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Heats of Formation of Energetic Oxetane Monomers and Polymers

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HEATS OF FORMATION OF ENERGETIC OXETANE MONOMERS AND POLYMERS

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ABSTRACT

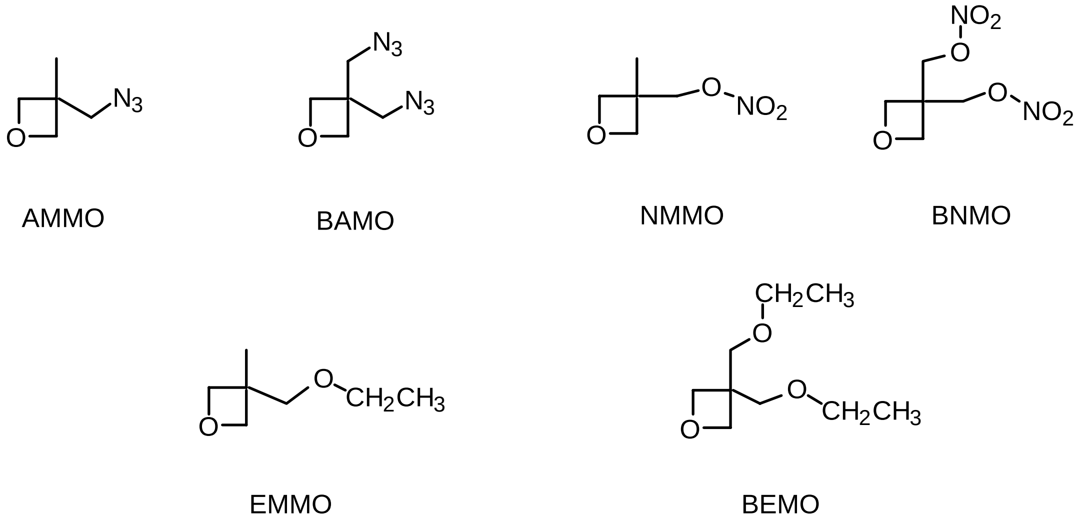
Energetic oxetane polymers have shown promise as performance-enhancing ingredients in gun and missile propellants. In order to correctly predict the performance of energetic materials containing these polymers, it is important to have accurate, experimentally determined values for the polymer heats of formation (ΔH_f). In support of a theoretical study on gun propellant performance, heats of combustion were experimentally determined for a series of oxetane polymers and monomers (see below) using combustion calorimetry, and from these, ΔH_f values were calculated. Polymers included BAMO/AMMO, BAMO/NMMO (polyol and TPE), and BNMO/NMMO mixtures. In order to calculate the ΔH_f of the polymers from heat of combustion data, a number of assumptions were made regarding the polymer structure and molecular weight. A comparison of the ΔH_f values for the monomers and polymers were made, and these values were compared to heats of formation measured elsewhere.

INTRODUCTION

Energetic binders made from oxetanes have been investigated for use in gun propellants and in other applications where an energetic binder would be useful. In order to predict the performance of an energetic material, it is important to have accurate, experimentally determined values for the material's heat (enthalpy) of formation (ΔH_f). While there are reports in the literature[1-4] of measured ΔH_f values for energetic oxetanes, these are generally limited to monomers and single-component polymers. In this study, heats of formation were determined for a series of oxetane monomers (including two previously unreported), as well as polymers and polymer mixtures, using combustion calorimetry. The compounds studied were based on the energetic monomers azidomethylmethyloxetane (AMMO), *bis*-azidomethyloxetane (BAMO), nitratomethylmethyloxetane (NMMO) and *bis*-nitratomethyloxetane (BNMO), and the non-energetic monomers ethoxymethylmethyloxetane (EMMO) and *bis*-ethoxymethyloxetane (BEMO). Samples of these materials were prepared at the Aerojet Corp. in Sacramento, California. Chemical structures of the monomers are shown in figure 1.

The following equation relates the heat of formation (ΔH_f) of a material to its heat of combustion (ΔH_c):

$$\Delta H_{f\,(\text{material})} = \Delta H_{f(\text{combustion products})} - \Delta H_{c(\text{material})}$$



AMMO BAMO NMMO BNMO

EMMO BEMO

Figure 1. Oxetane monomer structures.

The value for $\Delta H_{c(material)}$ is determined directly by combustion calorimetry. The material is ignited and burned in a sealed pressure bomb which contains pure oxygen atmosphere. The bomb is immersed in a water bath during combustion, and the resulting temperature rise of the bath is measured and used to calculate the value for $\Delta H_{c(material)}$. A value for $\Delta H_{f(combustion\ products)}$ is then calculated. In the case of CHNO compounds, the combustion products are N_2, CO_2, H_2O and small amounts of HNO_3. Since the heat of formation of nitrogen gas is zero (by definition for the elemental form), it does not contribute to the product heat of formation. The amount of nitric acid produced during combustion is measured by performing an acid-base titration of the liquid water remaining in the bomb. A correction for this HNO_3 is then calculated using the standard heat of formation of the acid. (In practice, these data are entered into the calorimeter computer, which then automatically includes this correction in the reported $\Delta H_{c(material}$.) The heats of formation of CO_2 and H_2O are determined by calculating the moles of these species produced during combustion (which is based on the C and H content of the material), and multiplying by their respective standard heats of formation:

ΔH_f (CO_2) = -94.051 kcal/mol

ΔH_f (H_2O) = -68.315 kcal/mol

So, for example, complete combustion of the AMMO monomer produces 5 moles of CO_2 and 4.5 moles of H_2O per mole of AMMO, which gives a $\Delta H_{f(combustion\ products)} = -777.67$ kcal/mol. The measured ΔH_c of AMMO was -6384.09 cal/g (which includes the correction for HNO_3). This is multiplied by the molecular weight of AMMO (127.147 g/mol)) to give a molar ΔH_c of -811.72 kcal/mol. Therefore:

$\Delta H_{f\ (AMMO)} = (-777.67) - (-811.72) = +34.04$ kcal/mol (or +0.2677 kcal/g).

RESULTS

Table 1 summarizes the experimental heats of formation determined by this study. For comparison, values measured elsewhere are given in the right column, if available. In general, our results agreed well with those values reported elsewhere, which gives us confidence that our values for previously unreported materials are accurate.

Table 1. Summary of Heat of Formation Measurements.

Material	**Measured Heats of Formation**		
(ingredient wt. %, if mixture)	kcal/mol	kcal/g	lit. (kcal/mol)
AMMO	+34.04	+0.2677	+43.00[a]
BAMO	+103.60	+0.6161	+124.00[a]; +102.039[b]
BEMO	-151.17	-0.8680	-
BNMO	-89.82	-0.4316	-75.90[c]
EMMO	-113.38	-0.8709	-
NMMO	-79.99	-0.5437	-79.67[d]
Poly-BAMO	+88.79	+0.5280	+89.12 to +124.00[c]
Poly-BEMO	-289.69	-1.6626	-164.00[d]
Poly-NMMO (polyol)	-82.78	-0.5626	-94.00 to –73.90[c]
Poly-BAMO(50%)/AMMO (50%) (TPE)	+41.16	+0.2842	-
Poly-BAMO(73%)/NMMO (27%) (polyol)	+46.09	+0.2848	-
Poly-BAMO(73%)/NMMO (27%) (TPE)	+35.55	+0.2196	-
Poly-BNMO(66%)/NMMO (34%) (TPE)	-101.26	-0.5548	-

Notes: (a) from reference 1, p. 22-10; (b) from reference 2, p. IIB-2-10; (c) from ICT Thermochemical Data Base; (d) from reference 3, pp. 87-4 & 87-5

A. General Experimental Notes. A Parr Instruments 1261 combustion calorimeter was used to conduct all experiments. Samples were burned in a 250 ml platinum-lined Parr bomb (Model 1105), using a platinum combustion crucible and platinum igniter wire. Sample sizes ranged between 0.3 and 1 gram, depending on burn characteristics. For volatile liquid samples, a tape seal was made over the sample combustion crucible to prevent evaporation prior to ignition. (The heat of combustion of this tape is known, and was accounted in the calculations. See results for AMMO for complete description, below.) Solid samples were pressed into pellets (if in powdered form) or, if in chunk form, were cut to the appropriate weight. In some cases, benzoic acid in pellet form was added to the combustion crucible along with the sample to facilitate complete combustion. Accuracy of material weight is ± 0.1 mg (not accounted for in error figures below). Post-burn gases were tested for presence of CO (which indicates incomplete combustion), and any runs where CO was detected were discarded. After each combustion, the inner bomb surfaces were rinsed with deionized water, and these washings were titrated for nitric acid using a 0.0709 sodium carbonate solution and methyl orange indicator. The titration data were entered into the calorimeter and heats of combustion were corrected automatically for nitric acid by the calorimeter software.

B. Oxetane Monomer Heat of Formation Results and Calculations.

1. **AMMO Monomer**. Aerojet lot # C923-64, liquid. AMMO does not burn cleanly in the oxygen bomb without a burn enhancer. Therefore, benzoic acid was added to each burn run, resulting in clean burns. Since AMMO is a liquid with significant volatility, the combustion crucible was sealed with cellophane tape to prevent mass loss due to evaporation. The liquid was added to the crucible with a syringe, by piercing the tape seal with the syringe needle. (The ΔH_c of the tape is known from separate measurements, and is deducted from the measured ΔH_c of AMMO.) Result: $\Delta H_c = 6384.09 \pm 13.63$ cal/g (average of 3 runs), which gives $\underline{\Delta H_f = +34.04 \pm 1.73}$ $\underline{\text{kcal/mol} = +0.2677 \pm 0.0136 \text{ kcal/g.}}$
2. **BAMO Monomer**. Aerojet SRR 70881, lot # 072798. BAMO burned fairly well without burn enhancers. However, each run left approximately 1 mg of an unburned, brown residue that, when washed with water, partially dissolved. No correction was made for this. Result: $\Delta H_c = 5037.63 \pm 7.71$ cal/g (average of 5 runs), which gives $\underline{\Delta H_f = +103.60 \pm 1.30 \text{ kcal/mol} = +0.6161 \pm 0.0077 \text{ kcal/g.}}$
3. **BEMO Monomer**. Burned cleanly on each run, using tape seal method to avoid evaporation errors (as with AMMO). Result: $\Delta H_c = 7522.11 \pm 8.77$ cal/g (average of 5 runs), which gives $\underline{\Delta H_f = -151.17 \pm 1.52 \text{ kcal/mol} = -0.8680 \pm 0.0088 \text{ kcal/g.}}$

4. **BNMO Monomer**. Aerojet lot # CR3 RX2. Burned as pressed pellets, this compound burned very well. Results: ΔH_c = 3140.82 ± 8.58 cal/g (average of 5 runs), which gives $\underline{\Delta H_f = -89.82 \pm 1.79}$ kcal/mol = -0.4316 ± 0.0086 kcal/g.
5. **EMMO Monomer**. Lot # 957-44K, liquid. EMMO is the most volatile of all the monomers analyzed, so experiments were conducted using tape-seal method (see AMMO, above). EMMO burns cleanly by itself, so no burn enhancers were needed. Results: ΔH_c = 7859.28 ± 15.23 cal/g (average of 4 runs), which gives $\underline{\Delta H_f = -113.38 \pm 1.98}$ kcal/mol = -0.8709 ± 0.0152 kcal/g.
6. **NMMO Monomer**. Burned cleanly with benzoic acid burn enhancer. Results: ΔH_c = 4741.86 ± 11.47 cal/g (average of 5 runs), which gives $\underline{\Delta H_f = -79.99 \pm 1.69}$ kcal/mol = -.5437 ± 0.0115 kcal/g.

C. Oxetane Polymer Heat of Formation Results and Calculations.

The following calculations use the assumption that the average molecular weight of the polymer is large in comparison to the monomer (i.e., the average number of repeating units, *n*, is greater than about 20). In effect, this neglects the weight of the "additional" –H and -OH groups at the chain ends, and it is then an excellent approximation that the polymer chain molecular weight is an integral multiple of the monomer molecular weight.

1. **Poly-NMMO (polyol)**. Lot # 727-64, viscous liquid. Burned fairly well with benzoic acid burn rate enhancer. Result: ΔH_c = 4722.87 ± 4.89 cal/g (average of 4 runs). Using the above assumption, one gram of poly-NMMO will burn to produce 1.496 grams of CO_2 and 0.5510 grams of H_2O. This gives a product ΔH_f = -5.286 kcal/g poly-NMMO. This gives $\underline{\Delta H_f = -82.78 \pm 0.72}$ kcal/mol = -0.5626 ± 0.0049 kcal/g.
2. **Poly-BEMO**. Lot # C647-91. Burned cleanly without burn enhancers. Result: ΔH_c = -6723.89 ± 19.42 cal/g (average of 6 runs), which gives $\underline{\Delta H_f = -289.69 \pm 3.38}$ kcal/mol = -1.6626 ± 0.0194 kcal/g.
3. **Poly-BAMO/AMMO (TPE)**. Lot # C923-58. Weight ratio of BAMO:AMMO = 0.50 : 0.50. This was a difficult material on which to obtain satisfactory combustion.

Burned as pressed pellets, the material tended to leave relatively large amounts of unburned residue. Combustion was slightly cleaner using benzoic acid as a burn enhancer, but unburned residue remained after each run. This residue was combusted separately (using benzoic acid to complete the combustion), and a correction for unburned material was determined. Result: ΔH_c = -5552.72 ± 15.29 cal/g (average 3 runs, corrected for unburned material). Based on a polymer empirical formula of $C_5H_{8.5694}N_{4.2917}O_1$, calculated $\underline{\Delta H_f = +41.16 \pm 2.22}$ kcal/mol = +0.28422 ± 0.0153 kcal/g.

4. **Poly-BAMO/NMMO (polyol).** Lot # 927-44A, sticky, highly viscous liquid. Ratio of BAMO:NMMO = 0.73 : 0.27. Burned very well using benzoic acid as a burn enhancer. Result: ΔH_c = -4941.35 ± 2.41 cal/g (average of 3 runs). Based on a polymer empirical formula of $C_5H_{8.2971}N_{4.5144}O_{1.8914}$, calculated $\underline{\Delta H_f = +46.09 \pm 0.39}$ kcal/mol = +0.28479 ± 0.0024 kcal/g.
5. **Poly-BAMO/NMMO (TPE).** Aerojet lot # ETPE-21, in the form of 1-2 cm rubbery chunks, with light conglomerations of finer particles. Ratio of BAMO:NMMO = 0.73 : 0.27. Burned fairly well without burn enhancers, although small amounts of soot remained after each burn (generally < 0.3 mg). The soot was occasionally found outside the crucible in a 1-2 cm patch on the inner wall of the combustion bomb, indicating possible ejection of the material from the combustion crucible. Use of burn rate enhancers resulted in combustion of bomb gasket, even with small amounts of sample. Result: ΔH_c = -4876.19 ± 9.57 cal/g (average of 4 runs, no correction for unburned residue). Based on a polymer empirical formula of $C_5H_{8.2971}N_{4.5144}O_{1.8914}$, calculated $\underline{\Delta H_f = +35.55 \pm 1.55}$ kcal/mol = +0.21963 ± 0.0096 kcal/g.
6. **Poly-BNMO/NMMO (TPE)**. Lot # C965-167B, rubbery chunks. Ratio of BNMO:NMMO = 0.66 : 0.34. Generally good burns, although some had unburned residue. Some runs were burned with benzoic acid as a burn enhancer, with slightly better results. No correction for unburned material was made. (Attempts to quantify heat of unburned material gave inconsistent results. In any case, the correction is probably insignificant, due to relatively small weight of unburned residue.) ΔH_c = -3597.86 ± 7.70 cal/g (average of 5 runs). Based on a polymer empirical formula of

$C_5H_{8.4215}N_{1.5785}O_{5.7354}$, calculated <u>$\Delta H_f$ = -101.26 ± 1.41 kcal/mol = -0.55479 ± 0.0077 kcal/g.</u>

7. **<u>Poly-BAMO</u>**. Lot # 979-205, solid powder pressed into pellets. Burned in a similar fashion to poly-BAMO/NMMO (TPE), leaving a small amount of soot in the crucible and on bomb wall. (No correction was made for this, but was estimated to be <5cal/g.) Result: ΔH_c = -4949.47 ± 12.21 cal/g (average of 3 runs), which gives <u>ΔH_f = +88.79 ± 2.05 kcal/mol = +0.5280 ± 0.0122 kcal/g.</u>

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