

Fuel Derived Methylidyne Radical Reactions with Ammonia and Substituted Amines Probed by Synchrotron VUV Photoionization Mass Spectrometry

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Scientific Context

In a well-known environment context one of the major challenges is to improve combustion efficiency and reduce pollutant emission through the use of fossil fuel alternatives. Prediction of harmful compounds such as NO_x from combustion processes is an active subject of research, especially due to the increasing use of fuels derived from biogenic sources (e.g., biomass, agricultural wastes). Biofuels contain oxygenated and nitrogenized species and are used as additives and substitutes for usual fossil fuels. However, regarding the fuel structure biofuel combustion could contribute to the formation of reactive harmful nitrogenized pollutants. Ammonia and its amine derivatives are emitted as gases in the atmosphere from a variety of sources (e.g., biomass burning, vegetation, combustion, industries) and are therefore of special interest in combustion environments. Accordingly, an improved utilization of biomass-derived nitrogen-containing compounds as fuels and a better understanding of the role of amines in combustion both require a systematic study of the chemistry of ammonia and substituted amines with combustion relevant radicals.

Processes occurring during biofuel combustion are complex and lead to a wide range of products whose branching ratios could be temperature and pressure dependent. Furthermore products are formed through various reaction intermediates, like free radicals, which may have different reactivities and short life times that need to be identified and quantified in order to take them into account in combustion models. Reactive species dominate the chemistry of combustion and lead to chain-terminating, chain-branching or chain-propagating regarding the physical parameter and the molecular structure of the oxydated compound. However it is a real challenge experimentally and theoretically to measure the proportion of each exit channel involving reactive intermediates in trace amount. There is few results at room temperature and atmospheric pressure and less at higher or lower value. Therefore, fuel derived radicals reactivity with any relevant biofuel compound are relevant for predictive biofuel combustion.

In this work we looked over the general mechanisms for the reaction of methylidyne radical (CH), one of the most important reactive intermediates detected in hydrocarbon flames, with ammonia and different amines (methylamine, dimethylamine and trimethylamine).

Experimental Procedure

In order to probe the reaction products we used the experimental setup displayed in *Figure 1* of the ALS synchrotron of LBNL in California. [1,2] The reactions occurred in a flow tube at low

pressure (4 Torr) and close to room temperature (373 K). The CH radicals were generated by the photodissociation of a precursor (bromoform) via successive absorption of photons by using an excimer laser at 248nm and 4 Hz repetition rate. The products are sampled from the flow through a small pinhole in the middle of the tube and are detected by using time-resolved multiplexed photoionization mass spectrometry using the ALS Berkeley synchrotron-generated tunable VUV light source. This technique provides photoionization spectra including the discrimination of isomers which have been used to infer the products of the reactions and gives fundamental information about the reaction mechanisms required for predictive combustion models. [3,4] The photoion spectra are fitted with integrated experimental or calculated photoelectron spectra to give isomeric branching ratios for a given atomic mass.

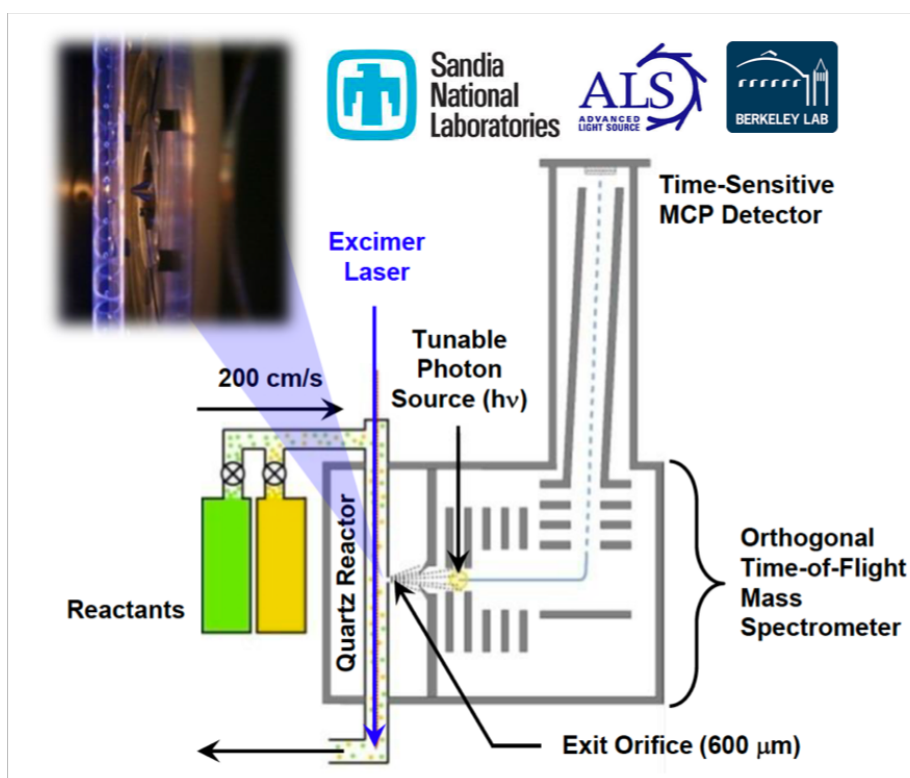


Figure 1. The multiplexed VUV photoionization mass spectrometry setup of the Advanced Light Source (ALS) synchrotron at the Lawrence Berkeley National Laboratory (CA-USA).

Results

For the reaction of CH radical with ammonia based on the mass spectrum and the photoion spectrum of m/z 29 displayed in Figure 2 we detected only one product identified as methanimine. Additional experiments were performed with deuterated bromoform as the radical precursor in order to gain additional information on the isomerization pathways. Only one main product signal was observed at m/z 30 with an identical photoion spectrum to that of m/z 29 from the CH + NH₃ reaction. The absence of significant signal at m/z 29 from the CD + ammonia reaction indicating an absence of D-loss from the initial adduct. These results are in agreement with previous study in the literature [6] and supports a dative-bond mechanism displayed in Figure 3 for the CH + NH₃ reaction. An initial H₃N–CH complex is formed with no energy barrier by a Lewis acid/base-type reaction. Then the adduct isomerizes through a H-

atom transfer to form a more stable $\text{H}_2\text{N}-\text{CH}_2$ reaction intermediate. Finally the most likely fate, based on our observations, of the complex is a direct dissociation to $\text{HN}=\text{CH}_2 + \text{H}$.

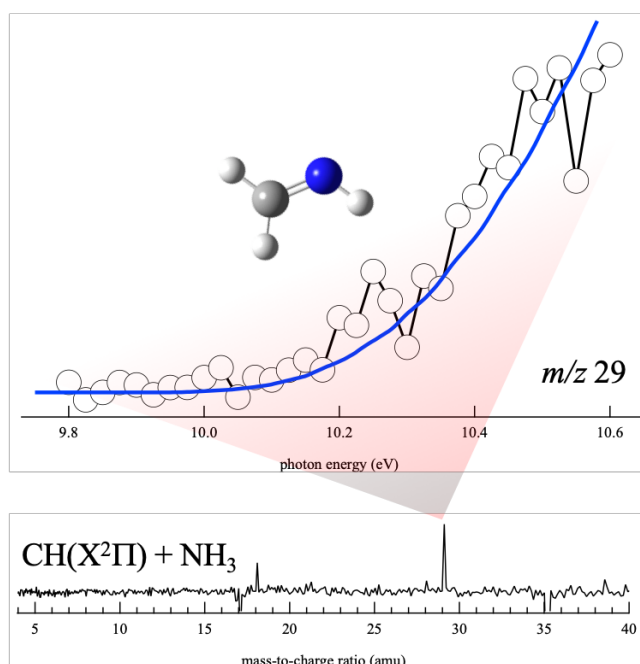


Figure 2. Mass spectrum of the $\text{CH}(\text{X}^2\Pi) + \text{NH}_3$ reaction and the photoionization spectrum of m/z 29 normalized to an integrated experimental photoelectron spectrum of $\text{HN}=\text{CH}_2$.

Regarding the reaction between CH with different amines (methylamine, dimethylamine and trimethylamine) only singly methyl substituted imine was detected and a similar addition-elimination mechanism to that proposed for the $\text{CH} + \text{NH}_3$ reaction was discussed to interpret the products detection. We detected H- and CH_3 -loss products through isomerization of an initial adduct suggesting that a methyl group transfer is a competitive pathway. However a more direct insertion pathway into a methyl C-H bond might become competitive as the number of methyl group increases.

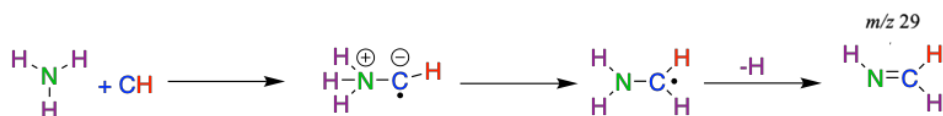


Figure 3. Proposed mechanism for the reaction of CH radical with NH_3 .

Conclusion and perspectives

The dative reaction mechanism proposed for the CH reactions with ammonia and amines is not sufficient to explain all the detected products and an alternative mechanism is likely to compete for bigger amines. However, the donor-acceptor type mechanism is likely to occur over a wide range of temperatures with an independent rate coefficient [7], including under combustion conditions (> 1000 K). This suggest that this enounced mechanism will still play a role even at combustion-relevant temperatures. Those reactions will contribute to the molecular

growth scheme in combustion environments and our work provides valuable data for the understanding of the formation of nitrated-PAHs. Further reactions involving imines which are highly reactive molecules due to their C=N double bond may lead to bigger N-bearing molecule intermediates toward the nitrogenization of large hydrocarbons (*e.g.*, pyridines, indoles, carbazoles) which are suspected to be more mutagenic and carcinogenic than their unsubstituted Polycyclic Aromatic Hydrocarbons (PAHs).

References

- [1] Taatjes, C. A., Hansen, N., Osborn, D. L., et al. (2008). *Physical Chemistry Chemical Physics*, 10(1), 20-34
- [2] Osborn, D. L., Zou, P., Johnsen, H., et al. (2008). *Review of Scientific Instruments*, 79(10), 104103.
- [3] Capron, M., Bourgalais, J., Kailasanathan, R. K. A., et al. (2015). *Physical Chemistry Chemical Physics*, 17(37), 23833-23846.
- [4] Bourgalais, J., Spencer, M., Osborn, et al. (2016). *The Journal of Physical Chemistry A*, 120(46), 9138-9150.
- [5] Bock, H., & Dammel, R. (1987). *Chemische Berichte*, 120(12), 1961-1970.
- [6] Blitz, M. A., Talbi, D., Seakins, P. W., et al. (2011). *The Journal of Physical Chemistry A*, 116(24), 5877-5885.
- [7] Zabarnick, S., Fleming, J. W., & Lin, M. C. (1989). *Chemical Physics*, 132(3), 407-411.