

High temperature sources of phenyl and benzyne radicals and their reactions.

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Recent results have emphasized the importance of *o*-benzyne radicals (*o*-C₆H₄) [1] along with phenyl radicals (C₆H₅) [2] in aromatic pyrolysis and soot formation. In the varied conditions of combustion systems, these radicals participate in dissociation [3], recombination, and addition reactions [4] and lead to soot formation by a variety of routes. It is therefore important to measure the high temperature reactions of these radicals and determine their pressure dependencies. High temperature thermal dissociation sources of these radicals are limited, and their characterization is also limited. Recently, diiodobenzene [5], dimethylbenzene [6], and phthalic anhydride [4] have been used successfully as sources for *o*-C₆H₄, although the low volatility of diiodobenzene and phthalic anhydride could limit their more general use.

We have used halo-benzenes (C₆H₅X, X=F,Cl,Br,I) as a source of phenyl and *o*-benzyne radicals over a very wide temperature range in a diaphragmless shock tube. We have measured the initial dissociation of these molecules and studied dissociation and recombination reactions of *o*-benzyne and phenyl radicals by laser schlieren densitometry and time-of-flight mass spectrometry at temperatures between 1275 K and 2900 K. The dissociation mechanisms for the halobenzenes vary from predominantly C-X scission in iodo-benzene to almost exclusively H-X elimination from fluorobenzene with C₆H₅Br/Cl exhibiting a mixture of scission and elimination. Secondary reactions between the parent molecules and radical products are also important with the fluoro and chloro benzenes. The use of halobenzenes as radical sources will be discussed along with results on the dissociation of *o*-benzyne and recombination of phenyl radicals.

References

- (1) Comandini, A.; Brezinsky, K.; *J. Phys. Chem. A* **2011**, 115, 5547-5559.
- (2) Tranter, R. S.; Klippenstein, S. J.; Harding, L. B.; Giri, B. R.; Yang, X.; Kiefer, J. H. *J. Phys. Chem. A* **2010**, 114, 8240.
- (3) Wang, H.; Laskin, A.; Moriarty, N.; Frenklach, M.; *Proc. Combust. Inst.* **2000**, 28, 1545-1555.
- (4) Friedrichs, G.; Goos, E.; Gripp, J.; Nicken, H.; Schönborn, J.; Vogel, H.; Temps, F.; *Z. Phys. Chem.* **2009**, 223, 387-407.
- (5) Xu, C.; Braun-Unkhoff, M.; Naumann, C.; Frank, P.; *Proc. Combust. Inst.*, **2007** 31, 231-239.
- (6) Zhang, X.; Maccarone, A.; Nimlos, M.; Kato, S.; Bierbaum, V.; Ellison, G.; Ruscic, B.; Simmonet, A.; Allen, W.; Schaefer, H.; *J. Chem Phys.* **2007**, 126, 044312.