

# Reaction kinetics of the OH radical with fulvenallene

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The fulvenallenyl radical ( $C_7H_5$ ) has six different resonance structures similar to both the propargyl and the cyclopentadienyl radicals, making it the most stable  $C_7H_5$  structure. It was only recently detected in low-pressure flames<sup>1</sup> and during toluene pyrolysis.<sup>2</sup> Its self-recombination was postulated to form phenanthrene ( $C_{14}H_{10}$ ) although there are no data available. Despite its importance for polycyclic aromatic hydrocarbon formation, fulvenallenyl is still very elusive and there is very limited chemical information available about its formation and reactivity.

We have investigated the formation of the fulvenallenyl radical by reaction of the OH radical with fulvenallene ( $C_7H_6$ ) over the 300 to 450 K temperature range. The reaction rate coefficient is found to be  $8.8(\pm 1.7) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at room temperature with a negative temperature dependence that can be fit from 298 to 450 K to  $k(T) = 8.8(\pm 1.7) \times 10^{-12} (T/298 \text{ K})^{-6.6(\pm 1.1)} \exp[-(8.72(\pm 3.03) \text{ kJ mol}^{-1}) / (R((1/T) - (1/298 \text{ K})))]$   $\text{cm}^3 \text{ s}^{-1}$ .<sup>3</sup> The absolute value of the reaction rate coefficient at room temperature together with its decrease with increasing temperature suggests that at and below room temperature, association is likely to dominate over the abstraction leading to negligible fulvenallenyl formation. The most likely reaction product at these temperatures is one of the four addition isomers, including the resonance stabilized 2- $C_7H_6OH$ . At 450 K, the slow apparent rate coefficient suggests that dissociation of the initial reaction complex back to the reactants is likely to be rapid. At this temperature and at combustion temperatures ( $>800 \text{ K}$ ), abstraction from the  $-CH-H$  of fulvenallene is likely to be the main mechanism, as predicted by da Silva and Bozzelli.<sup>4</sup> The present study demonstrates for the first time that kinetic studies of fulvenallene are feasible and suggest that the OH + fulvenallene reaction is a potential source of fulvenallenyl at combustion temperatures.

## References

- (1) Hansen, N.; Kasper, T.; Klippenstein, S. J.; Westmoreland, P. R.; Law, M. E.; Taatjes, C. A.; Kohse-Hoeinghaus, K.; Wang, J.; Cool, T. A. *J. Phys. Chem. A* **2007**, 111, 4081-4092.
- (2) Matsugi, A.; Miyoshi, *Proc. Comb. Inst.* **2013**, 34, 269-277.
- (3) Thapa, J.; Spencer, M.; Akhmedov, N. G.; Goulay, F. *J. Phys. Chem. Lett.* **2015**, 6, 4997-5001
- (4) da Silva, G.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, 113, 12045-12048.