ACYL AZIRIDINE REACTIVITY IN THE LINER AND PROPELLANT ENVIRONMENTS

Bruce N. Broline
Boeing Aerospace Company
Seattle, Washington

ABSTRACT

In order to clarify the mode of action of acylaziridine bond promoters, a monofunctional acylaziridine was synthesized and its reactivity of this model compound with 1-propanol in the presence and absence of ammonium perchlorate was studied. The major process identified involved ring-opening of the aziridine ring by the alcohol to give isomeric amides. Following this study, the reactivity of the model bond promoter with hydroxyl terminated polybutadiene polymers was investigated employing carbon-13 nuclear magnetic resonance spectrometry as the primary analytical tool.

INTRODUCTION

Compounds containing the acylaziridine group such as HX-752 and HX-868 have been extensively employed as bonding agents in HTPB propellents and as bond promoters in liner formulations. Despite the widespread use of these reagents, surprisingly few studies have been reported concerning the mode of action and reactivity of this class of compounds in the HTPB propellant and liner environments. Prior experiments concerning the reactivity of acylaziridines were directed toward the behavior of these reagents in CTPB polymer systems. Since CTPB polymers are more acidic and less nucleophilic than the modern HTPB polymers, the extension of data obtained on CTPB polymers to HTPB polymers may yield erroneous conclusions.

The study of acylaziridine bond promoter reactivity and mode of action could be attempted by investigating the cure chemistry of a particular propellant, but this approach yields serious analytical problems. The products obtained in such a study would be part of a complex polymer system making the identification and quantification of reaction products a most formidable and time-consuming task. In such situations, one is often reduced to merely observing starting materials disappear with little knowledge of the reaction products. A second approach is the design of a model system that accurately mimics the propellant ingredients with monofunctional compounds. The major advantage of such a system is that distinct, isolable, reaction products will be formed, greatly simplifying the analytical process. The development and study of such a model system is the approach we selected.

SYNTHESIS OF THE MODEL BOND PROMOTER AND REFERENCE COMPOUNDS

The model bond promoter selected for this study was 1-benzoyl-2-ethylaziridine(1). This compound possesses the required conjugated acylaziridine group and is monofunctional. The presence of the methyl substituent on the aziridine ring adds some complications due to the possibility of isomer formation, but it is required for a good model system since the stability and reactivity of small ring systems are substantially affected by ring substitution. The methyl substituent also serves as a label whose location in the reaction products will provide information concerning the mechanism of the various reaction pathways. This mechanistic detail would not be available if a model compound with fewer substituents were employed in this study.

The model compound was prepared by the Schotten-Baumann reaction of benzoyl chloride with 2-methylaziridine as shown below. This reaction gave the model compound (1) in 93% yield after distillation (B.P. = 61-62°C at 0.06 Torr) and of 98% purity as estimated by NMR spectrometry. Further purification could be accomplished by column chromatography on silica gel employing dichloromethane as the eluent.

Approved for public release; distribution unlimited.
Having the desired model compound in hand, our efforts turned to preparation of 5-methyl-2-phenyloxazoline (2) and 4-methyl-2-phenyloxazoline (3). Aoylaziridines are known to form oxazolines on heating, treatment with acids or halide salts, and it was desirable to have authentic samples of these two isomers (2 and 3) to allow unambiguous structural assignments.

The synthesis of 5-methyl-2-phenyloxazoline (2) is outlined below and began with the Schotten-Baumann reaction of benzoyl chloride with 1-amino-2-propanol to give the amide 4 in 64% yield after recrystallization (m.p.=92.5-95.5°C). This material was converted to the desired oxazoline by dehydration with p-toluenesulfonic acid in refluxing toluene to give 2 in 44% yield. The yield for this reaction was low, but sufficient material was obtained for characterization and no attempt was made to optimize the yield.

The initial attempt to prepare 4-methyl-2-phenyloxazoline (3) followed the route described above for the isomeric oxazoline 2. Unfortunately, attempted dehydration of the amide 5 led only to polymer formation. The successful method for the preparation of 3 involved the potassium iodide catalyzed rearrangement of the model compound 1 in acetone at room temperature. Treatment of 2-alkyl substituted N-acylaziridines is known to yield 4-alkyl substituted oxazolines; thus, the azoylaziridine 1 on treatment with potassium iodide gave 4-methyl-2-phenyloxazoline (3) in 95% yield. The material obtained was 95% pure, contaminated with 5% of the 5-methyl isomer (2).
CHARACTERIZATION OF GENERAL REACTIVITY

The initial characterization of reactivity involved determination of the reactivity of the model bonding agent with alcohols. The alcohol employed, 1-propanol, contains a primary hydroxyl group (as are the majority of the hydroxyl groups in the HTPB polymer) and has a boiling point high enough to allow reaction temperatures as high as 97°C. In addition, this alcohol is water soluble providing a simple method for its removal from reaction mixtures.

The first set of reaction conditions investigated were designed to favor reactions between the alcohol and acylaziridine. Thus, the model compound was treated with an excess of 1-propanol in the presence of ammonium perchlorate at 65°C. Under these conditions, the model compound was consumed in less than four hours. The NMR, IR, and mass spectra of the crude reaction mixture showed this material to be mainly products 6 and 7 resulting from ring-opening of the acylaziridine by 1-propanol as shown below. In addition, small amounts of the oxazolines 2 and 3 were present. The upfield region of the 200 MHz NMR spectrum of a typical reaction mixture is shown in Figure 1a. The small doublets centered at 1.37 and 1.31 ppm are due to the oxazolines 2 and 3 respectively. The triplet at 0.93 ppm and the sextet centered at 1.59 ppm as well as the doublets centered at 1.18 and 1.29 ppm are assigned to the amides 6 and 7.

The relative positions of the two methyl doublets at 1.14 and 1.25 suggest that the major component of the mixture is the isomer 7. This assignment was verified by the carbon-13 and mass spectra of the reaction mixture. The proton coupled and decoupled carbon-13 spectra are shown in Figure 2. The two resonances at 69.2 and 72.7 ppm are due to the carbons adjacent to the ether oxygen and their multiplicity in the proton coupled carbon-13 spectrum is consistent only with the isomer 7 being the major component. The concentration of the four components was determined by integration of the proton spectrum and are shown in Table 1, entry 1.

The second set of reaction conditions investigated involved an acylaziridine to 1-propanol ratio that more closely resembled the ratio found in a typical propellant formulation. Thus, a ratio of 1-propanol to acylaziridine of 2.7:1 was used with the ratio of acylaziridine to ammonium perchlorate equal to 1:1. This mixture was stirred at 65°C for four hours. The upfield portion of the NMR spectrum of the material obtained is shown in Figure 1b. Integration of this spectrum gave the results shown in Table 2, entry 2. Once again, the amide 7 was the major product (83%) with minor amounts of the isomer 6 (9%) and 3 of the oxazolines 2 and 6 of the oxazoline 3 were also present.

An investigation of the reactivity of the model bond promoter 1 with 1-propanol in the absence of ammonium perchlorate was also conducted. This experiment was directed toward a better understanding of the behavior of acylaziridines in the liner environment. Treatment of 1 with excess 1-propanol at 65°C for one week resulted in the reaction of 62% of the acylaziridine 1. In addition to the starting material, 45% of the amide 7, 12% of the amide 6, 2% of the oxazolines 2, and 3% of the oxazoline 3 were present (see Table 1, entry 3).
Figure 1 200 MHz Proton NMR Spectra of 1-Propanol Addition Products
Figure 2  Carbon 13 NMR Spectra of the 1-Propanol Addition Product. (2a - Decoupled Spectrum; 2b - Coupled Spectrum)
### Table I. Product Ratios for 1-Propanol Reactivity Studies

<table>
<thead>
<tr>
<th>ENTRY</th>
<th>1-Propanol Aziridine</th>
<th>AP Aziridine</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.0</td>
<td>0.63</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>7</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
<td>0.69</td>
<td>0</td>
<td>9</td>
<td>2</td>
<td>6</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>24.0</td>
<td>0</td>
<td>38</td>
<td>2</td>
<td>3</td>
<td>12</td>
<td>45</td>
</tr>
</tbody>
</table>

A second reaction pathway that may be available to acylaziridines in the liner and propellant environments is reaction with isocyanate curing agents. Simple N-acyl substituted aziridines are known to react with isocyanates at temperatures between 100-170°C to yield substituted imidazolidones as shown below. The mechanism of this reaction is likely to involve ring-opening to the acylaziridine to yield a zwitterion intermediate that reacts with the isocyanate to give the observed products. Since the environment at the propellant to liner interface is quite polar, it was thought that such reactions may be possible. Treatment of the model compound 1 with phenyl isocyanate in the presence and absence of ammonium perchlorate did not give addition products.

![Chemical Structure](image)

The reactivity of the oxazolines 2 and 3 was assessed to determine their stability under the reaction conditions. Perchlorate salts of oxazolines are known to polymerize on heating and anhydrous hydrochloride salts of oxazolines have been shown to rearrange to N-chloroamides. Additional possible reactions include acid catalysed ring opening by 1-propanol and hydrolysis of the oxazoline by water absorbed on the ammonium perchlorate.

The reactivity tests were carried out by treating one equivalent of the oxazoline (2 or 3) with forty equivalents of 1-propanol and ammonium perchlorate (2.7 equivalents). The resulting mixture was stirred at 65°C for one week at which time the reaction mixture was worked up and analysed by NMR. In both cases, no reaction was observed, only unreacted oxazoline was recovered.

### DISCUSSION OF 1-PROPAHOL REACTIVITY STUDIES

As can be seen by inspection of Table I, the major process under all conditions results from alcohol addition to the aziridine ring of 1 to give the amides 6 and 7. Comparison of entries 1 and 2 shows that the product distribution is only slightly affected by the alcohol concentration and that decreased alcohol to aziridine ratios give a higher amount of oxazoline 2 at the expense of amide 7. Also, the amounts of the products 2 and 6 are very similar for entries 1 and 2. The data given in entry 3 shows that alcohol addition to the aziridine is the major process even in the absence of ammonium perchlorate. Thus, ammonium perchlorate accelerates the reaction rate, but has only a small effect on the product distribution.

These data demonstrate that a major pathway available to acylaziridines in HTPB systems is reaction with hydroxy groups to yield amides. It is also important to note that the products shown in Table I account for the majority of the acylaziridine consumed. Mass balance considerations limit the amount of acylaziridine homopolymerization to be less than 15%. Thus, a possible role of action of acylaziridine bonding agents and bond promoters involves cross linking of the polymer network through reaction with free HTPB hydroxy groups.
REACTION OF R-45M HTPB POLYMERS

The second phase of this study involved the determination of the reactivity of the model bond promoter with the R-45M HTPB polymer employed in propellant formulations. The study of HTPB polymer reactivity is complicated by the fact that the polymer has an average molecular weight of approximately 2800 and a functionality slightly over 2 hydroxyl groups per molecule. Since the R-45M polymer reactivity is restricted to hydroxyl reactions, and these hydroxyl groups are present only in very low concentrations, the analytical process is very difficult.

Our approach to the solution of the analytical problems involved the use carbon-13 NMR spectrometry. While C-13 NMR is not noted for sensitivity, it offers the advantage that the carbon atoms adjacent to the hydroxyl groups can be directly observed. The sensitivity problems were overcome by using a relaxation reagent permitting more rapid spectral acquisitions and the use of 20mm sample tubes. It should be noted that our goal for this phase of the study was to define reactivity trends and not to obtain quantitative data.

The initial stage of this study involved the characterization by C-13 NMR of the reaction products obtained in the 1-propanol reactivity studies (See Table II). The amide 7 should serve as a reasonably good model for the reaction product of the model bonding agent and the R-45M polymer (as shown below). The chemical shifts of the G, B, Y, and E carbons of 7 should be very similar to the R-45M reaction product 8.

Homopolymers of the bond promoter such as 9 can also be identified by C-13 NMR. The C-13 spectrum of 9 has been reported and a portion of the data are shown in Table II. The C-13 spectrum of the R-45M polymer has been previously reported and our data on this polymer are in good agreement with the literature data. The isomeric R-45M terminal carbons exhibit C-13 peaks at 58.2, 63.5, and 68.9 ppm (see figure 3b).

The first experiment involved treatment of R-45M (14.1g) with ammonium perchlorate (3.0g) and the model bond promoter (2.0g). This mixture was stirred at 65°C. The reactivity of the model bond promoter was much slower than observed with 1-propanol; after 196 hours, the model bond promoter was not totally consumed. The terminal carbon region of the C-13 NMR spectrum of the material obtained from this experiment is shown in figure 3b.

The three peaks due to unreacted R-45M are present along with a major peak at 61.1 which is assigned to be the oxazoline 2. There is also a peak at 163.4 which is also assigned to the oxazoline 2. The two peaks at 68.9 and 72.8 are assigned to the carbon of the addition product 8. The carbonyl carbon of 8 at 166.9 provides additional support for assignment of the amide 8. An additional peak at 178.6 is due to unreacted model bonding agent. A very rough estimation of the ratio of the compounds 1, 2, and 8 is 20%, 30%, and 50% respectively. Significantly, no peaks consistent with the homopolymer 9 were present in this spectrum.
A second reactivity study involved heating a mixture of R-45M (7.7g) with the model bond promoter 1 (1.0g) at 65°C for 700 hours. No reaction was observed by C-13 NMR.

MECHANISTIC CONSIDERATIONS

A reaction manifold for the model bond promoter is shown in Figure 4. In the presence of 1-propanol \((\text{R}=\text{C}_3\text{H}_7)\) and ammonium perchlorate, the amide 7 was major product. This demonstrates that the mechanism for this reaction involves a carbonium ion intermediate. Initial protonation of 1 followed by ring opening would give the most stable carbonium ion 10. This ion (10) then partitions between reaction with propanol to give 7 or intra-molecular ring closure to give the oxazoline 2. In the absence of ammonium perchlorate, the formation of ion 10 is slowed, and the amide 6 becomes a more important product as shown in Table I.

The use of R-45M as the alcohol in place of 1-propanol yields reaction rates that are significantly decreased. This is probably caused by the decreased polarity of the R-45M polymer as compared to 1-propanol and by the decreased solubility of ammonium perchlorate in R-45M. The reduced rate gives added support for the carbonium ion pathway. In the presence of R-45M, ring closure of the carbonium ion 10 is faster than hydroxyl attack to give the oxazoline 2 as the major product. The second major product is the amide 8 resulting from ring opening of the acylaziridine by the hydroxyl groups of the R-45M polymer.

CONCLUSIONS

This study has demonstrated that an important reaction pathway for acylaziridine bond promotors and bonding agents in the HTPB propellant environments involves reaction with the hydroxyl groups of the polymer. The rearrangement of acylaziridines to oxasolnes was also identified as a major process. Significantly, homopolymerization of the model bonding agent was not identified as a major process. These data suggest that these reagents function by increasing the local crosslink density of the propellant in the area adjacent to the ammonium perchlorate particles through reaction with hydroxyl groups of the polymer.

In addition, this work has provided information concerning the mechanism of amide and oxasoline formation. The structures of the major products suggest that the predominant process involves formation of a carbonium ion that is either captured by alcohol to give amides or closes to yield oxasolnes. This carbonium ion pathway is reasonable since the propellant ingredients provide a very polar environment that will favor ionic pathways.

In conclusion, this study has demonstrated the value of an experimental approach that begins with simple, easily defined systems and graduates to the more complex cases. The application of this approach has significantly improved our understanding of acylaziridine reactivity in the liner and propellant environments.
Table II. Carbon - 13 NMR Data for Selected Compounds

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>δ</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>179.1</td>
<td>32.1</td>
<td>34.4</td>
<td>17.6</td>
<td>-</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>166.3</td>
<td>43.9</td>
<td>72.7</td>
<td>16.6</td>
<td>69.2</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>163.6</td>
<td>61.4</td>
<td>76.2</td>
<td>21.1</td>
<td>-</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>163.3</td>
<td>61.9</td>
<td>74.0</td>
<td>21.3</td>
<td>-</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>171.2</td>
<td>53.6</td>
<td>46.0</td>
<td>16.0</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3a Terminal Carbon Region of the C-13 NMR Spectrum of R-45M Polymer

Figure 3b Terminal Carbon Region of the C-13 NMR Spectrum of the R-45M Reaction Product
Figure 4: Reaction manifold for the model bond promoter.
REFERENCES

16. Carbon -13 NMR spectra were obtained at 50 MHz in deuteriochloroform. Chemical shifts are referenced to the center line of deuteriochloroform at 77.0 ppm.