculated is -0.9 kcal/mol, in good agreement with the -1.3 kcal/mol determined at the CCSD(T) level and 1.3 kcal/mol lower than determined in our previous work.<sup>34</sup>

The Minimum Energy Crossing Point (MECP) between triplet and singlet PESs was determined using energies and analytical gradients evaluated at the  $\omega$ B97X-D/6-311+G(d,p) level using an unrestricted formalism. The MECP geometry was determined using EStokTP, an open-source software recently developed by us.<sup>62</sup> The MECP was searched by minimizing the energy on the singlet PES imposing the constraint that the singlet and triplet energies be equal.<sup>63</sup> The search for the constrained local minimum was performed via the Sequential Least-Squares Quadratic Programming (SLSQP) algorithm,<sup>64,65</sup> which solves the nonlinear minimization problem by producing a sequence of quadratic approximations to the objective function via BFGS-type low-rank updates of the approximate Hessian. At each step, the equality constraints are imposed on the approximate quadratic minimization problem by means of the Augmented Lagrangian method.<sup>65,66</sup>

The above method was implemented in EStokTP by interfacing the solver to the open source optimization library NLOpt,<sup>66</sup> which contains a C language re-implementation of the original Fortran code for SLSQP. Optimizations were started from the <sup>3</sup>W1 structures and converged within about 50 steps, with accuracies of  $10^{-10}$  Hartrees using  $10^{-4}$  tolerances. Rate constants of individual channels were determined using conventional and variational transition state theory (VTST). In particular, rate constants of barrierless H loss reactions from the singlet PES were determined using VTST, adopting  $\omega$ B97X-D/6-311+G(d,p) geometries and frequencies and CASPT2 energies. The rate constant for ISC was determined using non adiabatic transition state theory (NA-TST). Because

in the present work we extend our implementation of NA-TST, which has some specificities compared to other approaches reported in the literature, it is useful to discuss in greater details about how our spin-forbidden microcanonical rate constant was determined. Microcanonical rate constants were computed using the MC-RRKM code at the E,J resolved level. For a spin-forbidden reaction in the framework of NA-TST, this means that the  $k(E,J)$  rate constant is evaluated as:

$$k(E,J) = \frac{\int_0^{E-E_0} \rho^{TS}(E',J) p_{hop}(E - E_0 - E') dE'}{h\rho(E,J)} \quad (7)$$

where  $\rho^{TS}$  and  $\rho$  are the density of states,  $E'$  is the energy in internal degrees of freedom at the MECP,  $J$  the angular momentum,  $E$  the rovibrational energy, and  $p_{hop}$  the probability of intersystem crossing. Energy resolved rate constants are then computed as suggested by the Miller E,J model<sup>67</sup> as:

$$k(E) = \frac{\sum_J k(E,J) y(E,J)}{\sum_J y(E,J)} \quad (8)$$

where  $y(E,J)$  is defined as:

$$y(E,J) = \frac{(2J+1)\rho(E,J)}{(\sum_J (2J+1)\rho(E,J))(Z + k(E,J))} \quad (9)$$

where  $Z$  is the intermolecular collision rate. In this model, the energy dependent rate constant  $k(E)$  is obtained from the E,J dependent rate  $k(E,J)$  by weighting over an  $y(E,J)$  distribution obtained under the assumption that the  $J$  distribution after an intermolecular collision is independent of the angular momentum of the molecule before collision.<sup>67</sup>

The probability of intersystem crossing  $p_{hop}$  was determined using two different models: the double passage Landau-Zener model:<sup>68</sup>

$$p_{hop}^{LZ}(E) = P_{LZ} + P_{LZ}(1 - P_{LZ}) \quad (10)$$

$$P_{LZ} = 1 - \exp\left(-\frac{2\pi H_{S0}^2}{\hbar|\Delta F|} \frac{1}{\sqrt{2E_{\perp}}}\right) \quad (11)$$

and the weak coupling ISC approximation originally suggested by Nikitin:<sup>69,70</sup>

$$p_{hop}^{WC}(E) = \pi^2 \beta^{4/3} A i^2(-\varepsilon \beta^{2/3}) \quad (12)$$

$$\beta = \frac{4H_{SO}}{\hbar} \sqrt{\frac{H_{SO}}{\bar{F}|\Delta F|}} \quad (13)$$

$$\varepsilon = \frac{E_{\perp}|\Delta F|}{2H_{SO}\bar{F}} \quad (14)$$

$$\bar{F} = \sqrt{|F_1 F_2|} \quad (15)$$

where  $P_{LZ}$  is the Landau-Zener single passage ISC probability,  $H_{SO}$  is the spin orbit coupling factor,  $|\Delta F|$  is the norm of the difference between the  $F_1$  and  $F_2$  gradients of the two PESs at the MECP, calculated in (square root) mass weighted Cartesian coordinates,  $E_{\perp}$  is the energy in the hopping coordinate, which is equal to the  $E - E_0 - E^I$  factor, and  $Ai$  in Eqn. (12) is the Airi function.

The density of states  $\rho(E, J)$  in Eq. 7 was determined in the rigid rotor harmonic oscillator (RRHO) approximation. MECP frequencies were determined using the bordered Hessian of the constrained energy function minimized to locate the MECP:

$$H_{MECP} = H_{sing} + \lambda(H_{trip} - H_{sing}) \quad (16)$$

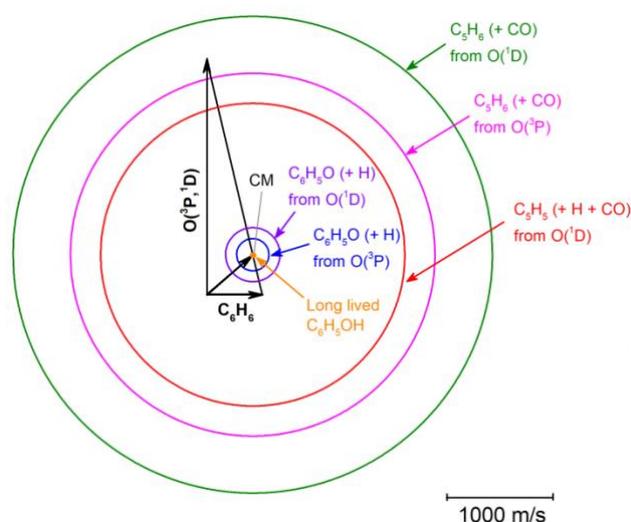
where  $H_{sing}$ ,  $H_{trip}$  and  $\lambda$  are the Hessians of the singlet and triplet PESs and the Lagrangian multiplier (comprised between 0 and 1), respectively.

Spin-orbit couplings ( $H_{SO}$ ) were evaluated using the state-interacting method at the MECPs using a Breit-Pauli Hamiltonian and a CASSCF wavefunction.<sup>20</sup> The T2/S0 HSO coupling in this system, square averaged over the three triplet-singlet coupling elements, is about  $35 \text{ cm}^{-1}$  for both ISC1 and ISC2, thus exhibiting a small dependence on the MECP geometry.<sup>34</sup>

Master equation simulations were performed with our kinetic Monte Carlo stochastic MC-RRKM code. For the thermal simulations, the intermolecular energy transfer was described using a single exponential down model,<sup>71</sup> with the same average collision downward energy transfer ( $\Delta E_{down}$ ) parameter of  $260 \times (T/300)^{0.875}$  we used in the ME investigation of phenol decomposition, assuming that the bath gas is Ar.<sup>61</sup> The termination threshold for the Monte Carlo simulations was  $10^4$  reactive events. All DFT calculations were performed using Gaussian09,<sup>72</sup> while CCSD(T), DF-MP2, and CASPT2 calculations were performed with Molpro.<sup>73</sup>

### 3. EXPERIMENTAL RESULTS

In Figure 2 we depict the velocity vector (so called Newton) diagram of the experiment on the reactions  $O(^3P, ^1D) + C_6H_6$ . There, the superimposed circles delimit the maximum velocity that the indicated bimolecular primary products can attain by assuming that all the available energy (given by  $E_c - \Delta H_0^0$ ) is channeled into product translational energy.



**Figure 2.** Velocity vector (Newton) diagram of the experiment. The radius of each circle represents the maximum velocity that the indicated product can attain in the CM system if all the available energy is channeled into product recoil energy. The phenol adduct is centered at the CM (that is, it follows the “centroid” distribution) and has therefore zero velocity in this frame.

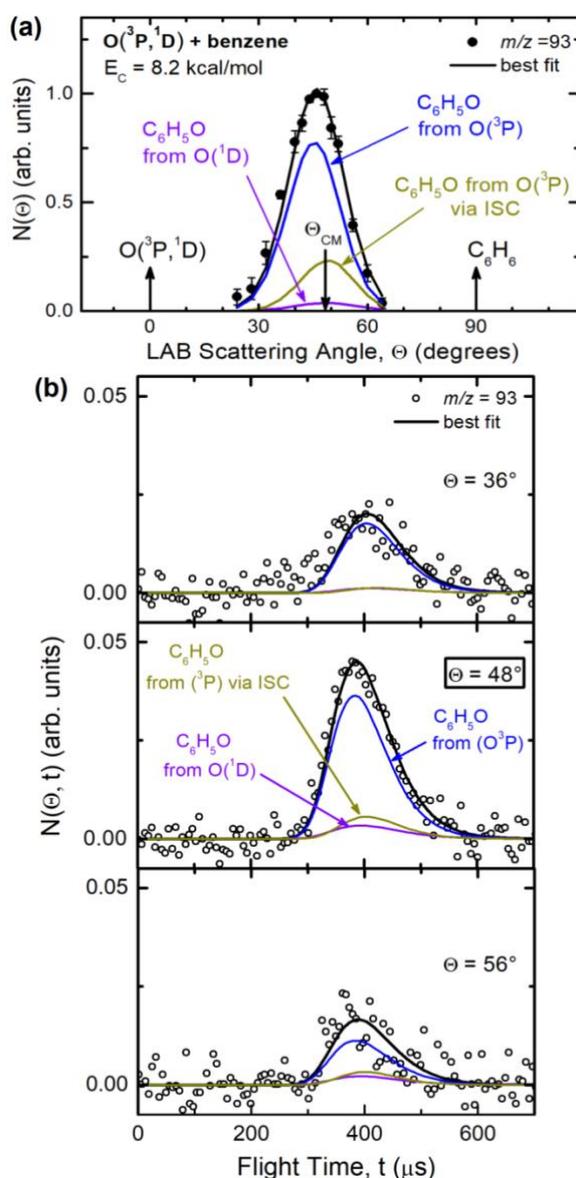
Because in this study we observe simultaneously products from the reaction of benzene with both  $O(^3P)$  and  $O(^1D)$ , one important issue is to distinguish their individual contribution. The estimated concentration of  $O(^1D)$  in the beam of atomic oxygen is  $\leq 0.10$ , that is, it is at least ten times smaller than that of  $O(^3P)$ .<sup>60</sup> From the PES in Figure 1 we can see that both  $O(^3P)$  and  $O(^1D)$  can give rise to the same two product channels forming  $C_6H_5O + H$  and  $C_5H_6 + CO$ , which, however, will have a very different exothermicity and, especially, a very different dynamics. In fact,  $O(^3P)$  can produce phenoxy + H adiabatically on the triplet PES over a significant exit potential barrier, but also non-adiabatically on the singlet PES, without exit-barrier, via ISC from the triplet

to the singlet PES. On the other hand, O(<sup>1</sup>D) can produce phenoxy + H adiabatically on the singlet PES with no exit barrier. Moreover, while O(<sup>3</sup>P) can produce C<sub>5</sub>H<sub>6</sub> + CO only non-adiabatically (via ISC), O(<sup>1</sup>D) can produce C<sub>5</sub>H<sub>6</sub> + CO adiabatically on the singlet PES and, in addition, the C<sub>5</sub>H<sub>6</sub> product can have enough internal energy to unimolecularly dissociate to C<sub>5</sub>H<sub>5</sub> + H (3-body process). It should be noted that dissociation of C<sub>6</sub>H<sub>5</sub>O to C<sub>5</sub>H<sub>5</sub> + CO is energetically not possible for O(<sup>3</sup>P) because of a high barrier of about 50 kcal/mol (see Figure 1) and negligible also for O(<sup>1</sup>D).<sup>51</sup> Furthermore, we note that previous CMB work on both O(<sup>3</sup>P) and O(<sup>1</sup>D) + benzene reactions has shown that some phenol adduct survives until the detector for the O(<sup>3</sup>P) reaction,<sup>10</sup> but not for the O(<sup>1</sup>D) reaction.<sup>51</sup> The phenol adduct observed at the detector can arise from radiative stabilization of the excited phenol intermediate (<sup>1</sup>W1 in Figure 1) or from the fact that phenol has a distribution of lifetimes and a small fraction of it could have a lifetime  $\geq 300$   $\mu$ s, sufficient to reach the detector. In the light of information from previous studies,<sup>10,51</sup> and taking into account that products arising from the much more exothermic O(<sup>1</sup>D) reactions are expected to fragment more strongly than those from O(<sup>3</sup>P) to daughter ions upon 70 eV electron impact ionization, we will exploit the following properties of the scattering to differentiate the contribution of O(<sup>3</sup>P) and O(<sup>1</sup>D) to the total reactive signal: (i) the different reaction energetics, (ii) the different reaction kinematics, (iii) the different reaction dynamics, and (iv) the theoretical information about the triplet and singlet PESs.

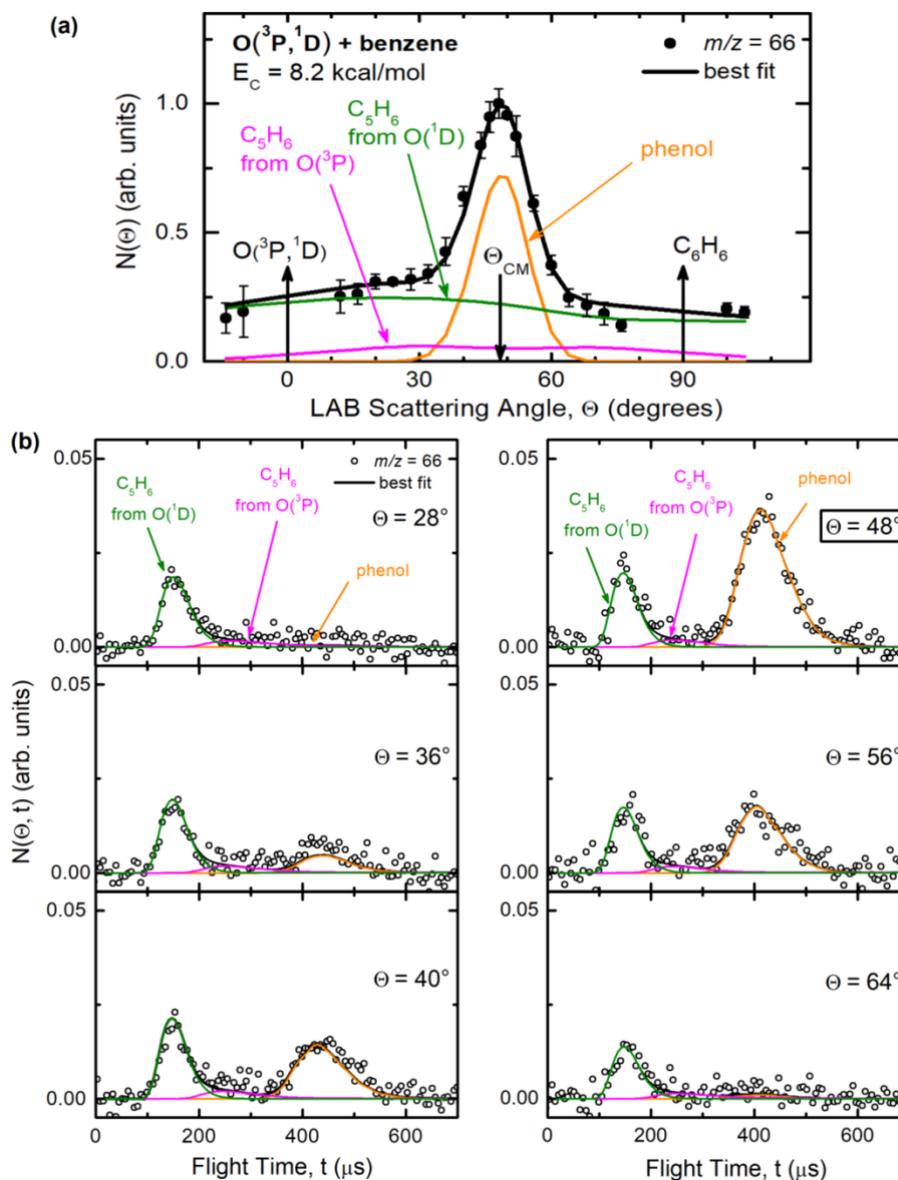
Reactive scattering signal was measured at  $m/z = 94$  (C<sub>6</sub>H<sub>6</sub>O), 93 (C<sub>6</sub>H<sub>5</sub>O), 66 (C<sub>5</sub>H<sub>6</sub>), and 65 (C<sub>5</sub>H<sub>5</sub>) with relative intensity of 0.01, 0.06, 0.08, and 1.00, respectively, when employing hard ionization detection (70 eV electron energy) (it was not necessary, neither useful to resort to soft ionization detection for this reactive system). The signal at  $m/z = 94$ , when corrected for the <sup>13</sup>C natural content (6.6%) of the signal at  $m/z = 93$ , corresponds to some phenol adduct that survives from the collision zone until the ionizer of the detector. LAB angular distributions,  $N(\Theta)$ , and TOF distributions,  $N(\Theta, t)$ , were measured for all three masses ( $m/z = 93, 66,$  and  $65$ ) corresponding to

possible bimolecular products of the  $O(^3P, ^1D) + C_6H_6$  reactions. The angular distributions for  $m/z = 93$ ,  $m/z = 66$ , and  $m/z = 65$  are shown in the parts (a) of the Figures 3, 4, and 5, respectively, while the TOF distributions at selected LAB angles in the corresponding parts (b) of the same Figures.

The various product channels corresponding to the H-displacement channels (1) and (4), to the  $C_5H_6$  and  $C_5H_5$  forming channels (2) and (5), and (6), respectively, and also to the phenol adduct (channel (3)), can be disentangled in the TOF measurements, as shown in the parts (b) of Figures 4 and 5. These two figures show the power of TOF analysis in these experiments, whereby different



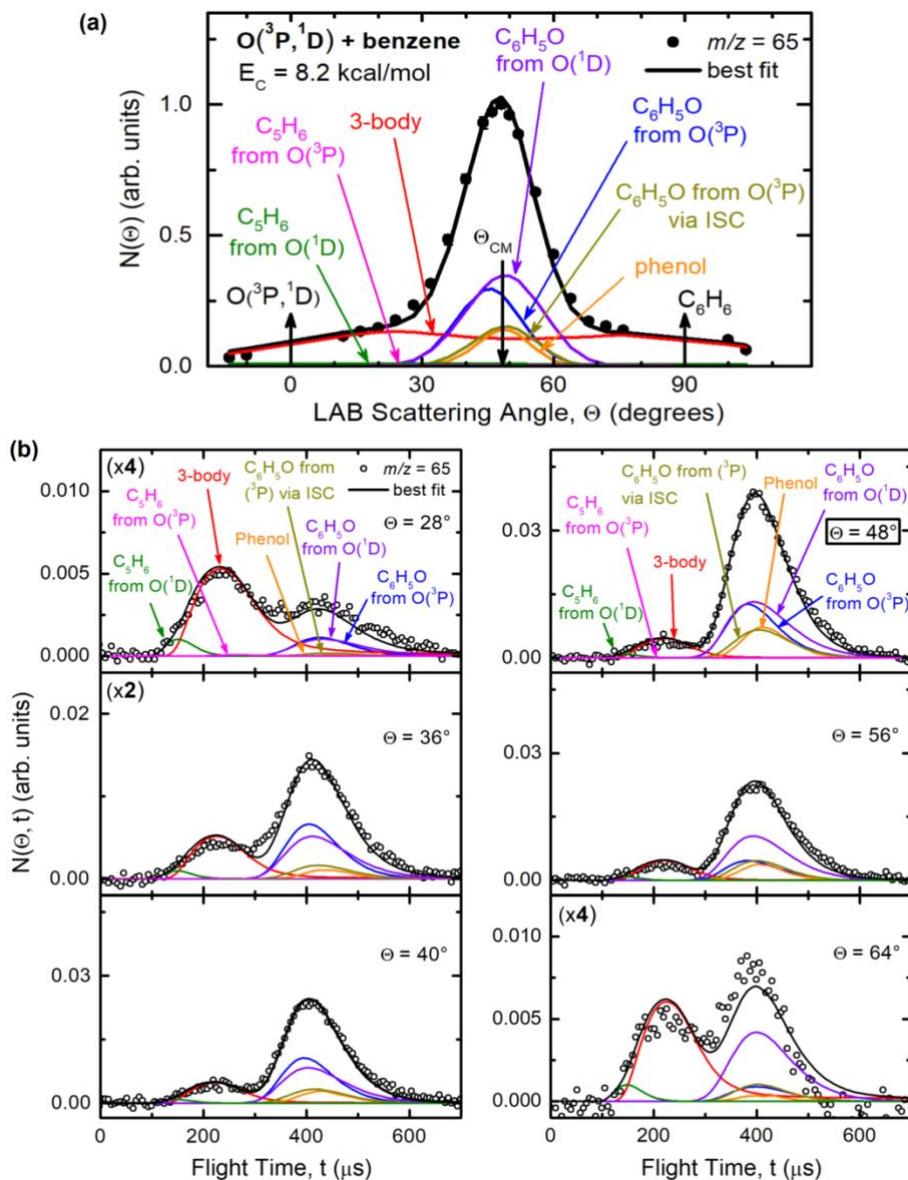
**Figure 3.** LAB angular distribution (a) and TOF distributions (b) of  $m/z = 93$  product (phenoxy) from the  $O(^3P, ^1D)$  reactions with benzene at  $E_c=8.2$  kcal/mol. Partial contributions from the two reactions channels (1) and (4) are represented with color-coded, labelled lines; the black line is the total best-fit.



**Figure 4.** LAB angular distribution (a) and TOF distributions (b) at selected LAB angles for  $m/z = 66$  products from the  $O(^3P, ^1D)$  reactions with benzene at  $E_c=8.2$  kcal/mol. Partial contributions from the reactions channels (2), (3), and (5) are represented with color-coded, labelled lines; the black line is the total best-fit.

Products (arising from different reaction channels) detected at the same  $m/z$  value, and usually not clearly distinguishable in the angular distribution at that  $m/z$  (Figures 4a and 5a), are instead separated (or partially separated) according to their different flight times in the TOF distributions at

specific LAB angles (Figures 4b and 5b). For each of the three masses at which angular distributions were measured (Figures 3a, 4a, and 5a), the variation of the various channel contributions with the LAB scattering angle  $\Theta$  is well exemplified in the parts (b) of the Figures 3,



**Figure 5.** LAB angular distribution (a) and TOF distributions at selected LAB angles (b) of  $m/z=65$  products from the  $O(^3P, ^1D)$  reactions with benzene at  $E_c=8.2$  kcal/mol. Partial contributions from the reactions channels (1)-(6) are represented with color-coded, labelled lines; the black line is the total best-fit.

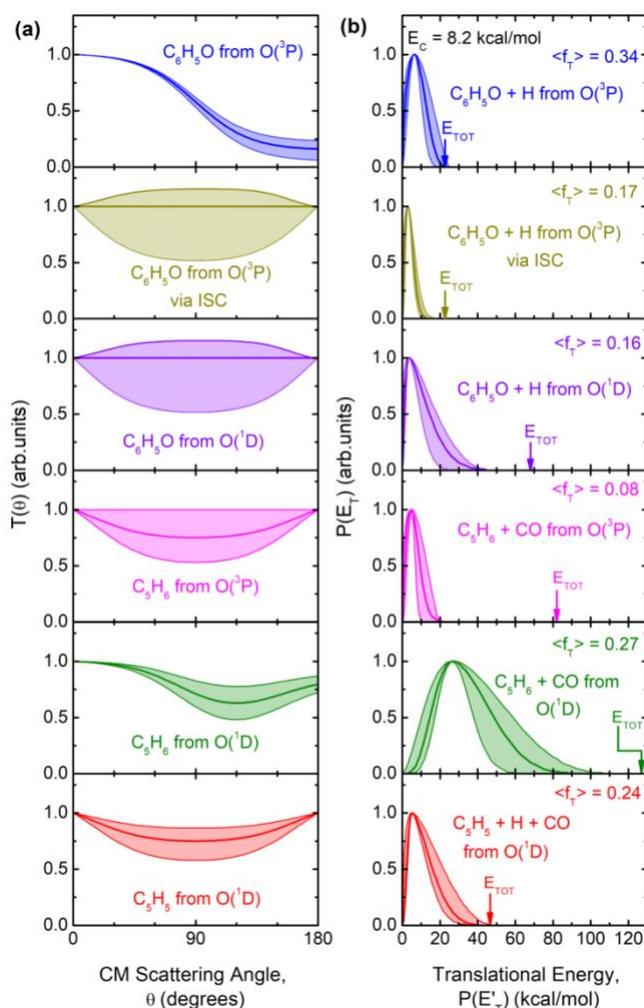
4, and 5. For instance, in Figure 4b the strong peak at about  $420 \mu s$  (corresponding to the CM velocity) for  $m/z = 66$  is due to the small quantity of phenol (parent mass 94) that survives up to the ionizer and is then dissociatively ionized to  $C_5H_6^+$ . Notably, in Figure 4b phenol cannot be observed

at  $\Theta=28^\circ$  and  $64^\circ$  for kinematic reasons, falling these angles outside those of the centroid distribution (which is represented by the phenol angular distribution depicted in Figure 4a). While the fast products distributed over much wider Newton circles are due to the cyclopentadiene ( $C_5H_6$ ) product (detected at its parent ion mass) from channel (2) and channel (5) (from the  $O(^3P)$  and  $O(^1D)$  reaction, respectively), the latter being much faster than the former because of the much larger exoergicity of channel (5) with respect to channel (2). Similarly, in Figure 5a the strong global peak at the CM angle for  $m/z = 65$  ( $C_5H_5^+$ ) is due to a small quantity of phenol daughter ion and to the daughter ions of phenoxy from both  $O(^3P)$  and  $O(^1D)$  reactions (channels (1) and (4), respectively), while the fast products distributed over much wider Newton circles are mainly due to the cyclopentadienyl radical ( $C_5H_5$ ) product (detected at its parent mass) from the 3-body channel (6) from the  $O(^1D)$  reaction, and to a smaller extent to the daughter ion of cyclopentadiene from channels (2) and (5).

The best-fit CM functions  $T(\theta)$  and  $P(E'_T)$  of the LAB angular and TOF distributions data reported in the Figures 3, 4, and 5 for the various product channels, are shown in Figure 6. Because the data shown in the Figures 3-5 carry the fingerprint of the three reaction channels (1)-(3) from  $O(^3P)$  and the three reaction channels (4)-(6) from  $O(^1D)$ , from the derived best-fit CM functions depicted in Figure 6 we have estimated the corresponding global BFs (see Table 1 below) and from these also the distinct BFs for the  $O(^3P)$  reaction channels and those for the  $O(^1D)$  reaction channels (see Table 2 below). In the following, we analyse the LAB angular and TOF distributions for the various  $m/z$  values to derive the best-fit CM  $T(\theta)$  and  $P(E'_T)$  functions for the various channels.

**3.1. The  $m/z = 93$  Data: H Displacement Channels.** The dynamics of the atomic hydrogen displacement channels leading to phenoxy formation from  $O(^3P)$  (channel (1)) and  $O(^1D)$  (channel (4)) were characterized by measuring product angular and TOF distributions at different LAB angles for the phenoxy radical parent ion,  $m/z = 93$  and also for its daughter ion,  $m/z = 65$ . Figure 3a shows that the  $m/z = 93$   $N(\Theta)$  is bell shaped and centered at around the CM angle ( $\Theta_{CM} =$

48°), but with a clear forward bias, while in Figure 3b the TOF spectra measured at three different LAB angles (CM angle of 48°, one angle in the forward direction ( $\Theta=36^\circ$ ), and another angle in the



**Figure 6.** (a): Best-fit CM angular distributions for the indicated products from the  $O(^3P)$  and  $O(^1D)$  reactions. (b): corresponding best-fit product translational energy distributions for the indicated channels. The total available energy is indicated by the arrow and the average fraction of energy released in product translation,  $\langle f_T \rangle$ , is also given. The shaded areas represent the error bars determined for the CM functions.

backward direction ( $\Theta=56^\circ$ ) exhibit a peak centered at around 380  $\mu s$ , which is somewhat faster than the peak of the phenol adduct (see Figure 4b). It should be noted that the phenol peak is centered at the CM velocity (since it follows the centroid distribution), while the peak of phenoxy, on the basis of energy and momentum conservation, has a velocity somewhat different from the CM velocity, because the product translational energy distribution peaks somewhat away from zero (see

Figure 6) and the phenoxy is left by a very light co-product (the H atom). Specifically, the TOF peak appears in the LAB frame at velocities larger than the CM velocity, that is, at flight times shorter than that of the CM (this being about 420  $\mu$ s, which is where the peak of phenol occurs, as can be seen in the TOF spectrum of phenol at  $\Theta=48^\circ$  in Figure 4b).

The primary products at  $m/z = 93$  were identified as  $C_6H_5O$  (phenoxy) from the  $C_6H_5O + H$  channel from both  $O(^3P)$  and  $O(^1D)$  reactions. Notably, part of the phenoxy yield from  $O(^3P)$  can originate adiabatically from the triplet PES and part non-adiabatically from the singlet PES (via ISC). We have exploited the different energetics, kinematics, and dynamics of the above three H displacement pathways to derive their best-fit CM functions and then estimate their relative contributions. The expected different fragmentation pattern that characterizes hot phenoxy originated from the  $O(^3P)$  or  $O(^1D)$  reaction was also noted. In fact, phenoxy from  $O(^3P)$  was mainly detected at  $m/z = 93$  (parent ion), while the presence of phenoxy from the  $O(^1D)$  reaction is mostly observed through its higher fragmentation at  $m/z = 65$  (Figure 5, see below). Since the heavy product  $C_6H_5O$  from channel (1) and the corresponding one from the  $O(^1D)$  reaction are kinematically constrained and hence scattered within two small, yet different Newton circles (Figure 2), their intensity is strongly amplified in the LAB frame (Figure 3a) because of the CM $\rightarrow$ LAB Jacobian transformation.<sup>53-57</sup> In Figure 3, the distinct contributions from the  $O(^3P)$  and  $O(^1D)$  reactions are represented as labeled color-coded curves, while the black line, which is in very good agreement with experimental data, represents the overall best-fit (total  $C_6H_5O$  product). The corresponding best-fit CM functions for the  $O(^3P)$  and  $O(^1D)$  reactions producing phenoxy + H are shown in Figures 6a and 6b. The combined fit of the  $m/z = 93$  and  $m/z = 65$  data turned out to be sensitive to the different dynamics of phenoxy formation from  $O(^3P)$  when this occurs directly on the triplet PES (for which, given the modest stability, and corresponding relatively short lifetime of the initial triplet diradical intermediate  $^3W1(A')$  (Figure 1), it is reasonable to expect a short-lived intermediate complex mechanism) or originates via ISC on the singlet PES (where, because of the

much larger stability, and expectedly long lifetime, of the  $^1W7$  intermediate, the formation of phenoxy is expected to proceed via a long-lived complex mechanism). Indeed, as can be seen in Figure 6, the  $T(\theta)$  of phenoxy from  $O(^3P) + C_6H_6$  occurring on the triplet PES is strongly forward biased. In fact, as can be seen in Figure 3a, its partial contribution to the LAB angular distribution peaks at an angle smaller than  $\Theta_{CM}$  (*i.e.*, in the forward direction with respect to the incoming O atom), while the  $T(\theta)$  for the  $O(^3P)$  reaction proceeding via ISC and that for the  $O(^1D)$  reaction are backward-forward symmetric with respect to  $\Theta_{CM}$ . The  $O(^3P)$  direct contribution on the triplet PES exhibiting a strongly forward peaked  $T(\theta)$  (see Figure 6a) reflects a strongly osculating complex mechanism, which approaches an almost direct scattering mechanism, while the backward-forward symmetric  $T(\Theta)$ s of phenoxy from  $O(^1D)$  and from  $O(^3P)$  via ISC reflect a long-lived complex mechanism.<sup>74,75</sup> The anisotropy of the  $T(\theta)$  of phenoxy from the triplet PES and the symmetry of the  $T(\theta)$  of the other two contributions to phenoxy formation are confirmed by the LAB data at  $m/z = 65$  and their analysis (see below, section 3.3).

The best-fit  $P(E'_T)$  of the phenoxy + H channel from the  $O(^3P)$  adiabatic reaction shown in Figure 6b(*rhs-top*) clearly shows that it peaks away from zero translational energy, at about 6.4 kcal/mol, corresponding to an average fraction of total available energy in product translation,  $\langle f_T \rangle$ , of 0.33. This indicates the existence in the PES of a significant exit potential energy barrier on the way to products. However, the  $P(E'_T)$  for channel (4) extends to an energy (about 40 kcal/mol) larger than that for channel (1) via ISC (which dies off at about 10 kcal/mol), and this is not surprising given the 45 kcal/mol larger exothermicity of channel (4) with respect to channel (1). Notably, the average fraction of total available energy released in translation,  $\langle f_T \rangle$ , is consequently much lower than for the  $O(^3P)$  direct reaction (which has  $\langle f_T \rangle = 0.33$ ), being 0.17 for the  $O(^3P)$  reaction via ISC and 0.16 for the  $O(^1D)$  reaction (Figure 6b). We remind the reader that the average product translational energy  $\langle E'_T \rangle$  is defined as  $\langle E'_T \rangle = \sum P(E'_T) E'_T / \sum P(E'_T)$ , and the average

fraction of total available energy,  $E_{TOT}$  ( $E_{TOT} = E_c - \Delta H^0_0$ ), channeled into translation,  $\langle f_T \rangle$ , is defined as  $\langle f_T \rangle = \langle E'_T \rangle / E_{TOT}$ .

**3.2. The  $m/z = 66$  Data: Phenol and CO + C<sub>6</sub>H<sub>5</sub> (Cyclopentadiene) Channels.** Let us now move on to examine the angular distribution at  $m/z = 66$ , which is characterized by a prominent peak centered at the CM angle, superimposed on two broad wings (Figure 4a). The central peak reflects the phenol adduct from the O(<sup>3</sup>P) reaction that fragments in the ionizer to C<sub>5</sub>H<sub>6</sub><sup>+</sup> (losing a CO molecule) and the measured distribution reflects that of the centroid (that is, it is just determined by the velocity and angular spreads of the two reactant beams and the detector acceptance angle (about 1°)). Note that phenol was also observed at its parent ion  $m/z = 94$ . In fact, we observed that the signal at this mass (at the CM angle) was higher than the 6.6% of the signal acquired at  $m/z = 93$ , attributed to the phenoxy forming channels (1) and (4), and corresponding to the reactive signal of the C<sub>6</sub>H<sub>5</sub>O isotopologue with <sup>13</sup>C natural abundance. Consequently, once subtracted the phenoxy <sup>13</sup>C contributions, the remaining  $m/z = 94$  signal could only be related to the phenol adduct C<sub>6</sub>H<sub>5</sub>OH, having a lifetime longer than its flight time from the collision region to the ionization zone of the detector (*i.e.*,  $\geq 300 \mu\text{s}$ ). It should be noted that formation of phenol is not possible under the single-collision conditions of the present CMB experiments, because the total energy is well above that of the possible bimolecular product channels and, therefore, the hot phenol intermediate will ultimately decompose into two product moieties. As we have discussed above, the small fraction of sufficiently long-lived phenol observed is expected to fragment very significantly in the ionizer of the MS detector by losing a CO molecule and giving a very significant ion signal at  $m/z = 66$ . This can very clearly be seen not only in the angular distribution measured at  $m/z = 66$  (see Figure 4a), where the peak perfectly centered at the CM angle can only originate from the phenol adduct, but also in the TOF data (Figure 4b), which show that the slow peak in the spectrum (peaking at about 420  $\mu\text{s}$ ) has a flight-time equal to that of the center of mass. Note that the phenol intensity is strongly amplified in the LAB frame because the C<sub>6</sub>H<sub>5</sub>OH adduct has

nominally zero velocity in the CM frame and the mass-spectrometer is a number density detector.<sup>10,53-55</sup>

In contrast, the two side wings of the product angular distribution at  $m/z = 66$  (Figure 4a) reflect unambiguously the formation of  $C_5H_6 + CO$  from both  $O(^3P)$  (channel (2)) (in minor part) and  $O(^1D)$  (channel (5)) (in dominant part). As can be seen, the LAB angular distribution of the  $C_5H_6$  product is very broad because of linear momentum conservation (cyclopentadiene is left by the heavy CO co-product). While the  $O(^3P)$  and  $O(^1D)$  contributions to CO formation cannot be distinguished in the  $N(\Theta)$ , they can readily be disentangled by the TOF measurements, because of the much larger exothermicity of channel (5) respect to channel (2). Therefore,  $C_5H_6$  formed from  $O(^1D)$  is expected to be much faster than  $C_5H_6$  from  $O(^3P)$ , as it is indeed observed experimentally (see  $m/z = 66$  TOF spectra in Figure (4b), which show the small  $O(^3P)$  contribution peaking at about 250  $\mu s$  and the very large  $O(^1D)$  one at about 150  $\mu s$ , as determined by the very different corresponding  $P(E_T)$  distributions (see Figure 6b). The fact that the peak attributed to  $C_5H_6$  from  $O(^1D)$  is much more intense than that from  $O(^3P)$  (see Figure 4b), despite the fact that the  $O(^1D)$  concentration in the atomic beam is about an order of magnitude lower than that of  $O(^3P)$ , is due to the much larger reactive cross section of the barrierless  $O(^1D)$  reaction with respect to the  $O(^3P)$  reaction. Moreover, while the  $O(^1D)$  reaction forming  $CO + C_5H_6$  occurs adiabatically on the singlet PES, the  $O(^3P)$  reaction can lead to  $C_5H_6 + CO$  only via the nonadiabatic process of ISC, which has a relatively low probability. Notably, although the LAB results obtained here are qualitatively similar to those obtained in the early pioneering CMB study of Sibener *et al.*<sup>10</sup> at a comparable  $E_c$ , where a small amount of phenol was also observed peaking at the CM, the earlier data<sup>10</sup> were not analyzed in terms of  $O(^3P)$  and  $O(^1D)$  contributions (although  $O(^1D)$  was known to be present in the atomic oxygen beam), because of lack of sufficient TOF resolution (12  $\mu s$ /channel TOF spectra and TOF path of about 17 cm, versus 6  $\mu s$ /channel and 24.3 cm, respectively, of the present study), and also of the more limited LAB angular range in which those earlier data were collected.

The CO forming channel from O(<sup>3</sup>P) was fitted using a symmetric, slightly polarized CM angular distribution, and a P(E'<sub>T</sub>) distribution peaking at about 4.7 kcal/mol and falling to zero at around 20 kcal/mol (see Figure 6b), which witnesses only 8% of the total available energy released into product translation (in turn, this corresponds to a very high internal excitation of the molecular CO and C<sub>5</sub>H<sub>6</sub> products of about 92% of the total available energy). In contrast, the P(E'<sub>T</sub>) distribution of the C<sub>5</sub>H<sub>6</sub> + CO channel from O(<sup>1</sup>D) peaks at about 25 kcal/mol and extends up to about 90 kcal/mol, featuring a much larger fraction ( $\langle f_T \rangle = 0.28$ ) of the total available energy (E<sub>TOT</sub> ≈ 128 kcal/mol) released in translation, with respect to the corresponding channel from O(<sup>3</sup>P). This clearly indicates that a significant fraction of the internal electronic energy (45.3 kcal/mol) of the atomic reactant is channeled into product translational energy.

It is worth comparing the TOF spectra at  $m/z = 66$  depicted in Figure 4b with those at the same mass depicted in Figure 1c of ref. 51. It should be noted that, in Figure 1c of Chen *et al.*,<sup>51</sup> the features  $\beta$  and  $\gamma$  in the TOF at  $m/z = 66$  (reported already corrected for the contribution of the O(<sup>3</sup>P) reaction) are due to the naturally abundant <sup>13</sup>C-isotopic C<sub>5</sub>H<sub>5</sub><sup>+</sup> detected with very large intensity at  $m/z = 65$ , and that, once corrected out leave only the fast peak  $\alpha$  (peaking at about 150  $\mu$ s) due to C<sub>5</sub>H<sub>6</sub> from the C<sub>5</sub>H<sub>6</sub> + CO channel from O(<sup>1</sup>D). In contrast, because our TOF data at  $m/z = 66$  are already corrected for <sup>13</sup>C-isotopic C<sub>5</sub>H<sub>5</sub><sup>+</sup>, but not for the O(<sup>3</sup>P) contribution, O(<sup>3</sup>P) reaction products are also present (phenol and C<sub>5</sub>H<sub>6</sub>, with the former strongly amplified at the CM despite its small contribution with respect to C<sub>5</sub>H<sub>6</sub> from channel (2)). Because we did not have two distinct experiments at the same E<sub>c</sub>, one with only a O(<sup>3</sup>P) beam and one with a beam containing both O(<sup>3</sup>P) and O(<sup>1</sup>D) (in equal amounts in the case of Chen *et al.*<sup>51</sup>) to make the correction due to O(<sup>3</sup>P) similar to that done by of Chen *et al.*, and being our goal rather that of deriving the dynamics of both O(<sup>3</sup>P) and O(<sup>1</sup>D) reactions with benzene, we have reported data at  $m/z = 66$  already corrected for <sup>13</sup>C natural isotopic abundance of  $m/z = 65$ . The peak that we see at about 150  $\mu$ s in all our TOF spectra shown in Figure 4b is the analogous of the peak  $\alpha$  in Figure 1c of ref. 51. However, and most notably, between the main fastest and slowest peaks observable in Figure 4b, the TOF spectra

indicate a small amount of a further contribution, whose velocity is intermediate between that of phenol and that of cyclopentadiene from the  $O(^1D) + \text{benzene}$  reaction. Although the intensity for this product is rather low in the present experimental conditions, at this mass-to-charge ratio it can be unambiguously identified as cyclopentadiene (via its parent ion) deriving from the reaction of benzene with  $O(^3P)$  (channel (2)).

### 3.3. The $m/z = 65$ Data: H Displacement, $\text{CO} + \text{C}_5\text{H}_6$ , and $\text{CO} + \text{C}_5\text{H}_5 + \text{H}$ (3-body)

**Channels.** Regarding the experimental data acquired at  $m/z = 65$ , the reactive signal was found to be very large (12.5 times larger than at  $m/z = 66$ , as already mentioned), giving a great deal of information. In particular, the angular distribution was measured in the same angular range where it was observed reactive signal at  $m/z = 66$ , that is, from  $-12^\circ$  to  $102^\circ$  LAB angle. A first comparison between the angular distributions at  $m/z = 66$  and  $65$ , reported in the Figures 4a and 5a, respectively, indicates that the oxidation of benzene occurs through different mechanisms with  $O(^3P)$  and  $O(^1D)$  reactants, which can be discerned from TOF measurements and by analyzing the different fragmentation patterns of the primary products detected at these  $m/z$  ratios. For instance, in both cases the angular distributions are characterized by a central peak. However, in the distribution acquired at  $m/z = 65$ , the peak is wider than that observed at  $m/z = 66$ , especially in the forward direction. Note that the phenoxy product from channels (1) and (4) easily loses a CO molecule in the ionizer giving the  $m/z = 65$  daughter ion. Moreover, in the angular distributions recorded at  $m/z = 66$  and  $65$ , there are two wings that extend over a wide LAB angular range. However, at  $m/z = 66$  it was found a somewhat higher intensity in the forward direction, while at  $m/z = 65$  the relative intensity of the two wings is comparable. This indicates that different primary products contribute at the two mass-to-charge ratios. In particular, the main difference between the two angular distributions (Figures 4a and 5a) is due to the 3-body channel (6) from  $O(^1D) + \text{benzene}$ , producing  $\text{CO} + \text{H} + \text{C}_5\text{H}_5$ , whose occurrence was assessed by the detection of the  $\text{C}_5\text{H}_5$  species via its parent ion at  $m/z = 65$ .

As discussed by Chen *et al.*<sup>51</sup> in the analogous pulsed CMB experiments at  $E_c=10$  kcal/mol, we note that for the 3-body channel (6) the momentum exerted by the H atom is negligible because of its small mass; we can then analyze only the momentum-matching condition for  $C_5H_5$  and CO. Because there is no reverse barrier for the H atom loss process from  $C_5H_6$  (see Figure 1), the kinetic energy of the H atom product is expected to be small. Since the momentum of the H atom would be small with respect to that of  $C_5H_5$  and CO products, in the data analysis we only used the masses of  $C_5H_5$  and CO products, neglecting the translational energy of the H atom, as previously done by Chen *et al.*<sup>51</sup> We remark that the  $T(\theta)$  distribution for the 3-body channel is backward-forward symmetric, slightly polarized (see Figure 6a), and this indicates a reaction mechanism associated with a long-lived complex.<sup>74,75</sup>

Besides the 3-body channel from  $O(^1D)$ , phenol (channel (3)), phenoxy (channels (1) and (4)), and cyclopentadiene (channels (2) and (5)) were also contributing at  $m/z = 65$  via their daughter ion. Cyclopentadiene is assumed to give a  $(m/z = 65)/(m/z = 66)$  intensity ratio of about 0.5.<sup>76</sup> Finally, if we compare the TOF spectra acquired at  $m/z = 66$  and  $65$  with those recorded at  $m/z = 93$ , we note that the relative intensity of the peaks changes with varying LAB angle of detection, especially focusing on the slower peak, whose maximum intensity occurs in proximity of  $\Theta_{CM} = 48^\circ$ . This trend can be explained by considering that products originating from the breakage of the C-C bond of the aromatic ring are more exothermic, and, therefore, by linear momentum conservation, scatter over wider Newton circles compared to species deriving from H displacement channels, which are kinematically constrained within small circles and therefore have an intensity strongly amplified at the CM angle (see Figure 2). In particular, in Figure 5b the large, slow peak centered at around  $400 \mu s$  originates from phenol (channel (3)), and phenoxy from  $O(^3P)$  (channel (1)) and  $O(^1D)$  (channel (4)). The faster and rather strong peak at around  $230 \mu s$  is mainly due to  $C_5H_5$  from the 3-body channel (6), in agreement with the results of ref. 51. The fastest shoulder (particularly well visible at  $\Theta=28^\circ$  - see also Figure SI-1) is due to  $C_5H_6$  from the  $O(^1D)$  reaction (channel (5)), in agreement

with Chen *et al.*<sup>51</sup> Because of the dominant contribution of the 3-body channel, the C<sub>5</sub>H<sub>6</sub> product contribution from channel (2) appears very weak in these  $m/z = 65$  TOF spectra. Overall, we note an excellent agreement with the results of Chen *et al.*<sup>51</sup> on the O(<sup>1</sup>D) + C<sub>6</sub>H<sub>6</sub> reaction.

We now wish to show that the simultaneous best-fit of the  $m/z = 93$  and  $65$  data, with the constraint of reproducing accurately the width and position of the main peaks in the angular distributions around the CM, and the shape and relative intensity at the various LAB angles of the corresponding overall peaks in the TOF distributions, has permitted us to derive unambiguously the best-fit CM functions for three contributing pathways to phenoxy formation. The LAB angular distributions at  $m/z = 93$  (Figure 3a) and  $65$  (Figure 5a) clearly show that the contribution to the total angular distributions of phenoxy from O(<sup>3</sup>P) via ISC and from O(<sup>1</sup>D), both peak near the CM, while the contribution of phenoxy from O(<sup>3</sup>P) via the triplet PES exhibits a peak at angles smaller than  $\Theta_{\text{CM}}$  (i.e., in the forward direction). Notably, the relative weights of the O(<sup>1</sup>D) and O(<sup>3</sup>P) contributions are opposite at the two masses, being that of O(<sup>1</sup>D) at  $m/z = 65$  comparatively much larger than at  $m/z = 93$ , because hotter phenoxy from O(<sup>1</sup>D) expectedly fragments more extensively in the ionizer. It is useful to examine also the relative contributions in the TOF spectra at  $m/z = 65$  (where the signal is strongest and the S/N highest). An examination of the TOF spectra at  $m/z = 65$  in the forward direction ( $\Theta=28^\circ$ ), at the CM ( $\Theta=48^\circ$ ), and in the backward direction ( $\Theta=64^\circ$ ) shows that the peak of phenoxy from O(<sup>3</sup>P) via ISC peaks closer to the CM velocity (the phenol velocity, see  $m/z = 66$  TOF) than the phenoxy from O(<sup>3</sup>P) occurring adiabatically on the triplet PES or from O(<sup>1</sup>D), and that it goes nearly to zero at  $\Theta=28^\circ$  because very little energy goes in translation for this channel. At the same time, because of the strongly forward peaking of the  $T(\theta)$  for phenoxy from O(<sup>3</sup>P) on the triplet PES, and because a large fraction of the total available energy goes in translation for this channel ( $\langle f_T \rangle = 0.34$ ), its contribution appears at  $\Theta_{\text{CM}}=48^\circ$  and at  $\Theta=28^\circ$  (forward direction), while it appears very weak in the backward direction (see TOF at  $\Theta=64$  in Figure 5b).

**3.4. Branching Fractions (BFs).** After the characterization of the CM  $T(\theta)$  and  $P(E_T)$  functions for the various product channels (Figure 6), the branching fraction of each primary product was estimated by using the procedure introduced by Schmoltner *et al.*<sup>11</sup> and widely employed by us in the study of a variety of multichannel reactions of  $O(^3P)$  with UHs.<sup>19,22</sup> The experimental BFs for the competing product channels of the  $O(^3P, ^1D) +$  benzene reactions at  $E_c = 8.2$  kcal/mol are listed in Table 1, while the BFs for the distinct  $O(^3P)$  and  $O(^1D)$  reactions are reported in Table 2. In Table 2 the BFs for the  $O(^3P)$  reaction are compared with the theoretical predictions from RRKM/ME simulations on the coupled triplet/singlet PES for the conditions of the CMB experiment. In addition, also the BFs derived from kinetic studies<sup>24</sup> at 900 K and 4 Torr are reported, compared with the RRKM/ME predictions for the same conditions from the present study. It is useful to take a closer look at the BFs in Table 1. If we add all the yields from the  $O(^3P)$  reaction channels (1-3) and those from the  $O(^1D)$  reaction channels (4-6), we find the following ratio: [yield  $O(^3P)$  reactions] / [yield  $O(^1D)$  reactions]=0.048 / 0.952, that is, under our experimental conditions only about 5% of the total reactive signal originates from the  $O(^3P)$  reaction with benzene, while the rest comes from the  $O(^1D)$  reaction. If we assume that the concentration of  $O(^1D)$  in the atomic oxygen beam is about 10% (upper limit) of that of  $O(^3P)$ ,<sup>60</sup> this would indicate that at the  $E_c=8.2$  kcal/mol the total reactive cross section of the reaction of benzene with  $O(^1D)$  is about 190 times larger than that with  $O(^3P)$ . This is plausible given that the  $O(^3P) +$  benzene reaction has  $k_{300K} \approx 1 \times 10^{-14}$  cc molec<sup>-1</sup> s<sup>-1</sup> ( $k_{900K} \approx 3 \times 10^{-12}$  cc molec<sup>-1</sup> s<sup>-1</sup>)<sup>24</sup> while the barrierless  $O(^1D)$  reaction with benzene is expected to be gas-kinetic ( $k_{300K} \approx 1 \times 10^{-10}$  cc molec<sup>-1</sup> s<sup>-1</sup>, with  $k$  only slightly decreasing with increasing temperature). Despite the relatively small fraction of the total reactive signal coming from the  $O(^3P)$  reaction, we were able to derive the detailed dynamics also for the  $O(^3P) +$  benzene reaction, along with that of the  $O(^1D)$  reaction. Both reaction dynamics will be compared with previous findings in the Discussion section.

As shown in Table 2, the trend of BFs for the various channels of the  $O(^3P) +$  benzene and  $O(^1D) +$  benzene reactions are found to be significantly different. For example, for  $O(^3P) +$  benzene

the H displacement channel (1) is dominant (overall BF =  $0.66 \pm 0.24$ ), while the analogous channel for  $O(^1D) + \text{benzene}$  (channel (4)) is minor (BF =  $0.04 \pm 0.02$ ). On the other hand, if we compare channels (2) and (5) we find that  $C_6H_5 + CO$  formation is significant in both  $O(^1D) + \text{benzene}$  (BF =

**Table 1.** Experimental BFs determined for the  $O(^3P, ^1D) + \text{reactions}$  at  $E_c=8.2$  kcal/mol. The experimental uncertainties vary between 25% and 50% depending on the reactive channel.

REACTANTS	PRIMARY PRODUCTS	Reaction channel	PES involved	BFs
$O(^3P) + C_6H_6$	$C_6H_5O + H$	(1)	triplet	<b><math>0.023 \pm 0.07</math></b>
	$C_6H_5O + H$	(1)	singlet via ISC	<b><math>0.009 \pm 0.004</math></b>
	$C_5H_6 + CO$	(2)	singlet via ISC	<b><math>0.015 \pm 0.007</math></b>
	Phenol	(3)	singlet via ISC	<b><math>0.001 \pm 0.0005</math></b>
$O(^1D) + C_6H_6$	$C_6H_5O + H$	(4)	singlet	<b><math>0.03(5) \pm 0.01</math></b>
	$C_5H_6 + CO$	(5)	singlet	<b><math>0.32(4) \pm 0.09</math></b>
	$C_5H_5 + CO + H$	(6)	singlet	<b><math>0.59(3) \pm 0.15</math></b>

**Table 2.** Experimental BFs determined for the  $O(^3P) + C_6H_6$  and  $O(^1D) + C_6H_6$  reactions at  $E_c=8.2$  kcal/mol, as obtained from Table 1 (see text), compared to the BFs predicted by RRKM/ME calculations on the coupled triplet/singlet PESs at  $E_c=8.2$  kcal/mol. The experimental uncertainties vary between 25% and 50% depending on the reactive channel. For the  $O(^3P)$  reaction also the BFs estimated in kinetic work<sup>24</sup> at 900 K and 4 Torr are reported and compared with our RRKM/ME predictions. For the  $O(^1D)$  reactions the experimental BFs are compared with those estimated from previous pulsed CMB work at  $E_c=10$  kcal/mol.<sup>51</sup>

REACTANTS	PRIMARY PRODUCTS	PES involved	BFs CMB expt. ( $E_c=8.2$ kcal/mol)	BFs RRKM/ME ( $E_c=8.2$ kcal/mol)	BFs Kinetic expt. <sup>24</sup> (900 K, 4 Torr)	BFs RRKM/ME (900 K, 4 Torr)
$O(^3P) + C_6H_6$	$C_6H_5O + H$	triplet	<b><math>0.48 \pm 0.15</math></b>	<b>0.26</b>	$0.33 \pm 0.13$	0.46
	$C_6H_5O + H$	singlet via ISC	<b><math>0.18 \pm 0.09</math></b>	<b>0.15</b>		0.13
	$C_5H_6 + CO$	singlet via ISC	<b><math>0.32 \pm 0.14</math></b>	<b>0.59</b>	$0.33 \pm 0.08$	0.14
	Phenol	singlet via ISC	<b><math>0.02 \pm 0.01</math></b>	<b>0</b>	$0.33 \pm 0.08$	0.27
					CMB expt. <sup>51</sup>	

					(E <sub>c</sub> =10 kcal/mol)	
<b>O(<sup>1</sup>D) + C<sub>6</sub>H<sub>6</sub></b>	C <sub>6</sub> H <sub>5</sub> O + H	singlet	<b>0.04 ± 0.02</b>		minor	
	C <sub>5</sub> H <sub>6</sub> + CO	singlet	<b>0.34 ± 0.10</b>		minor	
	C <sub>5</sub> H <sub>5</sub> + CO + H	singlet	<b>0.62 ± 0.15</b>		dominant	

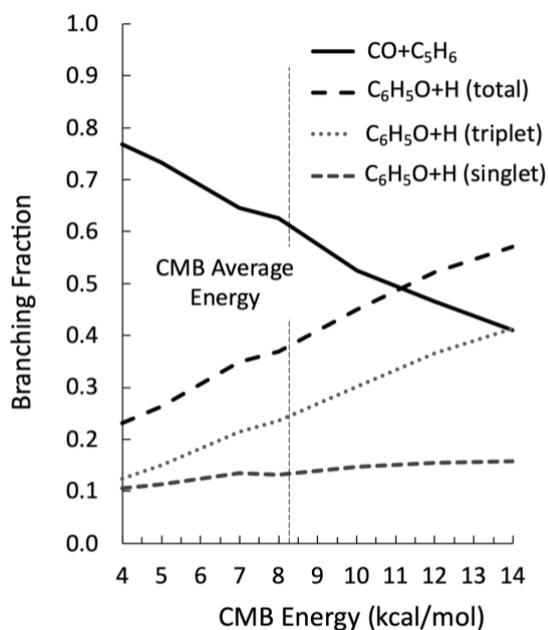
0.34± 0.10)) and O(<sup>3</sup>P) + benzene (BF = 0.32 ± 0.14). Notably, we detected the adduct (channel 3) from the O(<sup>3</sup>P) + benzene reaction as a minor product (BF = 0.02±0.01) and we confirmed that the three-body channel (6) is dominant in the O(<sup>1</sup>D) + benzene reaction (BF = 0.62±0.15), the latter corroborating the results by Chen *et al.*<sup>51</sup> However, in contrast to Chen *et al.*, for the O(<sup>1</sup>D) + benzene reaction we find a reversed yield of the C<sub>6</sub>H<sub>5</sub>O + H and C<sub>6</sub>H<sub>5</sub> + CO forming channels, despite the fact that the LAB data appear very similar. In particular, the branching ratio of channels [CO + stable C<sub>5</sub>H<sub>6</sub>]/[CO from the 3-body channel] is 0.55±0.20 in our case, while it is reported to be 0.12±0.03 in the previous study.<sup>51</sup> In contrast, the branching ratio of channels [C<sub>6</sub>H<sub>5</sub>O + H]/[3-body channel] is 0.065±0.025 in our case, while it is 0.38±0.06 in the previous study. We do not know the origin of this discrepancy, which is not expected to be justified by the 2 kcal/mol difference in the collision energy of the two experiments. However, it should be noted that, even if we add the H channel yield from O(<sup>3</sup>P) to the H yield from O(<sup>1</sup>D), the above large disagreement between the branching ratios from our study and those from the Chen *et al.* study would persist, because the yields of phenoxy + H from O(<sup>3</sup>P) and from O(<sup>1</sup>D) are comparable in our study (see Table 1). Interestingly, we note that a reasonable agreement between the two studies, considering the somewhat different E<sub>c</sub>, would be obtained if the branching ratios in Chen *et al.*'s study were actually interchanged, i.e. 0.12±0.03 for the [H]/[3-body] channels (versus our 0.065±0.025) and 0.38±0.06 for the [C<sub>6</sub>H<sub>5</sub>+CO]/[3-body] channels (versus our 0.55±0.20).

## 4. THEORETICAL RESULTS

**4.1. Branching Fractions under CMB Conditions.** The theoretical methodology described in section 2.2 was used to calculate the BFs for the reaction between O(<sup>3</sup>P) and benzene.

Calculations were performed using the same procedure adopted in our previous theoretical studies of reactions between  $O(^3P)$  and unsaturated hydrocarbons (see, for instance, ref. 22) which yielded in general a good agreement with experiments. In this instance, however, stochastic kinetic Monte Carlo simulations were performed accounting explicitly for the collisional energy distribution in CMB experiments, using experimental data to weight collision energy contributions within a 4-14 kcal/mol range, with an average value of 8.2 kcal/mol. The weak coupling model was used to compute crossing probabilities at the MECP, and NA-TST theory to evaluate rate constants. The computational results are compared with experiments in Table 2. It should be noted that the theoretical results differ slightly, by up to a factor of 1.2 in the BFs, from those reported in our previous study<sup>34</sup> because of the change of the energy barrier of  $^3TS2$ , the use of the weak coupling ISC model, and the simulation of CMB experiments using the collisional energy distribution rather than the average value. The results of simulations performed at values of collision energy of the CMB experiment between 4 and 14 kcal/mol, thus in the range corresponding to the experimental spread of the relative collision energy, are shown in Figure 7. It can be noted that BFs are significantly sensitive to the relative energy of the beams. When it is low, the main products are  $C_5H_6$  and  $CO$ . As the collision energy increases, the relevance of this channel progressively decreases because of competition by the H loss channels from the triplet and singlet PESs. It is interesting to notice how H loss from the singlet PES is significant in all conditions, though H loss from the triplet PES is largest even at the lowest CMB energies here explored. As can be observed, there is some disagreement between the experimental and calculated BFs (see Table 2). Experimentally, it is found that the main reaction channel leads to the formation of  $C_6H_5O + H$ , while, theoretically, the opposite is true ( $CO + C_5H_6$  larger than  $C_6H_5O + H$ ). However, the relative contributions to the H channel from the triplet and the singlet PESs are nicely captured by the model, which predicts that H is produced mainly from the triplet PES. In addition, it should be noted that there is considerable uncertainty, both in the experimental determinations and in the theoretical calculations. In particular, we observe that theoretical calculations rely on the ergodic

assumptions that the relative kinetic energy of the beams, following  $O(^3P)$  addition, is distributed among all molecular degrees of freedom. Our previous investigations of  $O(^3P)$  reactions with

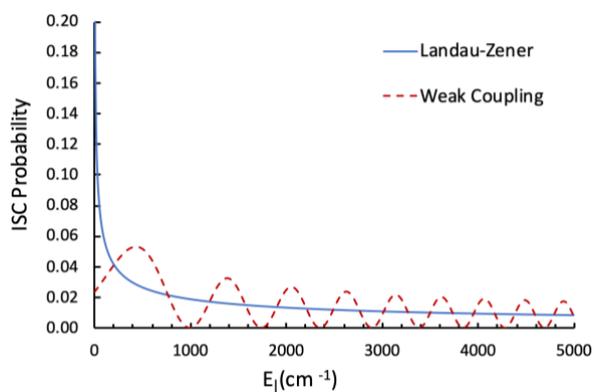


**Figure 7.** Branching fractions for the reaction between  $O(^3P)$  and benzene computed at different CMB collision energies. The vertical line corresponds to the nominal collision energy ( $E_c$ ) of the present experiments (8.2 kcal/mol).

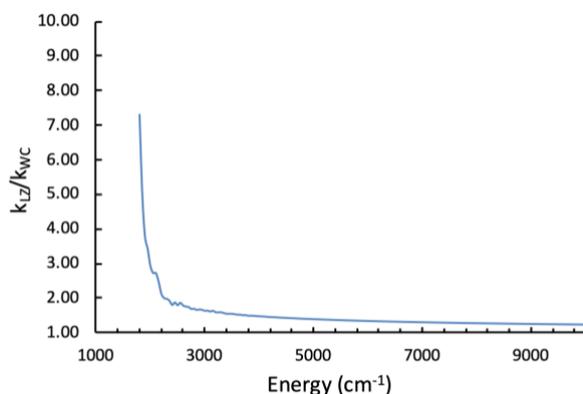
unsaturated hydrocarbons suggest that this may not always be the case for H loss channels. To determine the level of uncertainty in the present theoretical calculations, we performed additional calculations using a higher level of theory to compute ISC crossing rates (section 4.2), and checked the impact of selected model parameters on the BFs (section 4.3).

**4.2. Landau-Zener and Weak Coupling ISC Models.** Intersystem crossing probabilities and rate constants were computed at two levels of theory: the Landau-Zener (LZ) model, often used to study spin-forbidden processes, and the weak-coupling (WC) model (described in the method section). The WC model is expected to give a better theoretical description of ISC than the LZ model, which tends unphysically to a crossing probability of 1 when the energy in the reaction coordinate ( $E_{\perp}$ ) goes to zero and  $H_{SO}$  is small, as it is the case in the present system. A comparison of the ISC probabilities calculated with the two models as a function of  $E_{\perp}$  is shown in Figure 8. It can be observed that the LZ model, as expected, overestimates considerably the crossing probability

at low  $E_{\perp}$ . The two ISC probabilities first cross at  $E_{\perp} = 200 \text{ cm}^{-1}$  ( $\approx 0.6 \text{ kcal/mol}$ ). The ratio of rate constants calculated with Eq. (8) using the LZ and WC models are compared in Figure 9 as a



**Figure 8.** ISC probabilities computed as a function of the energy in the reaction coordinate  $E_{\perp}$ .



**Figure 9.** Ratio of ISC rate constants calculated using the LZ and WC models as a function of the total internal energy.

function of the total internal energy, referred to the bottom of the reactant well  ${}^3\text{W1}$  (see Figure 1). As could be expected, it can be noted that the LZ rate constant is considerably larger than the WC rate constant at low energies, and that the rates become comparable as energy increases. The impact of using ISC rate constants calculated using the LZ and WC models on the system reactivity is discussed in the next section.

**4.3. Impact of Model Parameters on Predicted Branching Fractions.** The impact of uncertainties and theoretical model approximations on the BFs predicted through master equation simulations is here investigated. In particular, we focus on the theoretical model used to determine ISC rates (LZ vs WC), on the spread of the collision energy in the CMB experiment, and on

uncertainties in the energy of some key stationary points of the PES. The results of this analysis are summarized in Table 3. It can thus be observed that performing the simulations using the LZ or WC has a small impact on the predicted BFs. The reason is that following O(<sup>3</sup>P) addition to the aromatic ring and assuming that the collision energy is distributed statistically among the internal degrees of freedom of the intermediate <sup>3</sup>W1, the average internal molecular energy is about 8000 cm<sup>-1</sup>, thus in the region where (see Figure 9) the LZ and WC ISC rates are similar. Simulations were performed using the average collision energy of 8.2 kcal/mol. The data reported in Table 3 can also be used to evaluate the impact of performing the simulations using the CMB collisional energy distribution or the average energy. As it can be observed, the impact is small but not negligible.

**Table 3.** Sensitivity of calculated branching fractions for the O(<sup>3</sup>P) + benzene reaction in CMB conditions to the adopted theoretical model and to uncertainties in model parameters.

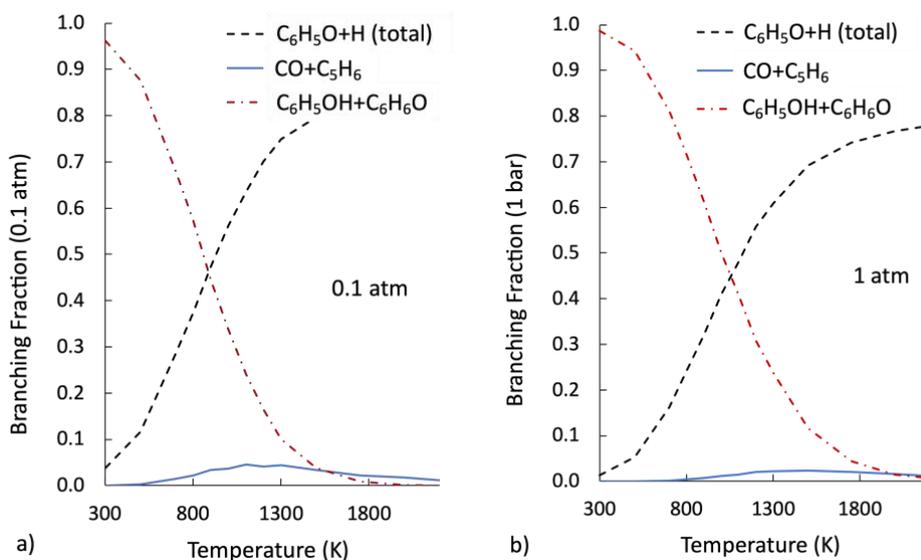
<b>Model</b>	C <sub>6</sub> H <sub>5</sub> O + H (triplet)	C <sub>5</sub> H <sub>6</sub> + CO	C <sub>6</sub> H <sub>5</sub> O + H (singlet)
Collision Energy Distribution	0.26	0.59	0.15
Landau-Zener ISC <sup>a</sup>	0.22	0.64	0.14
Weak Coupling <sup>a</sup>	0.25	0.61	0.14
-2 kcal/mol MECP Energy <sup>a,b</sup>	0.10	0.73	0.18
+2 kcal/mol MECP Energy <sup>a,b</sup>	0.53	0.38	0.08

<sup>a</sup> Simulations performed at the average collision energy of 8.2 kcal/mol. <sup>b</sup> Simulations performed using the weak coupling ISC model.

We then investigated the uncertainty in key energy barriers on the predicted BFs. Specifically, we focused on the energy barrier for the reaction of H loss on the triplet PES (<sup>3</sup>TS2) and on the MECP energy. Considering the multireference character of the MECP and the level of the theoretical calculations, it is reasonable to expect that both energies of these stationary points may have an uncertainty of at least 1 kcal/mol. As the two reaction pathways are in competition, the impact of these uncertainty was investigated by modifying the energy of the MECP by  $\pm 2$  kcal/mol,

thus condensing the whole uncertainty in this parameter. The results of the simulations indicate a significant effect on the BFs, with the triplet H loss channel BF changing by a factor of two, and the  $C_5H_6 + CO$  and singlet H loss channels being modified by about  $\pm 0.15$ . It is therefore reasonable to expect a significant model sensitivity to the computed energy barrier for the triplet H loss and to the MECP energy channel, and a smaller one for the singlet channels. It should be noted that the BF of the triplet channel is the one where the difference between calculated and experimental data is highest (see Table 2). We note that agreement between experimental BFs and theoretical predictions would improve significantly if the MECP energy was to be increased by 2 kcal/mol, from which the BF( $C_6H_5O + H$  from singlet) would become 0.08 (vs  $0.18 \pm 0.09$  experimental), the BF( $C_5H_6 + CO$ ) would become 0.38 (vs  $0.32 \pm 0.14$ ), and the BF( $C_6H_5O + H$  from triplet) would become 0.53 (vs  $0.48 \pm 0.15$ ).

**4.4. Thermal rate constants: pressure dependence and fits.** Rate constants were computed as a function of temperature at different pressures using the approach described in the method section and in our previous study.<sup>34</sup> Due to the inherent relevance in combustion systems, it is interesting at this point to discuss the dependence of the BFs of the main reaction channels on temperature and pressure in greater detail. The BFs calculated at 0.1 and 1 atm are reported in Figure 10. The BFs dependence on temperature predicted for the thermal simulations of Figure 10



**Figure 10.** Branching fractions for the reaction between O(<sup>3</sup>P) and benzene computed as a function of temperature at different pressures.

can be compared to the CMB simulations performed as a function of the CMB energy reported in Figure 7. It can be noted that the relevance of the BF of the CO + C<sub>5</sub>H<sub>6</sub> channel is much smaller in the thermal simulations than in the CMB simulations. This is determined by the impact of collisional stabilization of the singlet wells, most notably phenol (<sup>1</sup>W1) and two cyclohexadienone isomers (<sup>1</sup>W2 and <sup>1</sup>W6), which become the main products on the singlet PES (see Figure 1). Arrhenius fits of rate constants computed at different temperatures and pressures are reported in Table 4.

**Table 4.** Arrhenius fits in the form  $AT^{\alpha}\exp(-E_A/RT)$ . Units: cal, mol, s, cm<sup>3</sup>. In the fitting the rate constants for all the collisionally-stabilized wells (mainly <sup>1</sup>W1, <sup>1</sup>W2, and <sup>1</sup>W7) were merged into that of phenol (<sup>1</sup>W1).

Reaction	P [atm]	A [cm <sup>3</sup> /mol/s]	$\alpha$	E <sub>A</sub> [cal/mol]	R <sup>2</sup>	T Range [K]
C <sub>6</sub> H <sub>6</sub> + O → C <sub>6</sub> H <sub>5</sub> O + H	0.1	1.34E+08	1.76	5620	1.00	300-2200
	1	1.04E+08	1.79	5600	1.00	300-2200
	10	2.91E+08	1.66	5880	1.00	300-2200
	100	6.67E+09	1.28	6930	1.00	300-2200
C <sub>6</sub> H <sub>6</sub> + O → CO + C <sub>5</sub> H <sub>6</sub>	0.1	6.09E+15	-0.91	9840	0.99	300-2200
	1	2.22E+18	-1.58	14800	1.00	300-2200
	10	3.01E+19	-1.83	20300	1.00	800-2200
	100	5.63E+02	2.87	12900	0.99	1000-2200
C <sub>6</sub> H <sub>6</sub> + O → C <sub>6</sub> H <sub>5</sub> OH	0.1	1.80E+16	-6.73	-14031	0.98	300-1500
	1	3.49E+12	-0.78	1200	0.99	300-1500
	10	1.97E+23	-3.11	8560	1.00	500-1750
	100	5.61E+21	-2.63	7900	1.00	300-2000

DUPLICATE

0.1	1.40E+38	-7.68	14400
1	1.05E+28	-4.55	10500
10	1.46E+32	-6.88	7500
100	7.90E+33	-7.60	7500

## 5. DISCUSSION

The experimental results will be discussed in the light of the calculated triplet and singlet PESs and related theoretical predictions of product BFs from RRKM/ME calculations with inclusion of ISC. In particular, the shape of the CM product angular distributions and the fraction of the total available energy released as product translational motion for each reactive channel will be discussed analyzing the characteristics of the PESs involved (see Figure 1 and ref. 34), to achieve a comprehensive picture of the reaction mechanism.

**5.1. Product Angular Distributions and Lifetimes of Intermediates.** As may be seen in Figure 6, the best-fit CM  $T(\theta)$ s are backward-forward symmetric for all observed products of the  $O(^3P)$  and  $O(^1D)$  reactions, except for the phenoxy product from the direct  $O(^3P)$  reaction occurring on the triplet PES. It should be noted that all other product channels occur on the singlet PES (see Figure 1) and their backward-forward symmetric  $T(\theta)$  indicates that the reactions proceed via a long-lived complex mechanism,<sup>74,75</sup> which implies intermediate complexes living at least 5-6 rotational periods (which are of the order of picoseconds) before decomposing to products. Indeed, RRKM/ME computed lifetimes of  $^1W7$  and  $^1W2$  singlet intermediates (see Figure 1) are of the order of more than 100 ps, which corroborates the long-lived complex mechanism. In contrast, the lifetime of the  $^3W1(A')$  intermediate, which can lead adiabatically to the phenoxy + H products, having a rather shallow well of -12.8 kcal/mol, is much shorter (about 10 ps at  $E_c = 8.2$  kcal/mol and 7 ps at 800 K) than the lifetime of singlet intermediates. Consequently, for a range of impact parameters, a large fraction of the reactive  $O(^3P)$  + benzene collisions proceed nearly directly, that is, via a strongly osculating complex mechanism,<sup>74,75</sup> as witnessed by the strongly forward-biased angular distribution of phenoxy (Figure 6a-top panel). As observed previously in reactions of  $O(^3P)$

with UHs, in numerous cases the H displacement channel was found to behave not statistically, that is, if the energy following O attack on the carbons of the aromatic ring is not fully randomized within the triplet complex, the triplet dynamics may not be treatable by statistical theories. Indeed, the BF of the adiabatic H displacement channel from O(<sup>3</sup>P) + benzene is somewhat underestimated by the RRKM/ME simulations (BF=0.26 vs an experimentally derived value of 0.48±0.15) (see Table 2). It should be noted that following the electrophilic O atom attack on a ring carbon atom on the lowest A' triplet PES through the lowest entrance barrier of 3.8 kcal/mol, the initially formed triplet diradical <sup>3</sup>W1(A') undergoes preferentially H-elimination via an exit barrier (<sup>3</sup>TS2) to produce C<sub>6</sub>H<sub>5</sub>O + H (Figure 1). In contrast, following the electrophilic O atom attack at a ring carbon atom on the first excited <sup>3</sup>A'' PES through a slightly higher entrance barrier of 4.5 kcal/mol, the initially formed triplet diradical <sup>3</sup>W1(A'') undergoes preferentially and readily ISC onto the <sup>1</sup>A' singlet surface (Figure 1). As discussed in Section 4 (see also ref. 34) there are two minimum energy crossing points (MECPs) between <sup>3</sup>A'' and <sup>1</sup>A'. One of them (labeled ISC1) is located at -7.8 kcal/mol with respect to reactants, that is 0.8 kcal/mol above the <sup>3</sup>W1(A'') state, while the other one (labeled ISC2) is located at -9.2 kcal/mol, that is 0.6 kcal/mol below the <sup>3</sup>W1(A'') state. ISC is fast at these two MECPs, leading to the singlet state of the adduct followed by an almost barrierless isomerization to benzene oxide (<sup>1</sup>W7), which is located at -54.5 kcal/mol with respect to reactants (see Figure 1). Once formed, benzene oxide can undergo various isomerizations and dissociate to various products which have been detected experimentally. Specifically, <sup>1</sup>W7 isomerizes first via a barrier (<sup>1</sup>TS12) of 43.4 kcal/mol to the more stable (-81.5 kcal/mol) 2,4-cyclohexadienone (<sup>1</sup>W2) isomer. 2,4-cyclohexadienone can undergo C-H bond cleavage to phenoxy + H (located at -13.1 kcal/mol with respect to reactants) or, competitively isomerize to <sup>1</sup>W3 (-42.1 kcal/mol) and then <sup>1</sup>W4 (-48.8 kcal/mol) which ultimately decomposes, via <sup>1</sup>TS4 (-24.2 kcal/mol), to cyclopentadiene + CO, the most exothermic product channel, located at -73.6 kcal/mol with respect to reactants (see Figure 1). <sup>1</sup>W2 can also isomerize to phenol (<sup>1</sup>W1) through a higher barrier (<sup>1</sup>TS1) located at -30.6

kcal/mol. Phenol, in turn, can barrierlessly decompose to phenoxy + H, which is favored with respect to the competitive decomposition to benzyne ( $C_6H_4$ ) +  $H_2O$  (see Figure 1 in ref. 34).

It is appropriate here to comment on the nature of the co-product of the spin-forbidden CO forming channel. Clearly, the early suggestion<sup>37</sup> that the co-product of CO is the open chain hydrocarbon 3-penten-1-yne was erroneous, as demonstrated by the present and previous theoretical work<sup>24,48,51</sup> and by the direct observation of cyclopentadiene in the experiment by Taatjes *et al.*<sup>24</sup> by accurate measurements of the ionization efficiency curve of the product, and also by the present and previous<sup>10,51</sup> CMB studies.

It is interesting to examine the BFs of decomposition of the initial singlet intermediate benzene oxide ( $^1W7$ ) to  $C_6H_5 + CO$  and  $C_6H_5O + H$  in the case of the nonadiabatic reaction of  $O(^3P)$  and the adiabatic reaction of  $O(^1D)$  from the present CMB experiments. As shown in Table 2, for the  $O(^3P)$  reaction via ISC the experimental BF of the  $C_5H_6 + CO$  channel (BF =  $0.32 \pm 0.14$ ) is nearly twice that of the  $C_6H_5O + H$  channel (BF =  $0.18 \pm 0.09$ ), while for the  $O(^1D)$  reaction the BF of the ( $C_5H_6 + CO$ ) and ( $C_5H_5 + H + CO$ ) channels together (BF =  $0.34 + 0.62 = 0.96$ ) is nearly 25 times larger than that of the  $C_6H_5O + H$  channel (BF = 0.04). Clearly, the much more internally-excited cyclohexadienone ( $^1W2$ ) formed in the much more exothermic  $O(^1D)$  reaction, preferentially isomerizes to the intermediate  $^1W4$  rather than dissociating to phenoxy + H, and  $^1W4$  via  $^1TS4$  leads readily to  $C_6H_5 + CO$  products (see Figure 1).

We have not attempted a statistical estimate of the product BFs for the  $O(^1D)$  reaction. The two main reasons are: (i) given the high entrance energy in the singlet wells, a statistical treatment is not warranted as the reaction dynamics is expected to be dominated by nonstatistical effects; (ii) it is difficult to calculate individual channel rates because of secondary decompositions. As a matter of fact, although Chen *et al.*<sup>51</sup> in their CMB study of the  $O(^1D) + C_6H_6$  reaction did perform statistical calculations of individual micro-canonical rate coefficients and also of individual product micro-canonical BFs for the reaction as a function of energy (from 5 to 40 kcal/mol), they could not

compare the experimentally estimated BF<sub>s</sub> with the statistically computed BF<sub>s</sub> at  $E_c=10$  kcal/mol energy because of the secondary dissociations.

**5.2. Product Recoil Energies and PESs.** In discussing the product energy releases we will refer again to the features of the triplet/singlet PES. Following the  $O(^3P)$  attack to the aromatic ring via the lowest energy barrier of 3.8 kcal/mol ( $^3TS1$  in Figure 1), the diradical triplet intermediate  $^3W1(A')$  (located at  $-12.8$  kcal/mol) is formed. Because of its high energy content, it will decompose to phenoxy + H via  $^3TS2$  located at  $-0.9$  kcal/mol with respect to reactants (at 13.3 kcal/mol above the products). The  $P(E'_T)$  for the phenoxy + H products so formed on the triplet PES peaks far away from zero, at 6.4 kcal/mol (see Figure 6b-top panel), which is expected for a nearly direct reaction due to the presence of an exit barrier of about 13 kcal/mol (with respect to products) (see Figure 1). The  $P(E'_T)$  extends up to the limit of energy conservation ( $23\pm 3$  kcal/mol), and this is consistent with the experimental reaction exothermicity of 14.4 kcal/mol and  $E_c=8.2$  kcal/mol. The average fraction of total available energy ( $E_{tot}=E_c - \Delta H^0=8.2+14.4=22.6$  kcal/mol) released in translation is  $\langle f_T \rangle = 0.34$ , indicating that the phenoxy radical is highly internally-excited ( $\langle f_{int} \rangle = 0.66$ ). In contrast, the  $P(E'_T)$  of the phenoxy + H products formed via ISC (the ratio of BF<sub>s</sub>  $Phenoxy_{(from\ triplet)}/Phenoxy_{(from\ singlet)}$  is  $0.48/0.18=2.7$ ; see Table 2) peaks at an energy closer to zero (about 3 kcal/mol) and dies off at only about 10 kcal/mol, reflecting a significantly smaller fraction ( $\langle f_T \rangle = 0.17$ ) of product energy in translation. The peaking of the  $P(E'_T)$  close to zero is typical of reactions proceeding via a long-lived complex mechanism with a statistical product energy distribution. Notably, the  $P(E'_T)$  of phenoxy + H from the  $O(^1D)$  reaction, which evolves on the singlet PES, exhibits similar features, i.e., it peaks also at very low energy (3.5 kcal/mol), but extends up to about 40 kcal/mol, consistently with the larger exothermicity of the  $O(^1D)$  reaction; the average fraction of total available energy in translation of 0.16 indicates that the phenoxy radical from  $O(^1D)$  is highly internally-excited ( $\langle f_{int} \rangle = 0.84$ ). It should be noted that, overall, the amount of average internal energy of phenoxy from the  $O(^1D)$  reaction (about 50 kcal/mol) is much higher

than that for the phenoxy from O(<sup>3</sup>P) (about 6.5 kcal/mol), which is mostly formed adiabatically on the triplet PES (see above). This is the reason why phenoxy from O(<sup>1</sup>D) fragments in the ionizer to  $m/z = 65$  much more consistently than phenoxy from O(<sup>3</sup>P) does, as already discussed.

Regarding the C<sub>5</sub>H<sub>6</sub> + CO forming channel from O(<sup>3</sup>P) via ISC, the best-fit P(E'<sub>T</sub>) peaks at about 5 kcal/mol and dies off at about 20 kcal/mol, reflecting a very small fraction of total available energy in product translation ( $\langle f_T \rangle = 0.08$ ) (Figure 6b-fourth panel from top). This indicates that the two molecular products are very highly internally excited. In contrast, the P(E'<sub>T</sub>) for the same products formed from the O(<sup>1</sup>D) reaction peaks at about 26 kcal/mol and extends up to about 90 kcal/mol, reflecting a significantly larger fraction of energy in product translation ( $\langle f_T \rangle = 0.27$ ) (Figure 6b-fifth panel from top). This larger fraction of energy in translation indicates that a significant fraction of the internal (electronic) energy of excited atomic oxygen is converted in translational energy of the products. Interestingly, 73% of the total available energy ( $E_{\text{tot}} \approx 128$  kcal/mol) residing in internal excitation of the CO + C<sub>5</sub>H<sub>6</sub> products is large enough that a fraction of internally-excited cyclopentadiene can unimolecularly readily fragment to C<sub>5</sub>H<sub>5</sub> + H (see Figure 1). Indeed, the experimental data indicate that this is actually the dominant product channel, with a BF=0.62±0.15 (Table 2), to be compared with BF=0.34±0.10 and BF=0.04±0.02 for the C<sub>5</sub>H<sub>6</sub> + CO and C<sub>6</sub>H<sub>5</sub>O + H channels, respectively, from O(<sup>1</sup>D). This result is in agreement with the findings of Chen *et al.*<sup>51</sup> at  $E_c=10$  kcal/mol, according to which the 3-body channel is dominant, while the phenoxy and CO channels are minor.

The total available energy for the 3-body channel is about 47 kcal/mol. The best-fit P(E'<sub>T</sub>), derived as described in section 3.3, peaks at about 5 kcal/mol and extends up to about 36 kcal/mol, corresponding to a sizeable fraction of the total available energy released as product translational energy ( $\langle f_T \rangle \approx 0.24$ ). As it can be seen from Figure 6b, the P(E'<sub>T</sub>) distribution for the C<sub>5</sub>H<sub>6</sub> + CO and the C<sub>5</sub>H<sub>5</sub> + H + CO channels (5) and (6), respectively, is very different. In fact, the peak of the cyclopentadienyl radical from channel (6) occurs at about 220 μs in the TOF at  $m/z = 65$ , while that of cyclopentadiene from channel (5) occurs at about 140 μs (see Figure 5b).

The mechanism of  $C_5H_6 + CO$  formation sees the bridge addition of  $O(^1D)$  to two adjacent carbons of the ring forming benzene oxide ( $^1W7$ ), which then isomerizes by hydrogen migration to  $^1W2$  (2,4-cyclohexadienone), which competitively undergoes C-H bond cleavage to  $C_6H_5O + H$  or isomerization to  $^1W3$  and finally, via ring contraction, to  $^1W4$ , which leads to  $C_5H_6 + CO$  via  $^1TS4$ . Interestingly,  $C_5H_6$  is formed with enough internal energy to undergo fast barrierless unimolecular decay to  $H + C_5H_5$ , forming a 3-body reaction pathway (6), which is overall exoergic by about 38 kcal/mol with respect to the  $O(^1D) + C_6H_6$  reactants (Figure 1).

**5.3. Product Branching Fractions and Extent of ISC.** As mentioned above, the experimentally derived overall branching fractions for the six detected competing channels (1)-(6) from the overall  $O(^3P, ^1D) + C_6H_6$  reactions are reported in Table 1. A few important aspects to note from this Table are the following: (i) under our experimental conditions, about 95% of the total reactive yield is due to the  $O(^1D)$  reactions, with the overall reactive yield from  $O(^3P)$  being only about 5%; (ii) the dominant pathway is the 3-body channel (6) originating from the  $O(^1D)$  reaction, followed by channel (5), corresponding to the formation of  $C_5H_6 + CO$  from  $O(^1D)$ ; (iii) the other four possible channels are all minor, yet non negligible; (iv) the total yield of phenoxy + H from  $O(^3P)$  is very similar ( $BF=0.032\pm 0.011$ ) to that from  $O(^1D)$  ( $BF=0.035\pm 0.010$ ); (v) the  $C_5H_6 + CO$  channel from  $O(^3P)$  amounts to only about 5% ( $BF = 0.015\pm 0.007$ ) of that from  $O(^1D)$  ( $BF = 0.32\pm 0.09$ ); (vi) a small quantity of phenol is observed from the  $O(^3P)$  reaction (3).

As already mentioned, the individual BFs for the  $O(^3P)$  and the  $O(^1D)$  reaction are derived from Table 1 and listed in Table 2. There, the experimental BFs for the  $O(^3P)$  reaction channels are compared with our statistical predictions on the coupled triplet/singlet PESs, including ISC. As it can be seen from Table 2, experiment and simulations are in reasonable agreement when it comes to total formation of phenoxy + H ( $BF_{RRKM/ME} = 0.41$  vs  $BF_{CMB} = 0.66 \pm 0.24$ ), with the direct fraction of phenoxy + H on the triplet PES being theoretically underestimated ( $0.26$  vs  $0.48\pm 0.15$ ). Instead, theory somewhat overestimates the experimental  $C_5H_6 + CO$  channel BF ( $0.59$  vs  $0.32\pm 0.14$ ). Of

course, theory under single-collision conditions predicts zero phenol, while experimentally we derived a  $BF = 0.02 \pm 0.01$  for phenol surviving all the way up to the detector. When we sum up all triplet product yields and all singlet product yields for the various channels of the  $O(^3P)$  reaction we obtain that the extent of ISC is experimentally  $0.52 \pm 0.15$ , against a theoretical prediction of 0.74, which highlights a reasonable agreement between experiment and theory.

Table 2 also reports BFs derived from the kinetic study of the  $O(^3P)$  + benzene reaction by Taatjes *et al.*<sup>24</sup> at 900 K and 4 Torr, along with the results of our statistical simulations carried out at the same kinetic experimental conditions. Notably, the present theory somewhat overestimates the phenoxy + H channel (0.59 vs  $0.33 \pm 0.13$ ) and underestimates the  $C_5H_6$  + CO channel (0.14 vs  $0.33 \pm 0.08$ ), while providing a good estimate of the phenol formation channel (0.27 vs  $0.33 \pm 0.08$ ). Those values correspond to an extent of ISC of  $0.67 \pm 0.16$  from the kinetic experiment at 900 K and 4 Torr, in rather satisfactory agreement with a value of 0.41 returned by theory, which, assuming a theoretical uncertainty comparable to the experimental one of  $\pm 25\%$ , would fall within the lower experimental error bound.

It is interesting to examine the variation of the ISC with temperature for the  $O(^3P)$  + benzene reaction. The variations of the BFs and of the extent of ISC with temperature T (in the range 300-900 K) have been already reported in Figures 4a and 4b, respectively, of ref. 34 and discussed there.

**5.4. The Dynamics of the  $O(^1D)$  +  $C_6H_6$  Reaction.** As it can be seen from the singlet PES (blue curves in Figure 1), the best-fit CM functions reported in Figure 6, and the BFs reported in Table 2, the  $O(^1D)$  +  $C_6H_6$  reaction starts with the barrierless addition of  $O(^1D)$  to two adjacent carbons of the benzene ring forming benzene oxide ( $^1W7$ ) which can lead, via various isomerizations, dominantly to  $C_5H_6$  + CO and  $C_6H_5O$  + H, with a large part of the former products having enough internal excitation to undergo secondary dissociation of cyclopentadiene to cyclopentadienyl ( $C_5H_5$ ) + H (3-body channel (6)). The major channel is the formation of the three fragments  $C_5H_5$  + H + CO ( $BF=0.62 \pm 0.15$ ), with the channel forming  $C_5H_6$  + CO being about half

(BF=0.34±0.10) of the 3-body channel, and the channel forming C<sub>6</sub>H<sub>5</sub>O + H being minor (BF=0.04±0.02) (see Table 2).

We note that, on the one hand, our experimental results on O(<sup>1</sup>D) + benzene appear very similar to those reported by Chen *et al.*:<sup>51</sup> both studies find that the 3-body channel is the dominant one. On the other hand, in the pulsed CMB experiment of Chen *et al.*<sup>51</sup>, only TOF spectra of the products were measured at selected LAB angles, while in our continuous CMB experiments we were also able to directly measure with high accuracy the total LAB angular distribution for each product mass, and then the product TOF spectra at selected LAB angles. We remind the reader that the area of a TOF spectrum at a given LAB scattering angle corresponds to the intensity of the LAB angular distribution at that given angle. The availability of the angular distribution with a fine angular grid of data points provides more accurate information and facilitates the data analysis and the derivation of the CM functions (i.e., of the reaction dynamics). Deviations of the present results from previous work<sup>51</sup> concerning the relative importance of the H forming channel (4) and of the CO forming channel (5) with respect to the 3-body channel (6) have already been commented on in Section 3.4.

## 6. CONCLUSIONS

Although in the past decades the O(<sup>3</sup>P) + benzene reaction was extensively studied from both theoretical and experimental points of view because of its relevance in fuel combustion, the characterization of its detailed mechanism and dynamics, such as the primary product distribution and the role of ISC, remained to be done. In the present work, the O(<sup>3</sup>P) + benzene reaction dynamics were investigated experimentally by the CMB scattering method with MS detection and TOF analysis at E<sub>c</sub>=8.2 kcal/mol, and the primary products and their branching fractions determined. The experimental results were analyzed with the support of synergistic high-level quantum chemical calculations of the underlying triplet/singlet PESs and statistical (RRKM/ME) simulations on these PESs with nonadiabatic effects (i.e., ISC) taken into account, in order to gain a deeper and comprehensive understanding of the reaction mechanism and dynamics. This combined

experimental/theoretical study on the O(<sup>3</sup>P) + benzene benchmark system extends to aromatic hydrocarbons our recent combined experimental/theoretical studies<sup>19-23,29,32-34,77</sup> on O(<sup>3</sup>P) + C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> unsaturated hydrocarbons, and can serve as a gateway to more complex chemical pathways available in larger aliphatic/aromatic hydrocarbons.

Notably, although under our experimental conditions the concentration of O(<sup>1</sup>D) in the oxygen beam is ≤10%, its reactivity with benzene at E<sub>c</sub>=8.2 kcal/mol appears, as expected being the reaction O(<sup>1</sup>D) + benzene barrierless, to be much higher (by about two orders of magnitude) than that observed for O(<sup>3</sup>P) (whose reaction has an entrance barrier of 3.8-4.5 kcal/mol), in agreement with Chen *et al.*<sup>51</sup> and with the rate constants of the O(<sup>3</sup>P) reaction determined in previous kinetics studies.<sup>40-46</sup> The detailed dynamics of the O(<sup>1</sup>D) + benzene reaction determined in this study is in agreement with the results of the previous, detailed pulsed CMB study of Chen *et al.*<sup>51</sup> In particular, the 3-body channel leading to cyclopentadienyl + H + CO is assessed in both studies to be the dominant product channel (BF > 0.6), while the cyclopentadiene + CO and phenoxy + H channels serve a minor role.

The derived reaction mechanism of the O(<sup>3</sup>P) + benzene reaction sees the initial electrophilic attack of the O atom to the π-system of the aromatic ring (on a C atom) on both lowest triplet T<sub>1</sub>(<sup>3</sup>A') and T<sub>2</sub>(<sup>3</sup>A'') PESs, with formation of the triplet diradical adducts <sup>3</sup>W<sub>1</sub>(A') and <sup>3</sup>W<sub>1</sub>(A''). These adducts, under single collision conditions, can undergo competitive C–H bond cleavage on the ground triplet (T<sub>1</sub>) PES <sup>3</sup>A' and intersystem crossing (ISC1 and ISC2, at MEC<sub>P</sub>1 and MEC<sub>P</sub>2, respectively) from the excited (T<sub>2</sub>) PES <sup>3</sup>A'', to form benzene oxide. The latter readily isomerizes to 2,4-cyclohexadienone, which in turn can competitively dissociate to C<sub>6</sub>H<sub>5</sub>O + H and, via two successive isomerization steps involving ring contraction, to C<sub>5</sub>H<sub>6</sub> + CO. Because of the very long lifetime of the 2,4-cyclohexadienone and isomeric phenol intermediates, a small fraction of these adducts actually survive long enough (≥ 300 μs) to reach the mass spectrometer detector.

We have characterized the dynamics (center-of-mass product angular and translational energy distributions) of the main open reaction channels, namely those leading to (in order of decreasing importance and with branching fractions in parenthesis):  $C_6H_5O + H$  ( $0.66 \pm 0.24$ , of which  $0.48 \pm 0.15$  from the triplet PES and  $0.18 \pm 0.09$  from the singlet PES via ISC),  $C_5H_6 + CO$  ( $0.32 \pm 0.14$ ), and Phenol ( $0.02 \pm 0.01$ ). Therefore, under single collision conditions, at  $E_c = 8.2$  kcal/mol, the reactive interaction of  $O(^3P)$  with benzene mainly produces the radical channel phenoxy + H (overall BF = 0.66), but can also break apart the aromatic ring producing significant amounts of cyclopentadiene + CO (BF = 0.32). A small fraction of the adduct is also observed. Because some of the observed products can only be formed via ISC from the triplet to the singlet PES, we have inferred the extent of ISC from the product branching fractions. Our data suggest indeed that ISC is extremely relevant, accounting alone for  $52 \pm 15\%$  of product yield at the experimental  $E_c$ . It should be noted that this value is comparable to that ( $50 \pm 15\%$ ) observed in the reaction  $O(^3P) + 1$ -butene at a comparable  $E_c$ .<sup>22</sup> As summarized in Table 2, experimental and theoretical BFs determined in this work are in reasonable agreement with each other, as well as the extent of ISC (experimentally  $52 \pm 15\%$  and theoretically 74%). Significant differences between experimental and statistical BFs are mainly limited to the H displacement channel occurring adiabatically on the triplet PES, a process known for its non-fully statistical character. The impact of the model parameters on the theoretically predicted BFs has been examined.

Comparison of the theoretically predicted BFs at 900 K and 4 Torr with those at  $E_c=8.2$  kcal/mol has provided useful information on the variation of BFs with collision energy (temperature).<sup>34</sup> Notably, the overall predicted yield of product channels from the singlet PES (about 52% at  $E_c=8.2$  kcal/mol) remains essentially the same (54%) at 900 K and 4 Torr. However, at these thermal conditions the calculated fraction of stabilized product increases strongly (from BF=0.02 in the CMB conditions to BF=0.27 in the thermal conditions), while the fractions of  $C_6H_5 + CO$  and of  $C_6H_5O + H$  decrease ( $0.14$  vs  $0.32$  and  $0.13$  vs  $0.18$ , respectively). Clearly, while the extent of ISC

is comparable between the two experimental conditions (CMB at  $E_c=8.2$  kcal/mol and kinetics at 900 K and 4 Torr), in the thermal case the third-body stabilization plays a crucial role due to the multiple collision environment. It is, however, noteworthy (see Table 2) that the statistical calculations at 900 K and 4 Torr overestimate considerably (by nearly a factor of two) the overall amount of the radical channel (phenoxy + H) from the kinetic experiment (BF=0.59 theory vs 0.33 experiment), while underestimate by a similar amount the fraction of the molecular channel cyclopentadiene + CO (BF=0.14 vs 0.33). Most notably, the amount of the spin-forbidden molecular  $C_5H_6 + CO$  channel is comparable at  $E_c=8.2$  kcal/mol (BF =  $0.32 \pm 0.14$ ) and at 900 K and 4 Torr (BF =  $0.33 \pm 0.08$ ).

One of the main results of this work is that the CMB BFs measured in the present work and those determined in kinetic experiments<sup>24</sup> cannot be reproduced using the same statistical model, even if some of the model parameters are modified within their uncertainty range. This disagreement may be determined by different aspects, such as secondary chemistry contributing to the system reactivity in the kinetic experiments or dynamic effects not caught by the statistical model influencing the CMB dynamics. It is our opinion that this shortcoming may be addressed performing new kinetic experiments (or reinterpreting the existing ones<sup>24</sup> using appropriate reactor and kinetic models) and performing simulations of the CMB system using molecular dynamic approaches.

In the context of combustion processes, the most interesting and important result produced by this combined experimental/theoretical study of the complex mechanism of the  $O(^3P) +$  benzene reaction is that, once the theoretical statistical approach and description were reasonably validated by a satisfactory and encouraging comparison with the CMB experimental results, theory could be used to generate channel specific rate constants as a function of temperature and pressure in a wide  $T$  range (from 300 to 2200 K) and  $p$  range (from 0.1 to 100 atm) (see Table 4). We expect the valuable insights provided by these channel-specific kinetic rates to significantly support and expedite a much needed improvement of current hydrocarbon combustion models.

## ASSOCIATED CONTENT

**Supporting Information.** Previous experimental and theoretical studies on the  $O(^3P, ^1D) + \text{benzene}$  reactions. On the abstraction channel in the  $O(^3P) + C_6H_6$  reaction forming  $OH + C_6H_5$  (phenyl). Sensitivity of time-of-flight distributions to  $C_5H_6$  (cyclopentadiene) and  $C_5H_5$  (cyclopentadienyl) formation from  $O(^1D)$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHORS INFORMATION

### Corresponding Authors

\*(P.C.) E-mail: [piergio.casavecchia@unipg.it](mailto:piergio.casavecchia@unipg.it). Telephone: (+39) 0755855514.

\*(N.B.) E-mail: [nadia.balucani@unipg.it](mailto:nadia.balucani@unipg.it). Telephone: (+39) 0755855514.

\*(C.C.) E-mail: [carlo.cavallotti@polimi.it](mailto:carlo.cavallotti@polimi.it). Telephone: (+39) 0223993176.

## ORCID

Piergiorgio Casavecchia: [0000-0003-1934-7891](https://orcid.org/0000-0003-1934-7891)

Nadia Balucani: [0000-0001-5121-5683](https://orcid.org/0000-0001-5121-5683)

Carlo Cavallotti: [0000-0002-9229-1401](https://orcid.org/0000-0002-9229-1401)

Timothy K. Minton: [0000-0003-4577-7879](https://orcid.org/0000-0003-4577-7879)

## Notes

The authors declare no competing financial interests.

## ■ ACKNOWLEDGMENTS

Financial support from MUR (PRIN 2017, MAGIC DUST, Prot. 2017PJ5XXX) is gratefully acknowledged. GV, AC, NB, and PC acknowledge support also from Italian MUR and University of Perugia within the program “Department of Excellence–2018–2022–Project AMIS”. T. K. M. acknowledges the University of Perugia for a Visiting Scholarship grant in February/March 2017 (within the entrance Mobility Program of Researchers of International Fame).

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# TOC Graphic:

