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Low temperature rate coefficients for the reactions of 1CH2 with reactive and non-reactive species, and the implications for 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, 1CH2. For example, at room temperature an important reaction of 1CH2 is with acetylene (R1a), leading to the formation of propargyl (C3H3)[1]. The subsequent recombination of propargyl radicals is the major suggested route to benzene in Titan's atmosphere (R2)[2]. In addition to reaction of 1CH2 leading to products, there is also competition between inelastic electronic relaxation to form the ground triplet state 3CH2 (R1b). This ground state 3CH2 has a markedly different reactivity to the singlet, reacting primarily with methyl radicals (CH3) to form ethene (R3). As methyl radical recombination is the primary route to ethane (R4)[3], reactions of 1CH2 will also heavily influence the ethane budget on Titan.
1CH2 + C2H2 → C3H3 + H (R1a)
1CH2 + C2H2 → 3CH2 + C2H2 (R1b)
C3H3 + C3H3 → C6H6 (R2)
3CH2 + CH3 → C2H4 + H (R3)
CH3 + CH3 (+ M) → C2H6 (R4)
Thus this competition between chemical reaction and electronic relaxation in the reactions of 1CH2 with H2, CH4, C2H4, and C2H6 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 1CH2 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 1CH2 with nitrogen, hydrogen, methane, ethane, ethene, acetylene, and oxygen, have been studied. The results revealed an increase in the removal rate of 1CH2 at temperatures below 200 K, with a sharp increase of around a factor of 5 observed at 45 ± 5 K.

In addition to measuring total removal rates of 1CH2, the fraction of 1CH2 removed via electronic relaxation verses chemical reaction to products has also been investigated. Results for the reactive species ethane, ethene, and acetylene at 45 ± 5 K, and for hydrogen and methane at 73 ± 9 K indicate that following reactions with 1CH2, removal of 1CH2 is predominantly due to electronic relaxation (> 95 %) and not chemical reaction to products. This is in agreement with previous studies that show that with decreasing temperature, the fraction of reactive removal of 1CH2 to chemical products decreases while the fraction of removal by electronic relaxation increases[4][5].

These results indicate that 1CH2 formed in Titan's atmosphere will be rapidly relaxed to it's ground state via collisions with both reactive and non-reactive species, and thus will 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.

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