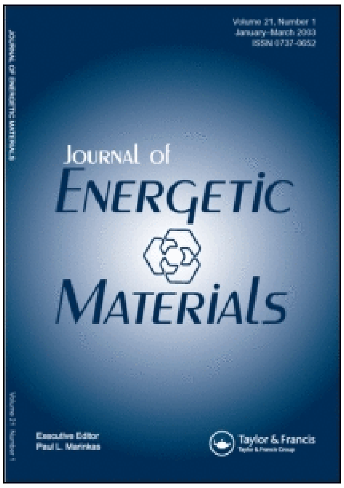

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High-Level Calculations on Nitrosooxyalanes: Possible New High-Energy Materials?

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As part of our survey of new potential high-energy materials, we have calculated the structures, vibrational frequencies and spectra, and various enthalpies of reaction for nitrosooxy-, dinitrosooxy-, and trinitrosooxyalane. Although the initial intent was to determine the properties of nitroalanes, in all cases the bonding to the central aluminum atom was through an oxygen atom of the NO_2 *group. All molecules optimized to a near planar structure. Calculations of their reaction energies showed that the higher the nitrosooxy content, the more negative the enthalpies of formation, with enthalpies of combustion or decomposition falling precipitously.*

Keywords: G2 calculations, high-energy materials, nitrosooxyalanes

Introduction

The search for new high energy (HE) materials is an ongoing one [1–3]. Good HE materials have certain characteristics,

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among them a high condensed-phase density, a high velocity of detonation, and metastable thermodynamics with regard to decomposition or combustion products. It is with this last property that modern computational chemistry has been able to assist the most, although models do exist to estimate other properties like density [4,5] and velocity of detonation [6], if appropriate other data are available.

We have been considering new molecules having high nitro group content for quite some time, considering carbon- [7], beryllium- [8], nitrogen- [9,10], and boron/nitrogen-backboned [11,12] molecules with relatively large numbers of nitro groups. Here we turn our attention to molecules based on aluminum. This is in part because aluminum has a very strong chemical propensity for oxygen; the enthalpy of formation of Al_2O_3 is $-1676\,kJ\,mol^{-1}$ or $-16.44\,kJ\,g^{-1}$ [13]. The parent "hydro-aluminum" is alane, AlH_3. Under normal conditions, alane is a colorless involatile solid that exists in various crystal forms. The most stable phase, α-AlH_3, is polymeric, with each Al center octahedrally surrounded by six hydrogen atoms [14]. Its measured enthalpy of formation is $-2.73 \pm 0.20\,kcal\,mol^{-1}$ or $-11.4 \pm 0.84\,kJ\,mol^{-1}$ [15]. It is trivial, then, to calculate its enthalpy of combustion as $-1285.3\,kJ\,mol^{-1}$ or $-41.8\,kJ\,g^{-1}$. This is a fairly substantial specific enthalpy of combustion and suggests that the appropriate derivatives of AlH_3 may also have high-energy properties.

Many high-energy materials are nitro derivatives [3]. As such, our first foray into potential high-energy aluminum compounds is an assessment of nitroalane derivatives. Here, we present results on our attempts to study the structures and properties, especially the thermodynamics, of various levels of nitro substitution of alane. To our knowledge, no studies on the substitution of nitro groups into alane have been performed to date.

Computational Details

All calculations were performed using the Gaussian 03 [16] suite of programs either on a desktop computer or on the IBM Cluster 1350 supercomputer located at the Ohio Supercomputer Center in Columbus, Ohio. G2 theory was utilized, which has been optimized for energy accuracy [17]. Molecules having formulas AlH_2NO_2, $AlH(NO_2)_2$, and $Al(NO_2)_3$ had their molecular structures optimized without constraint and vibrational frequencies calculated; all calculations yielded no imaginary vibrational frequencies, verifying that the ultimate structures obtained were true minimum-energy structures. Vibrations were visualized using the GaussView program, and vibrational spectra were plotted using the SWizard program [18] and can be supplied upon request.

The enthalpies of formation of the various molecules were determined using the following gas-phase chemical reaction:

$$\begin{aligned} AlH_3 + (3-n)/2N_2O_4 \rightarrow (AlH_n(NO_2)_{3-n} \\ + (3-n)/2H_2 \qquad (n = 2, 1, 0) \end{aligned}$$

All of the G2 energies of all species in the above reaction were determined, and the enthalpy change from that data was determined for each reaction. Then, using the known enthalpies of formation for the other species in the reactions, the enthalpy of formation for the appropriate $AlH_n(NO_2)_{3\text{-}n}$ molecule was determined. The experimental enthalpy of formation for N_2O_4 was taken from the NIST Chemistry Webbook [13]. The experimental enthalpy of formation of gas-phase AlH_3 is $+32.44\,\text{kcal}\,\text{mol}^{-1}$ $(+135.7\,\text{kJ}\,\text{mol}^{-1})$ based on vapor-phase data measured by Fredriksson and Carlsson [19].

Once the enthalpy of formation of the substituted alane was determined, the enthalpy of combustion or decomposition could be determined. The compound AlH_2NO_2 has an oxygen balance (OB%; a measure of the relative amount of oxygen present to completely oxidize all other atoms [20]) of −10.67%, indicating that the molecule does not have sufficient oxygen to completely oxidize the other atoms. Thus, for complete reaction, additional oxidant is necessary. As such, here we report an enthalpy of combustion for the reaction

$$AlH_2NO_2(g) + \frac{1}{4}O_2(g) \rightarrow \frac{1}{2}Al_2O_3(s) + H_2O(\ell) + \frac{1}{2}N_2(g)$$

The molecules $AlH(NO_2)_2$ and $Al(NO_2)_3$ have OB% of 26.67 and 43.64%, respectively, so these formulas have sufficient oxygen to oxidize all relevant other elements. Thus, here we report enthalpies of decomposition for these two compounds according to the following general al reaction:

$$AlH_n(NO_2)_{3-n}(g) \rightarrow \frac{1}{2}Al_2O_3(s) + \frac{n}{2}H_2O(\ell) + (3-n)/2N_2(g) + (9-5n)/4O_2(g) \quad (n = 0, 1)$$

Experimental enthalpies of formation for Al_2O_3(s) and $H_2O(l)$ are taken from the NIST Chemistry Webbook [13].

Results and Discussion

Optimized Structures

Initially, all nitro-modified alane molecules were constructed with initial molecular structures having the nitrogen atom of all nitro groups near the central aluminum atom, implying N-bonded nitro groups. However, in all cases, the optimized molecules show that an oxygen atom in the NO_2 moiety is bonded to the aluminum. As such, these molecules are not nitroalanes but nitrosooxyalanes. Figure 1 shows the optimized molecular structures of the four nitrosooxyalane molecules studied here. One of them, dinitrosooxyalane, exists as two different conformational isomers, depending on the relative orientations of the –ONO groups. We have labeled them as the cis (ONO pointing in the same direction) and trans (ONO pointing in the opposite directions) isomers. Although it is difficult to see from Fig. 1, nitrosooxyalane and cis-dinitrosooxyalane optimize as planar molecules, whereas trans-dinitrosooxyalane and trinitrosooxyalane optimize with the nitro groups twisted out of the expected plane of the molecule. In trinitrosooxyalane, the lower left –ONO group is almost planar, suggesting that the oxygen atoms on the other –ONO groups, at ca. 3.2 Å apart, are causing some electrostatic repulsive effects that twist the adjacent nitrosooxy groups out of the molecular plane.

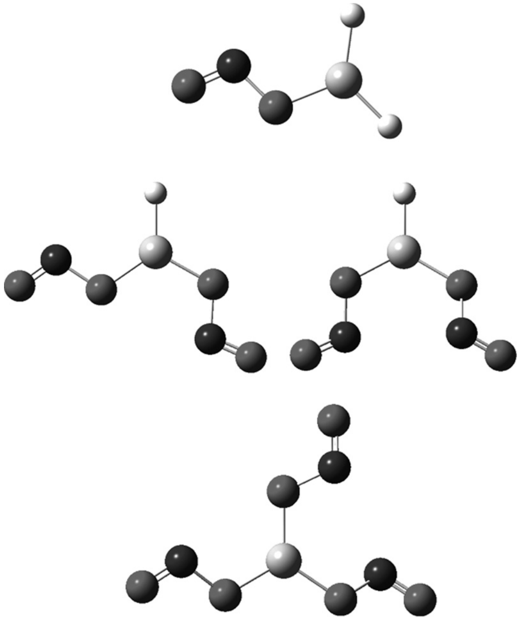

Figure 1. Optimized structures of nitrosooxyalanes. Top: nitrosooxyalane. Middle: cis-dinitrosooxyalane (left) and trans-dinitrosooxyalane (right). Bottom: trinitrosooxyalane. Legend: blue = oxygen, red = nitrogen, pink = aluminum, grey = hydrogen.

Table 1 lists representative bonding parameters for the four molecules. The bonding parameters are very similar from substance to substance but do show some trends. All bond distances to the central aluminum atom decrease with increasing ONO content. The two N–O bond distances within a molecule vary considerably, as befitting two different N–O bonds: a single bond between the nitrogen atom and the oxygen atom bonded to the aluminum atom and a double bond between the nitrogen atom and the terminal oxygen atom in each nitrosooxy group. The bond angles of the groups around the aluminum atom show that the three bonds are distributed as a distorted equilateral triangle, with bond angles between the groups ranging from 113 to 124°. One of the biggest differences between the cis and

Table 1

Bonding parameters for the optimized geometries of various nitrosooxyalane molecules (r in Ångstroms, angle in degrees)

	AlH_2NO_2	cis-$AlH(NO_2)_2$	trans-$AlH(NO_2)_2$	$Al(NO_2)_3$
r (Al-H)	1.577	1.566	1.565	—
r (Al-N)	1.772	1.751, 1.761	1.755	1.747
r (N-O)	1.196, 1.429	1.189, 1.454	1.190, 1.450	1.187, 1.463
α (H-Al-N)	113.3, 119.5	118.9, 124.9	119.4	—
α (Al-O-N)	113.6	112.1, 116.0	116.2	113.3
α (N-Al-N)	—	116.2	121.3	116.1, 120.4, 123.4
α (O-N-O)	111.3	110.8, 111.2	111.0	110.7, 111.0
δ (H-Al-N-O)	0.0	0.0	21.5	—
δ (N-Al-N-O)	—	0.0	21.5	13.4
δ (Al-O-N-O)	0.0	0.0	7.3	5.9

trans isomers of dinitrosooxyalane is the N−Al−N bond angle, which is 116° for the cis isomer and 121° for the trans isomer. This is likely due to repulsion between the lone pairs of the oxygen atoms. The O−N−O bond angles show little variation from one substance to the next. Finally, as mentioned above, nitrosooxyalane and cis-dinitrosooxyalane are essentially planar molecules, whereas the nitrosooxy groups in trans-dinitrosooxyalane and trinitrosoosyalane are twisted out of the plane of the core of the molecules.

As part of the molecular structure determination, vibrational frequencies were also calculated for all of the molecules. Persons interested in this information can contact the authors.

Energies of Reaction

Table 2 lists the enthalpies of formation of the various nitrosooxyalane molecules, as determined by the chemical reactions described above. We note that all enthalpies of formation are negative, indicating that these molecules are relatively stable with respect to their constituent elements in their standard states. Despite the differences in bonding parameters described above, the enthalpies of formation of the cis and trans isomers

Table 2

Calculated enthalpies of reaction for nitrosooxyalane molecules (kJ mol^{-1} unless otherwise specified)

	AlH_2NO_2	cis-$AlH(NO_2)_2$	trans-$AlH(NO_2)_2$	$Al(NO_2)_3$
ΔH_f	−64.2	−255.6	−255.3	−435.1
ΔH_{comb}	−1059.5	—	—	—
ΔH_{decomp}	—	−580.4	−580.1	−253.5
ΔH_{comb} (kJ g^{-1})	−14.13	—	—	—
ΔH_{decomp} (kJ g^{-1})	—	−4.85	−4.85	−1.54

of dinitrosooxyalane differ by only $0.3\,\mathrm{kJ\,mol^{-1}}$, an almost trivial difference that is well within the confidence limits of the G2 method [17]. The fact that alane, AlH_3, has a calculated enthalpy of formation of $+135.7\,\mathrm{kJ\,mol^{-1}}$ [19] illustrates aluminum's relative propensity for bonding to oxygen over hydrogen: as the number of nitrosooxy groups attached to the aluminum increases, the calculated enthalpy of formation gets more negative, by about 180–190 $\mathrm{kJ\,mol^{-1}}$ per –ONO group.

Table 2 also lists the enthalpy of combustion (for nitrosooxyalane) and the enthalpies of decomposition (for dinitrosooxyalane and trinitrosooxyalane) for these compounds, both in units of kJ per mole and kJ per gram. Paralleling the increasing negativity of the ΔH_f values as the –ONO content increases, the energy of reaction decreases precipitously, perhaps more so than any other series of nitro group-containing series we have studied previously. Indeed, in the case of $Al(NO_2)_3$, on a gram basis only a minimal amount of net energy is being released upon decomposition. Again, this is likely due to the aluminum atom's relative desire to bond with oxygen atoms. In these nitroxoosyalane molecules, the aluminum atom is already bonded to one or more oxygen atoms. Rearranging to Al_2O_3 does not seem to increase the amount of interaction of Al atoms with O atoms; in fact, in the cases of $AlH(NO_2)_2$ and $Al(NO_2)_3$, the relative ratio of Al to O atoms goes *down* upon formation of aluminum oxide as a product. Our conclusion is that though these may be interesting compounds for other reasons, they likely do not have much potential as high-energy materials.

Finally, to explore the possibility of N-bonded nitroalanes, we performed an HF/6-31G(d,p) calculation on $AlH_2(NO_2)$ with a structure constrained with a Al—N bond. The calculation converged on a structure that had good symmetry, but vibrational analysis indicated an imaginary vibrational frequency at $137i\,\mathrm{cm^{-1}}$, whose description was a wagging of the NO_2 group to bring the O atoms more proximal to the central aluminum atom (and thereby forming the nitrosooxy derivative). This indicates that this structure is not a minimum-energy geometry but a transition state. This also suggests that N-bonded nitroalane derivatives are unlikely to be isolated as stable compounds.

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