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SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-**TP**-1998-090
H.Y. Yoo and Jerry Boatz "Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials" **HEDM Conference Presentation** **(Statement A)**

Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials

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AFOSR HEDM CONTRACTOR'S MEETING
5/18-20, 1998
MONTEREY, CA

Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials

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One of the goals of the HEDM program is the development of high performance monopropellants which are also less toxic than currently used systems such as hydrazine. Included in this effort is the characterization of decomposition mechanisms, as an initial step toward identification of a suitable catalyst. *Ab initio* quantum mechanical calculations are performed on the decomposition mechanisms of $[NH_2Me_2]^+[NO_3]^-$, a potential monopropellant replacement for hydrazine. The potential energy surfaces of two gas-phase decomposition processes have been explored: (1) proton transfer and (2) methyl cation transfer reactions. These reaction pathways have been examined for both the isolated cation $[NH_2Me_2]^+$ and in the presence of a counter anion, $X=Cl^-$, $[NO_3]^-$. For $X=Cl^-$, transition states for both pathways have been located at the RHF/6-31G* level and the corresponding intrinsic reaction coordinates (IRCs) have been traced. Comparison of activation barriers and reaction enthalpies for these gas-phase decomposition pathways will be presented here.

$$[NH_2Me_2]^+[X]^- \rightarrow NHMe_2 + HX \qquad (1)$$

$$[NH_2Me_2]^+[X]^- \rightarrow NH_2Me + MeX \qquad (2)$$

Hydrazine is the state of the art monopropellant currently. However, it has several disadvantages including toxicity, volatility, and handling.

Researchers are continually looking for new monopropellant candidates which include energetic materials such as substituted ammonium salts.

Our research effort has concentrated on the decomposition routes of some HEDM materials. *Ab initio* quantum mechanical calculations have been carried out by our group to explore possible decomposition mechanisms.

The model compounds under study are $[NH_2Me_2]^+ [X]^-$, where $X = NO_3$ and Cl, and $[N(NH_2)_2Me_2]^+ [NO3]^-$.

- **To map out the potential energy surface of these model compounds**
- **To determine the energetics of decomposing species**
- **To design a catalyst that stabilizes the transition state**

Decomposition Mechanisms of $[NH_2Me_2]^+[X]^-$, $X = Cl$ or NO_3

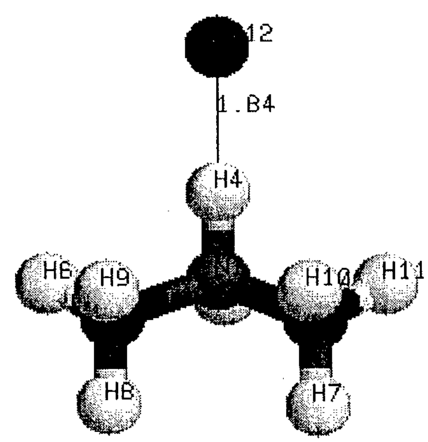
Proton Transfer

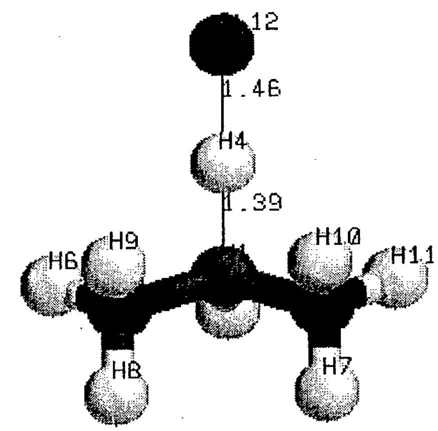
$$[NH_2Me_2]^+[X]^- \rightarrow NHMe_2 + HX$$

Methyl Cation Transfer

$$[NH_2Me_2]^+[X]^- \rightarrow NH_2Me + MeX$$

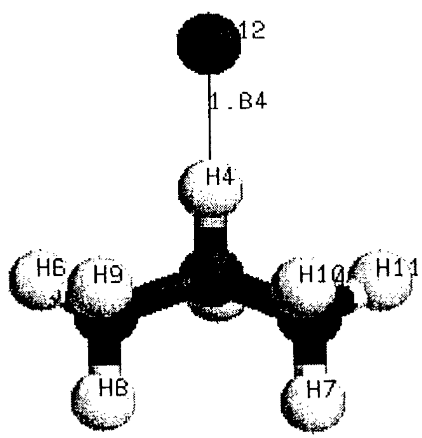
A Proton Transfer Transition Structure of $[NH_2Me_2]^+[Cl]^-$ At RHF/6-31G*(6d)

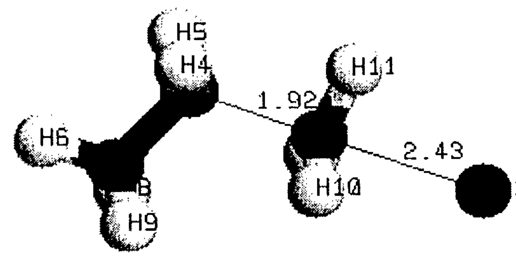




	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0**	**4.6**

A Methyl Cation Transfer Transition Structure of $[NH_2Me_2]^+[Cl]^-$ At RHF/6-31G*(6d)





	Intermediate Complex	Transition Structure
Energy (kcal/mol)	**0.0**	**41.6**

Calculated Reaction Energies of $[NH_2Me_2]^+[Cl]^-$

Proton Transfer

$$[NH_2Me_2]^+[Cl]^- \rightarrow NHMe_2 + HCl \qquad 10.7\ \text{kcal/mol}$$

Methyl Cation Transfer

$$[NH_2Me_2]^+[Cl]^- \rightarrow NH_2Me + MeCl \qquad 8.1\ \text{kcal/mol}$$

CONCLUSION

Based on the *ab initio* calculation studies of $[NH_2Me_2]^+[Cl]^-$

- **The activation energy of the proton transfer decomposition process is much lower than that of the methyl cation transfer pathway.**
- **The transition structure of proton transfer is much tighter than that of methyl cation transfer.**
- **The methyl cation transfer pathway is 2.6 kcal/mol less endothermic than the proton transfer process.**
- **Our calculations imply that the proton transfer is most likely the first step to occur in the decomposition process of $[NH_2Me_2]^+[Cl]^-$.**