

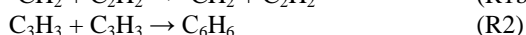
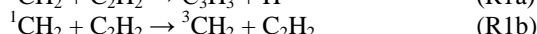
# Measurements of low temperature rate coefficients for reactions of $^1\text{CH}_2$ with species relevant to Titan's atmosphere

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The Cassini-Huygens mission to Titan revealed unexpectedly large amounts of benzene in the troposphere, and confirmed the absence of a global ethane ocean as predicted by photochemical models of methane conversion over the lifetime of the solar system. An important chemical intermediate in both the production and loss of benzene and ethane is the first electronically excited state of methylene,  $^1\text{CH}_2$ . For example, at room temperature an important reaction of  $^1\text{CH}_2$  is with acetylene (R1a), leading to the formation of propargyl ( $\text{C}_3\text{H}_3$ ).<sup>[1]</sup> The subsequent recombination of propargyl radicals is the major suggested route to benzene in Titan's atmosphere (R2).<sup>[2]</sup> In addition to reaction of  $^1\text{CH}_2$  leading to products, there is also competition between inelastic electronic relaxation to form the ground triplet state  $^3\text{CH}_2$  (R1b). This ground state  $^3\text{CH}_2$  has a markedly different reactivity to the singlet, reacting primarily with methyl radicals ( $\text{CH}_3$ ) to form ethane (R3). As methyl radical recombination is the primary route to ethane (R4),<sup>[3]</sup> reactions of  $^1\text{CH}_2$  will also heavily influence the ethane budget on Titan.



Thus this competition between chemical reaction and electronic relaxation in the reactions of  $^1\text{CH}_2$  will play an important role in determining the benzene and ethane budgets on Titan. Despite this there are no measurements of any rate constants for  $^1\text{CH}_2$  at temperatures relevant to Titan's atmosphere (60 – 170 K).

Using a pulsed Laval nozzle apparatus coupled with pulsed laser photolysis laser-induced fluorescence, the low temperature reaction kinetics for the removal of  $^1\text{CH}_2$  with  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{O}_2$  have been studied. The results revealed an increase in the removal rate of  $^1\text{CH}_2$  at temperatures below 200 K, with a sharp increase observed at  $45 \pm 5$  K.

In addition to measuring total removal rates, the fraction of  $^1\text{CH}_2$  removed via electronic relaxation versus chemical reaction to products has also been investigated. Results for  $\text{H}_2$  and  $\text{CH}_4$  at 70 K indicate that removal of  $^1\text{CH}_2$  is primarily by electronic relaxation, with chemical reaction to products accounting for only  $22 \pm 10$  % and  $36 \pm 18$  % of  $^1\text{CH}_2$  loss respectively.

These results indicate that the majority of  $^1\text{CH}_2$  formed in Titan's atmosphere will be rapidly relaxed to its ground state via collisions with both reactive and non-reactive species, and thus is likely to play a less significant role in the formation of larger hydrocarbons than previously thought. However, for a full understanding of the implications of these results, the new measurements are to be included in a 1D model of Titan's atmosphere to determine the impact of the laboratory measurements on observation/model agreement.

## References

- [1] K. Gannon *et. al.*, *J. Phys. Chem. A*, **2010**, *114*, 9413
- [2] E.H. Wilson, S.K. Atreya, *J. Geophys. Res.*, **2004**, *109*, 6002
- [3] M. Fulchignoni, *Nature*, **2005**, *438*, 785