COMMENTS

Comment on "The Reaction of Acetylene with Hydroxyl Radicals"

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In the above publication,[1] theoretical calculations are performed on the title reaction to determine the product channels and the rate coefficients for these channels as a function of temperature. The authors observe that "production of ketene is the main product channel at temperatures between 1200 and 2100 K and atmospheric pressure." This result is very important to understanding the acetylene/methane chemistry in the postflame region of moderately rich, nonsooting, hydrocarbon flames.[2] Measured hydrocarbon species profiles in several rich flames in ref 2, show that both acetylene and methane persist in the postflame gas for a considerable distance beyond the flame front. In addition, acetylene is converted into methane in this region resulting in rising methane concentrations as the distance from the flame front increases. The chemistry of the postflame region was modeled using the reactions (1) OH + C_2H_2 = ketene + H and (2) H + ketene = CH_3 + CO in ref 2. These reactions provide a path that can produce methane via OH reaction with acetylene. At the time of the publication of ref 2, reaction channel (1) was not generally accepted because of theoretical calculations indicating that it was not a major reaction channel.[3] The new theoretical calculations by Senosiain et al. indicate that reaction 1 is indeed a major reaction path under the experimental conditions of ref 2 and that another channel, forming CH_3 + CO (3), could also yield significant CH_4.

The results of Senosiain et al., and those of a recent theoretical examination of reaction 2,[4] support the use of reactions 1 and 2 in modeling the chemistry of rich flames as described in ref 2, and reaction 3 should be added to the mechanism. These reactions should improve modeling of the chemistry of rich combustion, which can influence emissions from practical combustion systems such as the automotive engine.[5] Methane and acetylene emissions increase rapidly as the fuel mixture is enriched beyond the stoichiometric fuel—air ratio in spark-ignited engines because of the persistence of acetylene and methane in the postflame gases of rich flames.[6,7] The authors of refs 1 and 4 are to be applauded for their crucial theoretical treatments of reactions 1—3.

References and Notes

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