CARBON DIOXIDE CHEMISTRY ON THE SURFACE OF TITAN. R. Hodyss[1], Sophie Piao[1], M.J. Malaska[1] and M. Cable[1], [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

Introduction: Titan (and other hydrocarbon worlds [1]) possess many of the basic elements of habitability, including a rich organic chemistry. However, the thick atmosphere of Titan shields the surface from radiation, which makes the incorporation of oxygen into organic compounds difficult, due to a reducing environment and low temperatures that slow chemical reactions. These obstacles may be overcome by impacts [2,3] or cryovolcanic heating of ice, which would mix organics with liquid water and allow chemical reactions that can incorporate oxygen [4,5]. We show that the reaction of carbon dioxide with amines can lead to oxygenated organics at Titan's surface without the need for external energy input. This reaction (carbamation) is shown in Figure 1.

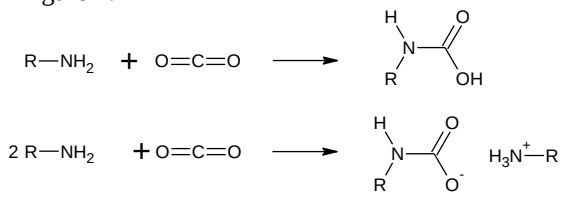

Figure 1. The carbamation reaction. An amine can react with carbon dioxide to form a carbamic acid (top). In the presence of excess amine, an ammonium carbamate salt is formed (bottom).

Carbamation occurs readily at Titan surface temperatures (94 K). Amines should be present on Titan's surface, formed by photochemical reactions of N_2 and CH_4 in the upper atmosphere [6]. Amine-containing molecules have been detected as a component of laboratory tholins made in terrestrial laboratories [7,8]. Carbon dioxide (CO_2) has been definitiviely identified in Titan's atmosphere, and there there is some spectral evidence that CO_2 is also present on the surface [9].

Experimental: We use a combination of micro-Raman spectroscopy and UHV FTIR spectroscopy to examine the reaction products and kinetics of the carbamation reaction. Raman spectra were acquired using a Horiba Jobin Yvon LabRam HR, with samples held in either a Linkam LTS 350 liquid nitrogen–cooled cryostage, or an Oxford Microstat cryostat. Infrared spectra and kinetic data were obtained using an ultra-high vacuum system equipped with an ARS 202 cold-head, and a Thermo Nicolet 6700 FTIR.

Results and Discussion: Figure 2 shows infrared spectra demonstrating the reaction of methylamine with CO_2, through the appearance of the =O stretch vibrations (1674 cm^{-1}) and the disappearance of the N-H bend modes as the reaction proceeds. Carbamic acid formation occurs with methylamine, ethylamine, dimethylamine and pyrrolidine, but not with trimethylamine

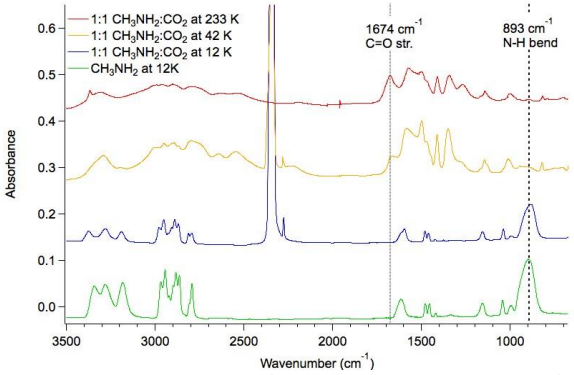

Figure 2. Mixtures of CO_2 and methylamine form methylcarbamic acid when warmed to Titan surface temperature. Short dashed lines highlight the formation of methylcarbamic acid product peaks. Long dashed lines show the disappearance of methylamine features.

or aniline. This indicates that primary and even secondary amines undergo carbamation at low temperatures. Reaction was observed with methylamine as low as 40 K, and with ethylamine at 100 K within minutes, demonstrating that carbamation is fast at Titan surface temperatures.

We will present data on the kinetics of the carbamation reaction for a variety of amines, as well as estimates of the quantity of carbamic acids that may be produced on Titan's surface and in the atmosphere.

Conclusion: The carbamation reaction proceeds rapidly under Titan surface conditions. The reaction is general for primary and secondary amines, but does not proceed for tertiary amines or aniline. Under Titan surface conditions (94 K, ~1 bar N_2), CO_2 reacts with CH_3NH_2 within seconds.

Carbamation will limit the lifetime of free CO_2 on Titan's surface, and provides a means for the incorporation of oxygen into organics through purely thermal reactions. These oxygenated species may serve as precursors to the formation of more complex prebiotic species of astrobiological interest.

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