

Crossed beam studies of the $O(^3P, ^1D) + \text{benzene}$ reaction dynamics: primary products and branching ratios

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The reaction of $O(^3P)$ with benzene is of considerable interest for modeling of aromatic oxidation and formation of polycyclic aromatic hydrocarbons (PAHs) and soot.

Early crossed molecular beam (CMB) studies¹ at collision energies (E_c) of 2.5-6.5-8.5 kcal/mol found the reaction to mainly lead to $H+C_6H_5O$ (phenoxy), with $CO+C_5H_6$ (cyclopentadiene) estimated to be $\leq 5\%$. Interestingly, this second channel can only occur via intersystem crossing, ISC, from the entrance triplet to the singlet potential energy surface (PES). The phenol adduct was also observed, which implies that its lifetime is $\geq 500 \mu s$.

Theoretical studies of the triplet/singlet PESs and statistical calculations of branching ratios (BRs) corroborated these findings².

CMB studies at $E_c \approx 10$ kcal/mol combined with PES calculations determined also the reaction dynamics of excited $O(^1D)+C_6H_6$ ³. Dominant products were found to be the 3-body channel $CO+H+C_5H_5$ (cyclopentadienyl), with $CO+C_5H_6$, C_6H_5O+H and $OH+C_6H_5$ being all minor. The CO and H channels were found to proceed via a long-lived complex mechanism. No phenol adduct was observed for the singlet reaction.

Recently, kinetics studies of $O(^3P)+\text{benzene}$ over the temperature range 300-1000 K and pressure range 1-10 Torr in a flow reactor by synchrotron photoionization mass spectrometry detected and quantified phenol and phenoxy radical products. Cyclopentadiene and cyclopentadienyl radical were also identified, with BRs at 900 K and 4 torr estimated to be the same (0.33) for phenoxy+H, phenol, and $CO+C_5H_6$. Both temperature and pressure dependences of the BRs were observed, indicating that 3-body stabilization at 4 Torr plays a significant role in the flow studies, leading both to very large fractions of stabilized phenol intermediate (especially at or below 500 K) and favoring ISC to $CO+C_5H_6$ products (especially at or above 700 K). The extent of CO formation from the $O(^3P)$ reaction under truly single-collision conditions remains an open, key question.

Here, we report a CMB study of $O(^3P, ^1D)+\text{benzene}$ at $E_c=8.2$ kcal/mol to assess the dynamics of phenoxy and CO formation from $O(^3P)$, determine the BRs and estimate the extent of ISC under single-collision conditions. Using an O-beam containing mainly $O(^3P)$ and a small amount ($\approx 10\%$) of $O(^1D)$, reaction channels from both $O(^3P)$ and $O(^1D)$ were observed and quantified. The dynamics of $H+\text{phenoxy}$, $CO+C_5H_6$, and $CO+H+C_5H_5$ channels from $O(^1D)$ agree with recent CMB work³. Phenol, $H+\text{phenoxy}$ (exhibiting a different formation dynamics than from $O(^1D)$), and a small amount of $CO+C_5H_6$ from $O(^3P)$ reaction were characterized.

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References

- [1] S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, Y. T. Lee, *J. Chem. Phys.* **72**, 4341 (1980).
- [2] T. L. Nguyen, J. Peeters, L. Vereecken, *J. Phys. Chem. A* **111**, 3836 (2007).
- [3] H.-F. Chen, C.-W. Liang, J. J. Lin, Y.-P. Lee, *et. al.*, *J. Chem. Phys.* **129**, 174303 (2008).
- [4] C. A. Taatjes, *et. al.*, *J. Phys. Chem. A* **114**, 3355 (2010).