Low temperature formation of cyanopolyynes

Sidaty Cheikh Sid Ely[1], Stephen J. Klippenstein,[2] Jean-Claude Guillemin[3] and Ian R. Sims[1,*]

[1] Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France
[2] Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.
[3] Ecole Nationale Supérieure de Chimie de Rennes, CNRS UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France
* Corresponding author: ian.sims@univ-rennes1.fr

It is thought that long chain cyanopolyyne molecules $H(C_2)_nCN$ may play an important role in the formation of the orange haze layer in Titan's atmosphere. The longest carbon chain molecule observed in interstellar space, $HC_{11}N$, is also a member of this series. We have proposed (1) a low temperature gas-phase synthetic route to produce these species involving successive radical molecule reactions as follows:

$C_2H + H(C{\equiv}C)_nH \rightarrow H(C{\equiv}C)_{n+1}H + H$ (1) $CN + H(C{\equiv}C)_nH \rightarrow H(C{\equiv}C)_nCN + H$ (2)

$C_2H + H(C{\equiv}C)_nCN \rightarrow H(C{\equiv}C)_{n+1}CN + H$ (3) $CN + H(C{\equiv}C)_nCN \rightarrow NC(C{\equiv}C)_nCN + H$ (4)

The first three reaction categories lead to growth of (cyano)polyynes. However, the fourth category of reaction could act as a 'termination reaction' for this chain as the dicyanopolyyne is likely to be relatively unreactive. Reactions of type (1) and (2) have been shown by us to be rapid down to ~20 K for the first member of the series, acetylene (n = 1) (1,2), but no further studies have been made owing to the fact that the necessary molecular reagents have to be synthesised.

Using a combination of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods (3,4) as well as a number of technical developments including a new pulsed CRESU (5), reaction types (1) and (2) have been studied for the next member of the series, diacetylene, H-C≡C-C≡C-H, and reaction types (3) and, crucially, (4) have been studied with the first member of the series, cyanoacetylene, H-C≡C-C≡N (6,7).

The experimental results will be compared to new variable reaction coordinate transition state theory (VRC-TST) calculations of the addition kinetics. The calculations also provide some indication of the expected addition sites and likely products. Master equation simulations are used to predict the pressure dependence of the kinetics, including the rate of radiative stabilization at low pressure. Additional calculations predict that the reactions of CN / CCH with NC_4N will be slow in Titan's atmosphere due to the presence of significantly positive barriers.

THURSDAY

References

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