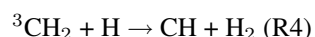
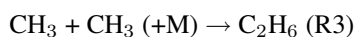
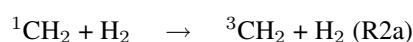
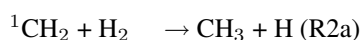
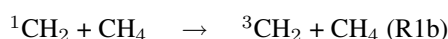
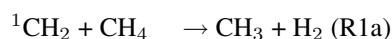


Low Temperature Studies of the Removal Reactions of $^1\text{CH}_2$ with Relevance to the Atmosphere of Titan

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The photolysis of methane by UV photons is the primary source of hydrocarbon radicals in the atmosphere of Titan and the giant planets. Although there is still significant uncertainty in the branching ratios of products, the production of the first singlet excited state of methylene, $^1\text{CH}_2$, is thought to be a significant channel. Reactions of $^1\text{CH}_2$ with methane (R1a) and hydrogen (R2a) are a significant source of methyl radicals, the recombination of which is the primary route to ethane on Titan (R3). The reaction of $^1\text{CH}_2$ with acetylene is also a source of propargyl, C_3H_3 , the recombination of which is the primary route to benzene on Titan. However, in addition to these reactions of $^1\text{CH}_2$ leading to chemical products, there is also competition between inelastic electronic relaxation to form ground triplet state methylene, $^3\text{CH}_2$ (R1b and R2b). Triplet methylene is much less reactive, and cannot undergo the complex insertion elimination reactions of singlet methylene. The main reaction of $^3\text{CH}_2$ occurs with other radical species such as H (R4).



Using pulsed laser photolysis laser-induced fluorescence, we have studied the reaction kinetics for the removal of $^1\text{CH}_2$ with N_2 , H_2 , CH_4 , C_2H_6 , C_2H_4 , C_2H_6 , and O_2 as a function of temperature. Low temperatures between 43 and 135 K were obtained using a pulsed Laval nozzle apparatus, while data at 160 K was obtained using a low flow reaction cell with cryogenic cooling. 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 for H_2 and CH_4 at 160 and 73 K. Results show that that removal of $^1\text{CH}_2$ by electronic relaxation increases with decreasing temperature.

These experimental 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 have been included in a 1D model of Titan's atmosphere. The model results show a significant reduction in ethane concentrations (10 – 50 %), due to reduction in CH_3 production via reactions R1a and R1b. In addition we also observe an increase in ethylene concentrations, the result of increased amounts of $^3\text{CH}_2$ reacting with H radicals to form CH (R4), which primarily react with methane to form ethylene.

Additional work is also underway to determine branching ratios between reaction and relaxation of $^1\text{CH}_2$ with ethane, ethylene, and acetylene. Model results have shown that if a similar trend to reactions with H_2 and CH_4 is observed, there would be significant reductions in benzene production on Titan.