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DEPSoCOR98: Tandem TGA/MS Studies of Single Propellants

6. AUTHOR(S)
David Scott Bohle

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
University of Wyoming
Laramie, WY 82071-3838

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. Michael R. Berman
AFOSR/NL
801 N. Randolph St., Rm. 732
Arlington VA 22203-1977

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There are no restrictions in either the availability or distribution imposed by the University of Wyoming for this report.

14. ABSTRACT
To prepare new economical HEDM derivatives from the condensation reactions of nitric oxide with organic substrates. Once prepared these derivatives were tested for energy content, thermal stability, and product output upon decomposition. The outcome of these experiments were then used to assess which cations, and conditions, are the best to metathesize with the heavy/dense alkali metals initially isolated. We now have an excellent understanding of what the main products will be from these reactions, and the optimal conditions for their formation. This has proven to be a surprisingly variable reaction, and a variety of products can form from the addition of NO to a given substrate, but the determining variables are the base employed, substrate/base ratio, and the temperature. Nitric oxide pressure is also a likely variable as well, indeed many of the products we have characterized are new because we used ca. 3 atm of NO pressure, whereas prior researchers typically use only 1 atm. These compounds are now being tested at Thiokol for propellant characteristics after having undergone safety tests beforehand.

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DEPSCoR98: Tandem TGA/MS Studies of Single Propellants

Professor Scott Bohle

Department of Chemistry
University of Wyoming
Laramie, WY 82071-3838

Bohle@uwyo.edu

Tel. 307-766-2795
Fax. 307-766-2807
Tandem TGA/MS Studies of Single Propellants

Objectives:

To prepare new economical HEDM derivatives from the condensation reactions of nitric oxide with organic substrates. Once prepared these derivatives were tested for energy content, thermal stability, and product output upon decomposition. The outcome of these experiments were then used to assess which cations, and conditions, are the best to metathesize with the heavy/dense alkali metals initially isolated.

Status of effort:

We now have an excellent understanding of what the main products will be from these reactions, and the optimal conditions for their formation. This has proven to be a surprisingly variable reaction, and a variety of products can form from the addition of NO to a given substrate, but the determining variables are the base employed, substrate/base ratio, and the temperature. Nitric oxide pressure is also a likely variable as well, indeed many of the products we have characterized are new because we used ca. 3 atm of NO pressure, whereas prior researchers typically use only 1 atm. These compounds are now being tested at Thiokol for propellant characteristics after having undergone safety tests beforehand.

Accomplishments/New Findings:

In prior progress reports we have outlined many of our accomplishments in what has proven to be a fertile area of research. At this point I will outline in broad brush strokes where we are with our understanding of this system, and describe some recent extensions to illustrate how we can apply the general rules we have developed.

The addition of NO to organic compounds with active hydrogens results in the formation of a new nitrogen-nitrogen double bond, and the first catenizing step to generate, possibly, a polynitrogen species. General considerations for the reaction are shown on the right, and we note that the number of known
N-catenized species are somewhat small, but have surprisingly good thermal stability. A surprising feature of all of these species however is the marked differences in the stabilities of their cis/trans (Z/E) pairs. For example, there are known diesters of cis-hyponitrite, and until recently, there were no known examples of E-diazenium diolates.

Some of the representative reactions from these diazenium diolate reactions are shown on the following page, Scheme 1. As can be seen, activating groups in the form of carbonyl groups or nitro substituents are required, and in all of these cases the resulting diazenium diolate function has a Z, or cis, configuration. In addition, all products are isolated as air stable crystalline solids which in general are pure, even after a simple filtration step from the reaction mixture. The cations can be readily exchanged by metathesis, for example with ammonium and hydrazinium cations. In many cases these reactions are accelerated by cooling them in an ice bath. This somewhat contra intuitive observation is most likely due to the increased solubility of NO in the solvent in these conditions, and the dependence of the reaction rate on the NO concentration. The thermal properties, as determined by DSC, of some of these species have been collected in Table 1.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{	ext{cecret}}$, °C</th>
<th>$T_{	ext{max}}$, °C</th>
<th>$\Delta H$, cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(N$_2$O$_2$K)$_3$</td>
<td>210.9</td>
<td>211.20</td>
<td>Exploses</td>
</tr>
<tr>
<td>Bu'COC(N$_2$O$_2$K)$_3$:3H$_2$O</td>
<td>127.51 and 142.23</td>
<td>178.54 and 201.28</td>
<td>-339.60</td>
</tr>
<tr>
<td>CH$_3$(N$_2$O$_2$K)$_2$</td>
<td>204.52</td>
<td>205.64</td>
<td>Exploses</td>
</tr>
<tr>
<td>CH$_2$(N$_2$O$_2$Na)$_2$:H$_2$O</td>
<td>235.5</td>
<td>244.40</td>
<td>Exploses</td>
</tr>
<tr>
<td>CH$_3$(N$_2$O$_2$Li)$_2$:H$_2$O</td>
<td>234.33</td>
<td>236.94</td>
<td>Exploses</td>
</tr>
<tr>
<td>[NEt$_4$)$_2$(CH$_2$(N$_2$O$_2$)$_2$]</td>
<td>172.10</td>
<td>177.24</td>
<td>-89.4</td>
</tr>
<tr>
<td>[N$_2$H$_4$)$_2$(CH$_2$(N$_2$O$_2$)$_2$]</td>
<td>156.10</td>
<td>157.91</td>
<td>-35.6</td>
</tr>
<tr>
<td>[C(NH$_2$)$_2$)$_2$(CH$_2$(N$_2$O$_2$)$_2$]</td>
<td>130.00 and 196.14</td>
<td>149.40 and 200.88</td>
<td>-73.0</td>
</tr>
<tr>
<td>CH$_2$CH(N$_2$O$_2$K)$_2$</td>
<td>202.40</td>
<td>203.61</td>
<td>Exploses</td>
</tr>
<tr>
<td>CH$_3$CH(N$_2$O$_2$Na)$_2$</td>
<td>254.15</td>
<td>259.60</td>
<td>-144.1</td>
</tr>
<tr>
<td>CH$_2$CH$_2$CH(N$_2$O$_2$K)$_2$</td>
<td>244.96</td>
<td>249.12</td>
<td>-341.3</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH(N$_2$O$_2$Na)$_2$</td>
<td>211.29</td>
<td>230.32</td>
<td>-177.7</td>
</tr>
<tr>
<td>HOCH$_2$CH$_2$CH$_2$CH(N$_2$O$_2$Na)$_2$:2H$_2$O</td>
<td>214.74</td>
<td>227.57</td>
<td>-190.4</td>
</tr>
<tr>
<td>CH$_3$N$_2$O$_2$Na</td>
<td>294.60</td>
<td>332.40</td>
<td>-180.00</td>
</tr>
<tr>
<td>CH$_3$CH$_2$N$_2$O$_2$K</td>
<td>275.00</td>
<td>281.92</td>
<td>-254.2</td>
</tr>
<tr>
<td>Bu'N$_2$O$_2$K</td>
<td>275.00</td>
<td>284.58</td>
<td>-50.2</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C(N$_2$O$_2$K)(COOK)</td>
<td>266.96</td>
<td>270.65</td>
<td>-155.1</td>
</tr>
<tr>
<td>CH$_2$(N$_2$O$_2$K)(COOK)</td>
<td>255.50</td>
<td>259.07</td>
<td>-442.1</td>
</tr>
<tr>
<td>CH$_3$C(NO$_2$)(N$_2$O$_2$Na)</td>
<td>214.10</td>
<td>224.69</td>
<td>-332.2</td>
</tr>
</tbody>
</table>
Recent Accomplishments:

As highlighted during a recent site visit by the program director to our campus, we have some exciting recent findings which we are in the process of publishing and trying to understand. As noted above, all of the diazenium diolates we have described have a Z or cis geometry of the two oxygens. We have recently found an exception, and in this case an E, or trans, ONNO geometry is trapped out in a cyclic structure during the condensation of NO with dimethylmalonate:

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{O} \\
\text{C} \\
\text{C} \\
\text{Me} \\
\text{CO}_2\text{Me} \\
\end{array}
\xrightarrow{\text{NO, 3 atm.}}
\xrightarrow{\text{O}^\circ\text{C}, 12\ \text{hr.}}
\xrightarrow{\text{MeOH, 4 KOH}}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{O} \\
\end{array}
\text{Isolated as a dipotassium salt}
\text{in 30\% yield}
\]

DSC: \(T_{\text{onset}}\ 322\ ^\circ\text{C}\)
\[\Delta H = -421\ \text{cal g}^{-1}\]
\[\rho = 2.027\ \text{g ml}^{-1}\]

A compound with these properties was briefly described by Traube in 1897, but the structure was wrong, the yield poor, and nothing further has been done with it. We find this result both fundamentally intriguing as well as practically important. Current efforts are underway to understand why in this case the Z/E isomerization is so facile; we hypothesize that this is due to stabilizing multiple bond interactions of the carbon bound NO group during the transition state. \textit{Ab initio} theory is currently being applied to this question to examine these potential energy surfaces. On a practical level though, these cyclic structures results in very high crystal densities, and even though the value above is for a dipotassium salt, we believe that we will be able to prepare other salts by simple metathesis.

Finally, to illustrate how we now have predictive capability in these nitric oxide condensation reactions, the following new trisdiazenium diolates have been prepared:
The combination of two $\text{C(N}_2\text{O}_2\text{)}_3$ groups into the bicyclic strained ring species is particularly significant, since these molecules have been examined as fuels for mixed propellant systems. In this case energy is stored in the ring as strain energy, and the oxidizer is potentially incorporated directly into the material, which is isolated as a stable salt.

**Summary:**
We have prepared a family of new HEDM materials directly from inexpensive reagents in a single step. These compounds have excellent thermal properties and are being tested by our collaborators at Thiokol for inclusion in new propellant formulations.

**Personnel Supported:**
Professor D. Scott Bohle, Principal Investigator
Dr. Navamoney Arulsamy, Postdoctoral Associate
Dr. Jerome Imonigie, Postdoctoral Associate
Chris Barnes, Blaine Doletski, and Michael Smithback Graduate Students
CJ Jones, Andrew Korich, Undergraduate summer research students

**Publications Resulting Directly from this Project: (Sept 1996-May 2001)**

1. Traube's "Azoxymalonate salt" is a Sydnone with a $\text{trans-N}_2\text{O}_2$ structure. Navamoney Arulsamy, D. Scott Bohle *Angew. Chemie Submitted.*


**Comprehensive List of Important Publications During This Project: (April 98 - May 2001)**


64. Theoretical, Thermal, and Coordination Chemistry of the Amphoteric Thiazate(\text{NSO}^-) Ion, Navamoney Arulsamy, D. Scott Bohle, Chen-Hsiung Hung, and Bryan D. Smith, *Inorganic Chemistry In Press*.


**Interactions/Transitions:**

a. This past summer Andrew Korich, from Katheleen Mondanaro’s group at St. Michael’s college in Vermont, spent eight weeks in our group and prepared two new trisdiazonium diolates.

b. We have continued our collaboration with the HEDM group at Thiokol for testing the critical properties of our new salts.

c. Results relating to this project have been presented at the HEDM conferences in Virginia(1997), Monterey(1998), Cape Caneveral(1999), and Park City(2000). In addition, these results have been presented at numerous Universities including: North Dakota State, Iowa State University, Colorado State University, and University of Utah.

c. Transitions. It is very gratifying that Thiokol and SRI have active interests in these compounds. Dr. Thomas Highsmith visited our campus in 2000, and he gave a very well received seminar. The groups at Edwards Airforce Base have expressed an ongoing interest in our graduating students. There is a strong possibility that one of my more talented undergraduates may choose to do his Ph.D. with Dr. Christie. In many ways the training this lab provides is just as important as are our research results; where else can young American scientists get this type of training in HEDM synthesis?
Honors and Awards.

During Grant:
9/99   Early Promotion to Full Professor.
4/99   Extraordinary Merit for Research, University of Wyoming
7/97   Ed King Lecturer in Inorganic Chemistry, University of Colorado, Boulder.
5/96   Dreyfus Teacher Scholar Award from the Dreyfus Foundation.

Lifetime:
9/99   Early Promotion to Full Professor.
4/99   Extraordinary Merit for Research, University of Wyoming
7/97   Ed King Lecturer in Inorganic Chemistry, University of Colorado, Boulder.
5/96   Dreyfus Teacher Scholar Award from the Dreyfus Foundation.
7/95   Humboldt Fellowship from Alexander von Humboldt Foundation(Declined).
5/95   Merit Award for Research, College of Arts and Science, University of Wyoming.
4/95   Hitchings-Elion Fellowship from the Burroughs-Wellcome Foundation.
4/95   Professor of the Year from the ACS Student Affiliate
1/95   Harmon Award for Arthritis Research
4/94   Cottrell Scholar Award from the Research Corporation.
10/89  Postdoctoral Fellowship from the National Institutes of Health.
7/89   Briggs Prize from the University of Auckland for Doctoral Thesis.
8/88   Postdoctoral Fellowship from the Universität Freiburg.
8/86   Student Paper Competition for the New Zealand Institute of Chemistry.
12/84  Postgraduate Scholarship from the University Grants Committee.
5/84   First Class Honours in MSc. degree examinations from the University of Auckland.