the absence of NO, when  $H_2O_2$  was used as a precursor for OH, which clearly indicates that NO is not required to form  $\alpha$ -dicarbonyl compounds from 2. Thus, the reaction step to form  $\alpha$ -dicarbonyl compounds is proposed to be

$$\mathbf{R} \rightarrow \text{RCOCOR'} + \text{OD} \quad (\mathbf{R}, \mathbf{R'} = \text{H or CH}_3) \quad (25)$$

Additional evidence was obtained from the effect of NO on the product ratio. If reaction 24 takes place, the branching factors for the two possible reactions of 2 (reactions 23 and 24) should depend upon the initial concentration of NO. As is shown in Figure 7, however, the product ratio  $\Delta$ [formic acid]/ $\Delta$ [ $\alpha$ -dicarbonyl compound] shows no dependence on the initial concentration of NO. This fact is consistent with the suggestion of Slagle et al.<sup>27b</sup> that the adduct formed in the  $C_2H_3 + O_2$  reaction has an extremely short lifetime and that it decomposes readily by the channel leading to the products. We can conclude that the lifetime of 2 is also very short.

Recently, Schmidt et al.<sup>20</sup> observed the regeneration of OH from  $OH + C_2H_2$  reaction directly by means of the laser fluorescence technique. Thus, reaction 25 was strongly supported. At the same time they observed the production of  $CH_2CHO$  radicals. Therefore,  $CH_2CHO + O_2 \rightarrow HCOCHO + OH$  may be, as they proposed, an additional pathway to form glyoxal.

From the yields of products listed in Table II the branching fractions for 2 to react by routes 23 and 25 are estimated to be  $0.4 \pm 0.1$  and  $0.7 \pm 0.3$ , respectively, for acetylene. Other reaction pathways such as reactions 1 and 2 are negligible under atmospheric conditions. For propyne the branching fractions for reactions 23 and 25 are  $0.12 \pm 0.02$  and  $0.53 \pm 0.03$ , respectively. In this case a possibility that some additional reaction channel is involved cannot be wholly excluded at present. For 2-butyne the branching fractions for reactions 23 and 25 are  $0.12 \pm 0.01$ and  $0.87 \pm 0.07$ , respectively. Other reaction pathways seem insignificant in this case, too.

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Registry No. HC=CH, 74-86-2; CH<sub>3</sub>C=CH, 74-99-7; CH<sub>3</sub>C=CC-H<sub>3</sub>, 503-17-3; OH, 3352-57-6.

# Thermal Decomposition of Energetic Materials. 8. Evidence of an Oscillating Process during the High-Rate Thermolysis of Hydroxylammonium Nitrate, and Comments on the Interionic Interactions

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Relatively dry, solid hydroxylammonium nitrate (HAN), (NH<sub>3</sub>OH)NO<sub>3</sub>, was examined by IR spectroscopy from 170 K to well above its decomposition point. The modes in the 2600-2950-cm<sup>-1</sup> range are assigned to  $-NH_3^+$  combination tones, rather than to  $\nu(OH)$  as was recently proposed for aqueous HAN solutions. Frequency-to-distance correlations for solid HAN cast doubt on the viability of using  $\nu$ (NH/OH) fundamentals to determine accurate interionic distances in HAN. Several of the thermolysis products of HAN (HNO<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>) were quantified in real time by rapid-scan FTIR and were found to oscillate when solid HAN and aqueous HAN solutions were pyrolyzed at a high rate (130 K s<sup>-1</sup>) with pressures  $\geq$  100 psi of Ar. The onset of the oscillation is delayed by increasing the initial H<sub>2</sub>O content. The period of oscillation at constant pressure increases with the heating rate. Some comments on the reactions that may lead to the decomposition products of HAN are made based on these findings.

# Introduction

Extremely concentrated aqueous hydroxylammonium nitrate (HAN), (NH<sub>3</sub>OH)NO<sub>3</sub>, and aliphatic ammonium nitrates are combustible at elevated temperature and pressure making them interesting as chemical propellants.<sup>1</sup> Many of the fundamental structural and decomposition questions about HAN and HAN solutions remain to be answered. In this paper the vibrational mode assignments and their relationship to interionic interactions in HAN have been reexamined in an attempt to clarify several contradictory aspects. Rapid-scan FTIR spectroscopy (RSFTIR) characterizes real-time, high-heating rate thermolysis of HAN and HAN solutions and has provided an intriguing view into the dynamics of the process. The most interesting observation is the temporal oscillations that take place among the product concentrations at elevated pressure.

#### **Experimental Section**

Samples of solid and aqueous HAN and HAN-d4 were generously supplied by R. A. Fifer and N. Klein, BRL, Aberdeen, MD. Multiple freeze-thaw cycles under vacuum were used in an effort to obtain H<sub>2</sub>O-free solid HAN. The percent deuteration

of HAN- $d_4$  was enhanced by the addition of D<sub>2</sub>O before the freeze-thaw cycles.

The calibrated pyrolysis cell, spectral methods, and data reduction for high-rate thermal decomposition at specific pressures and heating rates using RSFTIR are fully described elsewhere.<sup>2</sup> Ramp heating occurs until the final filament temperature  $(T_f)$ is reached.  $T_{\rm f}$  is then maintained for the remainder of the 10-s data collection. The Nicolet 60SX FTIR spectrometer with an MCT detector was set for 10 scans s<sup>-1</sup>, 2 scans per file, 4-cm<sup>-1</sup> resolution. Approximately 1 mg of sample was placed on the nichrome filament by a micropipet as necessary for the solutions. This procedure was carried out under an Ar blanket. The cell was then closed and the Ar pressure adjusted to the desired level. Thermolysis was conducted at 2, 15, 50, 100, 200, 500, and 1000 psi (1 psi = 6.9 KPa). The heating rates were  $130 \pm 10$  K s<sup>-1</sup> and the final filament temperature ranged from 600 K at 2 psi to 500 K at 1000 psi. These experiments were repeated a number of times to perfect the technique and because an occasional erratic result was obtained. While the details of the product concentrations vary slightly from run to run, the essential features are reproducible and accurate in all cases. Erratic behavior seemed to occur when the sample droplet size was allowed to vary too

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<sup>(1)</sup> For a review see Klein, N. BRL-TR-2641, Ballistics Research Laboratory, Aberdeen Proving Ground, MD, Feb 1985.

<sup>(2)</sup> Oyumi, Y.; Brill, T. B. Combust. Flame 1985, 62, 213.

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Figure 1. The microenvironment of  $NO_3^-$  ions about  $ND_3OD^+$  in crystalline HAN- $d_4$ . The hydrogen bond contacts are shown as dashed lines.

much. The absorbance values were converted to concentrationtime profiles (percent by volume) by the use of the absolute intensities of characteristic modes.<sup>2</sup>  $H_2O(g)$  was not quantified because the vibration-rotation fine structure complicated the integration process. IR-inactive species, such as N<sub>2</sub> and O<sub>2</sub>, were not quantified. HAN solutions are known to be unstable in the presence of certain metal ions.<sup>3,4</sup> Therefore, we compared the thermolysis results for HAN on a nichrome and a gold-plated nichrome filament using the same experimental conditions. No differences were detected.

The spectrum of neat HAN between 170 and 470 K was examined by using slow heating and cooling (5 K min<sup>-1</sup>) as appropriate. The sample resided in a semiconfined state between two NaCl plates,<sup>5</sup> and the temperature was measured by embedding a type J thermocouple between the plates and recording the temperature with a Fluke digital thermometer. Thirty-two scans at 1-cm<sup>-1</sup> resolution were recorded.

## Solid HAN and HAN- $d_4$

The details of recent crystal structure determinations of HAN and HAN- $d_4$  will appear separately.<sup>6</sup> HAN and HAN- $d_4$  are isostructural ( $P2_1/c$ , Z = 4) and possess remarkably similar distances and angles. Figure 1 shows the NO<sub>3</sub><sup>-</sup> environment surrounding a single ND<sub>3</sub>OD<sup>+</sup> ion. All of the hydrogen atoms engage in hydrogen bonding with one of the N-D bonds being bifurcated. The O(2)...O(4) distance is 2.800 (1) Å while the shortest interionic N···O distances lie in the range of 2.834-2.983 (1) Å. These distances would categorize HAN as a moderately strongly hydrogen-bonded solid. There is no H<sub>2</sub>O of crystallization in the lattice. Since the ions of HAN lie at  $C_1$  sites of the unit cell, none of the vibrational modes remains fully degenerate and all have "a" symmetry.

Many of the IR-active absorptions of HAN and HAN- $d_4$  at room temperature have been assigned previously in the solid and solution state.<sup>7-10</sup> Table I lists the frequencies observed in this work for solid HAN and HAN- $d_4$ . In addition to the fundamentals, a number of overtone/combination bands appear which have become enhanced by the N-H and O-H vibrational anharmonicity introduced by hydrogen bonding. The intensity of

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1473 m 1147 m 1455 m 1428 m, sh

(NH<sub>3</sub>OH)NO<sub>3</sub>

3140 sh, m

3043 vs, b

2991 vs, b

2920 sh, s

(1182 + 1554)

(1182 + 1535)

(1149 + 1535)

(1182 + 1473)

(1182 + 1455)

2880 s

2750 m

2711 m

2685 m

2653 m

2626 m

2386 w

1755 m

1554 m

1535 w

2(1182)

1846 w, b

 $\nu_{3}(NO_{3}^{-})$  $NH_{3}/D_{3}^{+}$  rock 1371 vs 1353 vs 1182 s 856 m 1149 s 797 m OH/D bend 1075 w 1020 w  $\nu_1(NO_3^-)$ 987 s 981 m v(N-O)  $\nu_{2}(NO_{3}^{-})$ 818 s 834 m

<sup>a</sup> vs = very strong, s = strong, m = medium, w = weak, b = broad, sh = shoulder.



Figure 2. (a) The mid-IR spectrum of solid, partially dry HAN at 297 K. The shoulder at 3140 cm<sup>-1</sup> is  $H_2O$  dependent and appears not to be a HAN fundamental. (b) Melted HAN at 350 K.

the shoulder at 3140 cm<sup>-1</sup> in solid HAN (Figure 2a) depends on the amount of adsorbed  $H_2O$  present in the sample and is, therefore, unlikely to be a HAN mode. We concur with most of the previous assignments on hydroxylammonium salts<sup>7-14</sup> and have added several further assignments to weak overtone and combination bands in HAN. Recently, it was suggested that the absorptions in the 2620-2750-cm<sup>-1</sup> range of aqueous HAN are produced by  $\nu(OH)^{9,11}$  of a very short  $NH_3OH^{\ddagger}...ONO_2^{-1}$  contact ion pair.9 The O...O distance (2.61 Å) that was subsequently

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tentative assignments

 $\nu_{as}(\rm NH/\rm D) + \nu(\rm OH/\rm D)$ 

 $NH_3/D_3^+ + OH/D$  bending

combination bands

 $\delta_{as}(NH_3/D_3^+) + lattice$ 

 $(\nu_1 + \nu_2)(NO_3)$ 

 $\delta_{as}(NH_3/D_3^+)$ 

 $\delta_{as}(NH_3/D_3)^{+}$ 

H<sub>2</sub>O

 $2\delta_{as}(ND_3^+)$ 

 $\nu_{\rm s}(\rm NH/D)$ 

TABLE I: Mid-IR Frequencies (cm<sup>-1</sup>) for Solid HAN and HAN-d<sub>4</sub> at 297 K<sup>a</sup>

(ND<sub>3</sub>OD)NO<sub>3</sub>

2422 w

2315 s, b

2258 s, b

2165 w, b

(856 + 1258)

(797 + 1258)

(856 + 1144)

2113 w

2023 w

1969 w

1559 w, b

1785 w

1258 w

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calculated from this frequency<sup>9</sup> is 0.19 Å shorter than exists in the crystalline HAN,<sup>6</sup> a fact that, if true, would be surprising. The resolution of these modes in the spectrum of the solid phase (Figure 2a) and in other hydroxylammonium salts<sup>7,12,14</sup> and alkylammonium salts<sup>15</sup> lends credence to their assignment to  $-NH_3^+$ combination bands rather than to an OH fundamental. These modes merge into an unresolved broad absorption in molten HAN at 350 K (Figure 2b) and by dissolution of HAN in  $H_2O$ .

The correlation between the O…O distance and  $\nu(OH)$ (2950-3100 cm<sup>-1</sup>) in crystalline HAN, as has been discussed by Novak for other hydrogen-bonded species,<sup>16</sup> is not satisfying. The O(2)---O(4) distance in HAN by X-ray diffraction is 2.800 (1) Å which should place  $\nu(OH)$  in the vicinity of 3300 cm<sup>-1</sup>. No absorptions in dry, solid HAN assignable to  $\nu(OH)$  occur above 3100 cm<sup>-1</sup>. It should be noted, however, that Novak found substantial deviations from his average correlation line thereby making the frequency-to-distance connection risky for predictions about individual compounds. A possible explanation for why the distance-to-frequency correlation is so poor in HAN is the fact that the  $-NH_3^+$  deformation modes in the 1420–1560-cm<sup>-1</sup> range have approximately half the frequency of the NH and OH stretching modes. All of these modes have the same symmetry in the solid phase. Consequently, Fermi resonance can occur causing splittings and shifts in the fundamentals that do not originate from interionic bonding differences. These problems cast doubt on the viability of calculating reliable, absolute interionic distances from the IR frequencies of HAN. Confidence about the accuracy of these distances could be raised only by independent confirmation using other experimental methods.

Solid HAN which was relatively free of H<sub>2</sub>O was cooled slowly to 170 K while its IR spectrum was recorded. There are normal frequency shifts and improved resolution at low temperature but no clear evidence of solid-solid phase transitions. Solid HAN was then heated through its melting point. All of the bands broaden upon melting but the NH and OH modes are, not surprisingly, the ones most profoundly affected owing to the fluctuations in the interionic distances brought on by the greater degree of ion mobility in the melt. The NH/OH stretching mode region, while broadened, is only slightly shifted toward higher frequency. Therefore, the hydrogen bonding in molten HAN is somewhat less, although not markedly so, than crystalline HAN.  $\nu_3(NO_3^{-1})$ broadens, splits, and diminishes in frequency by about 20 cm<sup>-1</sup> upon melting. As the temperature of the melt increases, gradual loss in the intensity of the NH<sub>3</sub>OH<sup>+</sup> modes occurs beginning above 420 K. This event accelerates as T further increases. The modes remaining at 470 K result from a small residue of NH4NO3 which has been identified before as a decomposition product of HAN.<sup>17</sup>

#### **High-Rate Thermolysis**

Of much greater practical interest is the rapid decomposition of HAN at high heating rates. The development of a mass balance equation was not the purpose of the present work because homonuclear diatomics and  $H_2O(g)$ , which originates both from desorption and decomposition, were not quantified. All of the other detected gas products were quantified. The rapid thermolysis of solid HAN at pressures below about 100 psi of Ar proved to be uninspiring. As shown in Figure 3 for 15 psi of Ar, the predominant product is HNO<sub>3</sub> followed by N<sub>2</sub>O and NO<sub>2</sub>. At this pressure the concentrations of these species remain relatively constant with time. If the pressure increases in steps to 50 psi, then the time dependence of the concentrations of HNO<sub>3</sub> and N<sub>2</sub>O has successively greater negative and positive slopes, respectively. They are approximately equal in concentration after 10 s when P = 50 psi.

The intriguing results were obtained by rapidly pyrolyzing HAN  $(dT/dt = 130 \text{ K s}^{-1})$  at pressures above 100 psi. Figure 4 showing the results for solid, damp HAN at 500 psi is representative of



Figure 3. The thermolysis products of solid HAN in 15 psi of Ar. The heating rate was 35 K s<sup>-1</sup> and  $T_f$  was 560 K. H<sub>2</sub>O and any IR-inactive species are not quantified.



Figure 4. The temporal oscillations of the product concentrations when 1 mg of solid HAN is thermolyzed at 130 K s<sup>-1</sup> and 500 psi of Ar.

the behavior. The concentrations of the products vigorously oscillate during the first few seconds of thermolysis before dampening to a more benign later stage. These temporal oscillations in the concentration somewhat resemble the behavior of less hostile, but genuinely oscillating, reactions.<sup>18</sup> For example, the gas evolution from a concentrated aqueous solution of  $NH_4Cl$  and  $HNO_2$  is observed to oscillate.<sup>19</sup> Unfortunately, the conditions of HAN decomposition make it difficult to establish the source of the oscillatory process. It is not yet known whether the oscillations are chemical or physicochemical in origin. However, no oscillations of this type have been observed in any previous thermolysis studies conducted by this method<sup>2,20,21,24-27</sup> which rules out their origin from inhomogeneities arising from convection of incomplete mixing within the cell. Beyond this, several observations in the present work at high heating rates are helpful for establishing a few of the operative factors.

First, according to the IR spectrum there is an initial burst of  $H_2O(g)$ , (not quantified) which is then joined by  $HNO_3(g)$  and  $NO_2(g)$  followed, usually, by  $N_2O(g)$ . The order of appearance

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**Figure 5.** The relationship of the initial  $[HNO_3] = [N_2O]$  crossover (see Figure 4) to the H<sub>2</sub>O content of the HAN sample  $(dT/dt = 130 \text{ K s}^{-1}, T_f = 510 \text{ K}, P = 500 \text{ psi of Ar})$ . Damp solid HAN was estimated to be 17.5 M.

of  $N_2O$  and  $NO_2$  was reversed in several instances, and we believe that the actual and apparent order of formation can be switched by small differences in the time interval between the onset of heating and the recording of the first interferogram containing gas product information. Once reaching the 20-30% range [NO<sub>2</sub>] remains relatively steady, while [N2O] and [HNO3] fluctuate and cross one another several times. The initial crossover of HNO<sub>3</sub> and  $N_2O$  can be delayed by increasing the initial  $H_2O$  content of the sample (Figure 5). On this basis we believe that some of the unusual features of the thermolysis process of HAN may be tied to the effect of  $H_2O$ . Possibly the initial vaporization of some of the adsorbed H<sub>2</sub>O may momentarily cool the sample which, in turn, affects the product distribution by altering the rates of the various competitive decomposition reactions. The oscillations are difficult to create in less than 12 M HAN solutions. Changing the heating rate  $T_{\rm f}$  at constant pressure also affects the frequency of the oscillations. Higher heating rates and final filament temperatures were observed to compress the oscillations into a shorter time interval.

Second, the detectable gas products are those that occur from HAN decomposition in the absence of a catalyst.<sup>17</sup>

$$45(NH_{3}OH)NO_{3} \rightarrow 26HNO_{3} + 20N_{2}O + 10N_{2} + 2NO_{2} + NH_{4}NO_{3} (1)$$

The concentrations observed in this work are not in the balance of eq 1 and  $N_2$  is, of course, not detected. However, secondary reactions involving the products will alter the product distribution.  $N_2O$  and  $NO_2$  are products well established by previous thermolysis studies on HAN.<sup>12,13,28</sup> The products from (1) would be expected to form by multiple pathways involving radical in-

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The dominant initially observed decomposition product from HAN is HNO<sub>3</sub>(g). The same is true of the other simple amine nitrate salts studied to date by these RSFTIR methods:  $[C(C+H_2NH_3)_4](NO_3)_4$ ,<sup>20</sup>  $[C(NHNH_2)_3]NO_3$ ,<sup>21</sup> and  $NH_4NO_3$ .<sup>20,21</sup> Therefore, an early step of HAN decomposition at high temperature may be rapid proton transfer from  $NH_3OH^+$  to  $NO_3^-$ (2), but, as shown below, this is not the only path by which HAN

$$(NH_3OH)NO_3 \rightarrow NH_2OH + HNO_3$$
 (2)

might produce HNO<sub>3</sub>. The NH<sub>2</sub>OH from (2) would be expected to degrade, perhaps by (3).<sup>22</sup> Any NH<sub>3</sub> produced by (3) should

$$6NH_2OH \rightarrow 2N_2O + 2NH_3 + 4H_2O \tag{3}$$

react with HNO<sub>3</sub> to produce  $NH_4NO_3$  which is a product formed during slow thermolysis of HAN (vide supra). However,  $NH_4NO_3$  will not survive under these rapid thermolysis conditions.<sup>20,21</sup> Two other routes, (4) and (5), to HAN decomposition liberate major

 $2(\mathrm{NH_3OH})\mathrm{NO_3} \rightarrow 2\mathrm{NO_2} + \mathrm{N_2} + 4\mathrm{H_2O} \tag{4}$ 

$$4(\mathrm{NH}_{3}\mathrm{OH})\mathrm{NO}_{3} \rightarrow 3\mathrm{N}_{2}\mathrm{O} + 2\mathrm{H}\mathrm{NO}_{3} + 7\mathrm{H}_{2}\mathrm{O} \qquad (5)$$

products observed in this study. There is reasonable evidence to suggest that  $N_2O$  is produced at a slower rate than are  $NO_2$  and  $HNO_3$  which would imply that reactions 3 and 5 may be slower than reactions 2 and 4.

It is noteworthy that several species believed to be present when HAN is decomposed slowly in solution are either not present or do not survive to appear in the gas phase during rapid decomposition. These species include HONO,<sup>23</sup> NO<sub>2</sub><sup>-,13</sup> and NO<sub>2</sub><sup>+,11-13</sup> NO has been identified among the products of HAN decomposition when time-delayed analysis is employed.<sup>28</sup> Both HONO(g) and NO(g) are readily detected products from other energetic materials.<sup>2,20,21,24-27</sup> The fact that they are not detected from HAN at any pressure (2–1000 psi) or heating rate used implies that both have a concentration <2% of the total products under these conditions.

Just as the present real-time rapid thermolysis experiments produce results that are at some variance with previous slow heating and time-delayed experiments, we anticipate that combustion experiments on liquid HAN droplets will yield findings that update those presented here. Further studies will be forthcoming on characterizing the thermolysis of aliphatic ammonium nitrate fuels at high rates and then, ultimately, the thermolysis of aqueous solutions of HAN mixed with these fuels.

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**Registry No.** (NH<sub>3</sub>OH)NO<sub>3</sub>, 13465-08-2; HNO<sub>3</sub>, 7697-37-2; N<sub>2</sub>O, 10024-97-2; NO<sub>2</sub>, 10102-44-0.