Chemical Activation in the Product Yields of the OH/C_2H_2/O_2 system: Yields as a function of oxygen and Temperature

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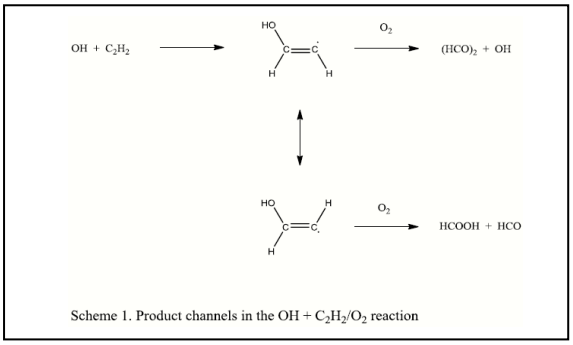
Acetylene, C_2H_2, is an important atmospheric marker for anthropogenic emissions and biomass burning. Atmospheric removal of acetylene is dominated by addition with OH. The adduct subsequently reacts with O_2 via a barrierless association reaction along two product pathways (Scheme 1).[1-3] The kinetics of the OH + C_2H_2 reaction have been studied by monitoring OH decay under pseudo-first-order conditions using both N_2 and O_2/N_2 bath gas mixtures. Experimental conditions are controlled so that the OH + C_2H_2 reaction rapidly recycles in the presence of oxygen. Monitoring OH decay in the presence, k_{O2}, and absence, k_{N2}, of O_2 allows the OH yield (Φ_{OH}) to be determined directly via $\Phi_{OH} = 1 - {}^{k_{O2}}/_{k_{N2}}$. Φ_{OH} shows no dependence on total pressure but does depend on bath gas composition (Figure 2). These observations can be rationalized as follows. OH adds to C_2H_2 to produce either a *cis* or *trans* conformer, with formation of either considered equally probable. The adducts form with ~130 kJ mol^{-1} excess energy and in N_2 become thermalized. The more stable *trans* adduct, leading to OH regeneration, is preferentially populated under thermal conditions. The dependence on f_{O2} is related to how much thermalization has occurred before the adduct has encountered O_2: high f_{O2} means reaction before the adduct is thermalized - *chemical activation* - where at the limit of pure O_2, the conformers react with O_2 where the populations are close to equal and hence Φ_{OH} ~0.5; at low f_{O2} the adduct distribution is close to thermal equilibrium, resulting in an increased Φ_{OH}. Temperature dependent Φ_{OH} have also been observed, resulting from enhanced *trans* populations as the temperature is lowered (Figure 3). In the presentation we will discuss the role of chemical activation in determining product distributions in what has mainly been considered a thermal environment, atmospheric implications, theoretical modeling of the system and the extension to higher alkynes.



Scheme 1. Product channels in the OH + C_2H_2/O_2 reaction

References
(1) Schmidt, V.; Becker, K. H. et al. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1985**, *89*, 321. (2) Hatakeyama, S.; Washida, N.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 173. (3) Glowacki, D. R.; Pilling, M. J. *Chemphyschem* **2010**, *11*, 3836.

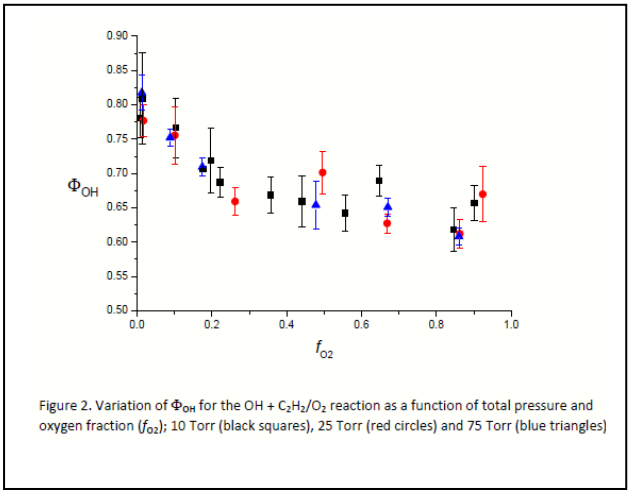


Figure 2. Variation of Φ_{OH} for the OH + C_2H_2/O_2 reaction as a function of total pressure and oxygen fraction (f_{O2}); 10 Torr (black squares), 25 Torr (red circles) and 75 Torr (blue triangles)

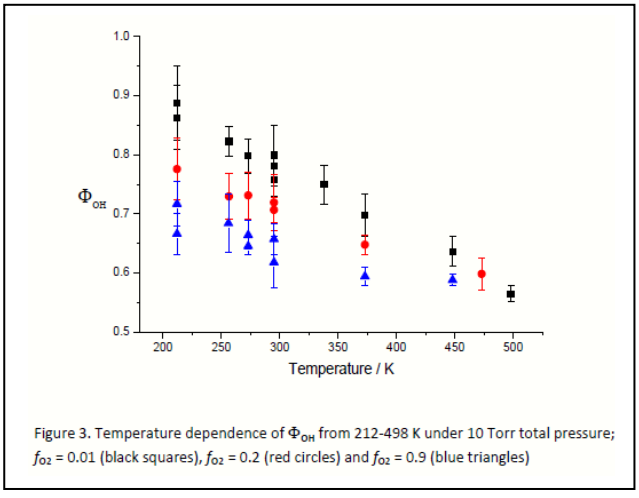


Figure 3. Temperature dependence of Φ_{OH} from 212-498 K under 10 Torr total pressure; f_{O2} = 0.01 (black squares), f_{O2} = 0.2 (red circles) and f_{O2} = 0.9 (blue triangles)

THURSDAY