CARBAMATION: A NEW MECHANISM FOR THE FORMATION OF OXYGENATED ORGANICS ON TITAN'S SURFACE. R. Hodyss[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 below:

$$R\text{-}NH_2 + CO_2 \rightarrow R\text{-}NH\text{-}COOH$$

While the surfaces of the moons of the outer Solar System are usually considered too cold (30-100 K) for significant chemistry to occur without the input of energy from exogenic sources (such as charged particles or VUV irradiation), this reaction 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]. There is some spectral evidence CO_2 is present on the surface, and CO_2 has been definitively identified in the atmosphere [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 for a variety of primary and secondary amines.

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 ultrahigh vacuum system equipped with an ARS 202 coldhead, and a Thermo Nicolet 6700 FTIR.

Results and Discussion: Figure 1 shows spectra of ethylcarbamic acid formation from CO_2 and ethylamine. We have observed carbamic acid formation in mixtures of methylamine, ethylamine and dibutylamine with CO_2 at cryogenic temperatures. This indicates that both primary and secondary amines undergo carbamation at low temperatures. Reaction was observed with methylamine as low as 40 K, and with ethylamine at 100 K, demonstrating that carbamation is fast at Titan surface temperatures.

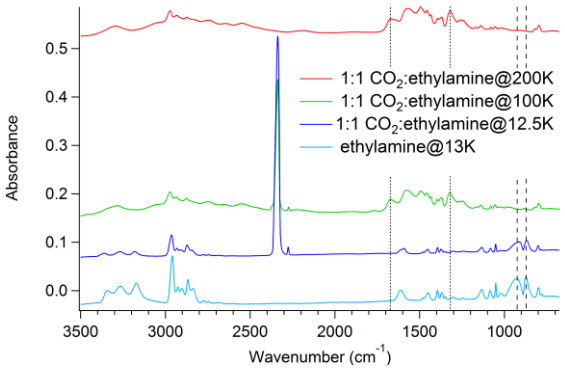

Figure 1. Mixtures of CO_2 and ethylamine form ethylcarbamic acid when warmed to Titan surface temperature. Short dashed lines highlight the formation of ethylcarbamic acid product peaks. Long dashed lines show the disappearance of ethylamine features.

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 existence of low temperature thermal reactions of organics to form more complex species opens new venues for organic synthesis in the Solar System. Most particularly CO_2 and small amines formed photochemically in Titan's atmosphere may react in solid aerosols as they drift to the surface, or on the surface or subsurface of Titan. 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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