Low-temperature Gas-Phase Formation of Methanimine (CH_2NH; X^1A') – the Simplest Imine – under Single-Collision Conditions

Zhenghai Yang, Iakov A. Medvedkov, Shane J. Goettl, Ralf I. Kaiser*

Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, USA

*Email: ralfk@hawaii.edu;

EXPERIMENTAL

EXPERIMENTAL: The reaction of the D1-methylidyne radical (CD; $X^2\Pi$) with ammonia (NH_3; X^1A_1) was investigated utilizing a crossed molecular beams machine.[1,2] The D1-methylidyne beam was produced through photodissociation (COMPex 110; 248 nm) of D1-bromoform ($CDBr_3$; Sigma Aldrich; ≥99.5%) held in a stainless-steel bubbler at a stagnation temperature of 283 K. Helium acted as carrier gas with backing pressure of 2.2 atm and the mixture was released via a pulsed piezoelectric valve at 60 Hz repetition rate.[3] The 248 nm laser output operated at 30 Hz and intersected molecular beam 1 mm downstream of the nozzle with output energy of 160 mJ pulse^{-1}. The selection of 60 Hz of the pulse valve and 30 Hz of the excimer laser allowed a background subtraction during the experiment data collection. The primary CD molecular beam was skimmed and then velocity-selected via a four-slot chopper wheel rotating at 120 Hz mounted between the skimmer and the interaction region and controlled by a high stable motion system (Faulhaber; 2057024B). The selected well-defined section of CD beam possesses a peak velocity (v_p) of 1762 ± 22 m s^{-1} along with a speed ratio (S) of 9.2 ± 1.1 and intersected perpendicularly with the crossing segment of the secondary pure ammonia (NH_3; Matheson; 99.99%) released at repetition rate of 30 Hz and backing pressure of 550 Torr with the peak velocity v_p of 1143 ± 34 m s^{-1}. The collision in the interaction region results in a CM angle of 38.2 ± 0.4° and a collision energy of 16.9 ± 0.3 kJ mol^{-1}. The molecular beam parameters are compiled in Table S1.

Products of reactive scattering were ionized by an electron impact ionizer operated at 80 eV and 2 mA. A quadrupole mass spectrometer (QMS) was exploited at time-of-flight (TOF) mode to filter the produced ions according to distinct mass-to-charge ratios (m/z). The designated ions first hit to a stainless-steel target coated with aluminum and initiated a cascade-of-electron pulse which then fly to an organic scintillator generating a photon pulse. The signal was finally detected by a Burle photomultiplier tube and collected via a multichannel scaler after filtered by a discriminator operating at 1.6 mV.[4] The detector assembly is rotatable and operated under ultrahigh-vacuum conditions of 7 × 10^{-12} Torr. To obtain reaction dynamics information, a forward-convolution routine is employed, and the data is transferred from the laboratory frame to the center-of-mass (CM) frame resulting in best-fits and the corresponding CM functions of $P(E_T)$, $T(\theta)$ and the contour flux map, $I(u, \theta) \sim P(u) \times T(\theta)$ with the CM scattering angle θ and product

velocity u.[2,5] The flux contour map depicts the flux of the reactive-scattering products and contains dynamics information of the scattering reaction.

Table S1. Peak velocities (v_p) and speed ratios (S) of the D1-methylidyne radical (CD), and ammonia (NH_3) beams along with the corresponding collision energy (E_C) and center-of-mass angle (Θ_{CM}).

Beam	v_p (m s^{-1})	S	E_c (kJ mol^{-1})	Θ_{CM} (deg)
CD	1762 ± 22	9.2 ± 1.1		
NH_3	1143 ± 34	10.3 ± 1.4	16.9 ± 0.3	38.2 ± 0.4

References

(1) Kaiser, R. I. Experimental Investigation on the Formation of Carbon-Bearing Molecules in the Interstellar Medium via Neutral−Neutral Reactions. *Chem. Rev.* **2002**, *102*, 1309-1358.

(2) Gu, X.; Guo, Y.; Zhang, F.; Mebel, A. M.; Kaiser, R. I. Reaction Dynamics of Carbon-Bearing Radicals in Circumstellar Envelopes of Carbon Stars. *Faraday Discuss.* **2006**, *133*, 245-275.

(3) Yang, Z.; Galimova, G. R.; He, C.; Doddipatla, S.; Mebel, A. M.; Kaiser, R. I. Gas-Phase Formation of 1, 3, 5, 7-Cyclooctatetraene (C_8H_8) through Ring Expansion via the Aromatic 1, 3, 5-Cyclooctatrien-7-yl Radical ($C_8H_9^{\bullet}$) Transient. *J. Am. Chem. Soc.* **2022**, *144*, 22470-22478.

(4) Doddipatla, S.; Galimova, G. R.; Wei, H.; Thomas, A. M.; He, C.; Yang, Z.; Morozov, A. N.; Shingledecker, C. N.; Mebel, A. M.; Kaiser, R. I. Low-Temperature Gas-Phase Formation of Indene in the Interstellar Medium. *Sci. Adv.* **2021**, *7*, eabd4044.

(5) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press, Cambridge, 2005.