

Thermal Decomposition of Ammonium Nitrate Based Composites

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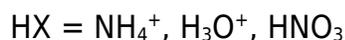
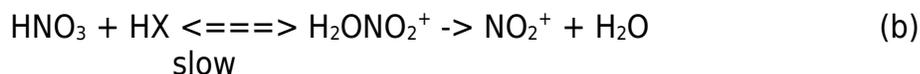
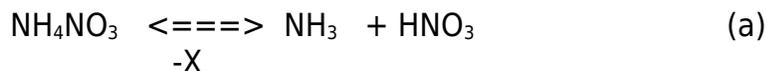
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ABSTRACT

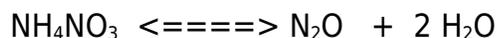
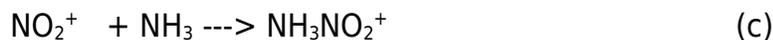
To evaluate the thermal stability of ammonium nitrate-water-in-oil emulsions, the thermal decomposition kinetics and resultant products were examined. As a baseline, the thermal stability of ammonium nitrate with individual components of the emulsion was determined. Only mineral oil had any effect on the decomposition. Generally, ammonium nitrate mixed with hydrocarbons has enhanced thermal stability. However, ammonium nitrate mixed, rather than emulsified, with mineral oil can decompose along a lower energy pathway than pure ammonium nitrate. The extent of decomposition along that pathway is not large before the decomposition process results in emulsification of the ammonium nitrate and, thus, in termination of that pathway. Mineral oil appears to be unique among the hydrocarbons in its ability to destabilize ammonium nitrate. Experiments utilized differential scanning calorimetry in combination with conventional isothermal techniques.

INTRODUCTION

Studies of the thermal decomposition of ammonium nitrate over the range 200°C to 380°C showed two modes of decomposition [1]. At all temperatures the first step is endothermic dissociation to ammonia and nitric acid. Between 200°C and 290°C, the subsequent reaction has been shown to be ionic with formation of NO_2^+ rate-limiting [2].

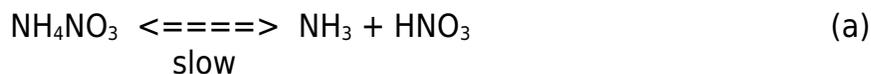


Scheme I

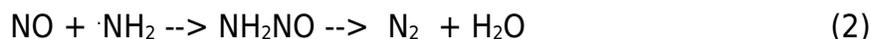


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Above 290° C, a free-radical decomposition mode is dominant; homolysis of nitric acid forming nitrogen dioxide and hydroxyl radical is proposed as the rate-determining step [1].



Over the entire temperature range, nitrous oxide is the major gaseous product, and N₂, the by-product. At 230°C a 25% yield of N₂ was observed, while at 340°C the N₂ content was 6%. At low temperatures reaction **1** was dominant, while at higher temperatures reaction **2** was suggested:



With this understanding of ammonium nitrate thermal decomposition, its decomposition as a component in an emulsion or in ANFO (ammonium nitrate/ 5 wt% fuel oil) was examined.

EXPERIMENTAL SECTION

Reaction vessels were formed from 1.5 to 2mm wide capillary tubing. For thermolysis studies at constant temperature, capillaries were sealed so that the total volume was about 40 uL. For samples heated in the DSC cell compartment, capillaries were sealed so that the volume was ~4uL. The ammonium nitrate-based emulsion (0.5-3 mg), formulation shown in Table I, was loaded by syringe. Mineral oil and other hydrocarbons were ground together with ammonium nitrate to form a solid slurry. The mineral oil used was Sontex 100 (Pennzoil, ~382 g/mol). The hydrocarbon was usually added at 5wt.% to approximate the amount of oil in the emulsion. Capillaries were sealed under air or in vacuum; the reaction rate was independent of atmosphere.

Decomposition kinetics were determined either by heating the sample in a constant temperature bath and monitoring the fraction reacted versus time or by employing the ASTM programmed heating rate method [3]. A Perkin-Elmer DSC 4 with a TADS processing system was used with glass-capillary DSC cells [4]. These glass cells could withstand more pressure (3000 psi, 224 atm.) than the commercial

metal pans, they eliminated possible reactions with the metal, and they permitted relatively easy recovery of sample and decomposition gases. Unless otherwise specified, temperatures were reference to an indium standard, and the scan rate was 20°/min.

The progress of the conventional thermolysis reactions was evaluated by determining loss of nitrate by ion chromatography (Dionex 2000 i/SP). The gas was measured in a gas burette and was characterized by Fourier-transform infrared spectrophotometry or by gas chromatography using either a mass selective (GC/MS) or a thermal conductivity detector.

RESULTS

Thermograms

Thermal scans of the decomposition of pure ammonium nitrate, ammonium nitrate/5 wt.% mineral oil slurry, and the aqueous emulsion are shown in Figure 1. In the pure ammonium nitrate and the 5% mineral oil systems, two endotherms were visible. The first at 128°C was the II to I phase change, and the second at 169°C was the solid-to-liquid transition. In pure ammonium nitrate there was a single exotherm with onset ~304°C, maximum 322°C, and an average heat of reaction of ~320 cal/g. For ammonium nitrate in 5% mineral oil there were two exothermic regions: the first, a peak (292°C) with a maximum lower than that of neat ammonium nitrate; the second, an apparent doublet (356°C and 387°C). The average total heat of reaction was ~730 cal/g, 26% of the total heat being released in the first exotherm.

The thermogram of the aqueous emulsion differed in several features from that of neat ammonium nitrate. The solid phase transitions were absent. Their disappearance was presumed to be due to the fact that ammonium nitrate was no longer in crystalline form; it was dissolved in small water droplets in the emulsion. There were two exotherms: the first at 331°C, and the second ~40° higher at 369° C. The average heat of reaction was ~690cal/g--the first and second exotherms contributing about equally. It was apparent that ammonium nitrate in the emulsion matrix was more stable to thermal decomposition than neat ammonium nitrate.

Kinetics

Employing the ASTM variable heating rate method [2], the energy of activation and frequency factor for thermolysis of ammonium nitrate were found. The values obtained by DSC were comparable to those obtained by isothermal methods (Table II). Since the thermograms of the ammonium nitrate emulsion and 5 wt.% mineral oil slurry exhibited two exotherms, two sets of activation energies were determined; but the physical significance of these exotherms was not immediately obvious.

The reaction of the ammonium nitrate emulsion and the 5 wt.% mineral oil slurry were examined by heating samples of ammonium nitrate with selected hydrocarbon mixtures in constant temperature baths in the range of 230° to 370°C. For the ammonium nitrate emulsion, the ammonium nitrate slurried with 10% dodecane, 10% mesitylene, and 10% tetralin, the first 70% of the isothermal thermolysis in the high temperature range appeared first-order and proceeded at a

rate only slightly slower than that of neat ammonium nitrate. Below 270°C, the decomposition was considerably slower than that of pure ammonium nitrate (Figs. 2, 3).

For the ammonium nitrate slurried with 5% mineral oil, the decomposition at high temperatures was slightly faster than that of neat ammonium nitrate. At temperatures below 250°C, although the overall decomposition was slower than neat ammonium nitrate, initially, it was much faster (Fig. 4). (These regions will be referred to as the early and late rate.) The point at which the reaction slowed depended on the thermolysis temperature. At 270°C, ~40% of the ammonium nitrate in mineral oil had decomposed before the reaction slowed; at 250°C it slowed at ~23% ammonium nitrate decomposition; and at 230°C at 14%. Arrhenius plots for these ammonium nitrate composite systems were constructed. Examples are shown in Figures 5-7. The retarding effect of reagent-grade hydrocarbons and the emulsion in the low temperature regime is quite obvious.

ANFO versus Emulsion

Scans of the decomposition of pure ammonium nitrate, ammonium nitrate/5 wt % mineral oil slurry, and the aqueous emulsion are shown in Figure 1. From the relative position of the first exotherms, it is apparent that the ammonium nitrate/mineral oil slurry is less stable to thermal decomposition than neat ammonium nitrate, while ammonium nitrate in the emulsion matrix is more stable. Since it is known that water retards the decomposition of ammonium nitrate [1], the presence of 15% water in the emulsion was considered a possible source of the stabilization. An anhydrous emulsion was prepared (Table I), and a DSC scan run. There was almost no difference between the thermograms of the aqueous and anhydrous emulsions (Fig. 8). To better understand the relation between the ammonium nitrate/mineral oil thermogram and that of the ammonium nitrate emulsion, a pseudo emulsion, with all the ingredients of the true emulsion added together but not emulsified, was prepared. Its thermogram resembled that of the ammonium nitrate/5 wt% mineral oil mixture more closely than it did the true emulsion (Fig. 9). In particular, it exhibited a low temperature exotherm. We conclude that the physical process of emulsifying caused the loss of the low temperature exotherm.

Concentration of the Hydrocarbon.

When the thermograms of ammonium nitrate in 5%, 16%, 32%, and 90% mineral oil were compared, it was observed that increased oil content raised the temperature of the first exothermic maximum without shifting the position of the second exotherm. Since it was the first exotherm which made the ammonium nitrate /mineral oil slurry initially less thermally stable than neat ammonium nitrate, the effect of increasing the oil content was to make the mixtures less unstable. Only with 90% mineral oil was the first exotherm at higher temperature than it was in neat ammonium nitrate (Table III). The total heat evolved did not differ dramatically, but the percentage of heat contributed by the first exotherm diminished steadily as mineral oil increased.

First-order plots (Fig. 10) derived from isothermal heating showed that as the amount of mineral oil was increased from 5% to 32%, the duration of the early, fast

decomposition was shortened so that only 11% of the nitrate content was lost at 32% mineral oil compared to 40% lost with 5% mineral oil. The slope of the late decomposition and, therefore, its rate constant were unaffected by added oil. The first exotherm, which apparently corresponds to the early, fast decomposition, was shifted to higher temperatures and became a less significant part of the total energy output as the oil content increased. However, added oil did not affect the position of the second exotherm, which we correlate to the late, slow decomposition; it is independent of the amount of hydrocarbon.

Half Scans

For the ammonium nitrate/5% mineral oil mixture and the aqueous emulsion, several scans were terminated after the first exotherm, and the samples were recovered for analysis. Visual examination showed that the oil had darkened and a whitish solid, presumably ammonium nitrate, was present. Ion chromatographic analysis of the half-scanned samples showed that the fraction of nitrate lost was equivalent to the fraction of energy released during the first exotherm (Table III). Ammonium ion was lost in a 1/1 ratio with nitrate loss. A partial scan through the first exotherm followed by cooling to 50°C and subsequent re-heating produced a thermogram with only the high-temperature doublet exotherm. Neither the phase changes in the ammonium nitrate/ mineral oil mixture nor the first exotherm were visible (Fig.11). A similar experiment on the ammonium nitrate emulsion showed only the second exotherm on the re-scan.

Decomposition Gases

The composition of gaseous decomposition products of ammonium nitrate in various hydrocarbons is reported in Tables IV and V. The most notable departure from neat ammonium nitrate decomposition is the production of CO₂ and the marked decrease in nitrous oxide with concomitant increase in N₂. Gases collected from complete and partial DSC scans were analyzed. Samples, which had only undergone the first exothermic reaction, exhibited markedly less carbon dioxide in the decomposition gases. This leads us to speculate that the second exotherm is responsible for the major CO₂ production. Gases collected from isothermal thermolysis showed that ammonium nitrate/mineral oil produced much less CO₂ at 340°C than at 250°C, even though heating times were adjusted so that the same fraction of nitrate was lost. This, coupled with the DSC data, suggests the formation of CO₂ is a secondary process. Ammonium nitrate begins to decompose with some interaction from the hydrocarbon, since the N₂ to N₂O ratio is far from that observed with neat ammonium nitrate. However after a time an intermediate is built up that forms carbon dioxide. At high temperature (340°C), the decomposition is complete before much of this occurs.

Pure Hydrocarbons

The thermograms of ammonium nitrate mixed with dodecane, tetradecane, or mesitylene looked qualitatively the same as that with 5% mineral oil; the ammonium nitrate phase changes and two exothermic regions were observed. However, the

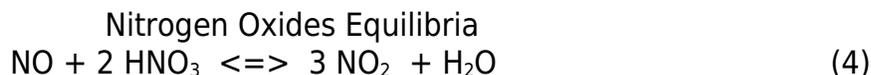
initial exotherm was not at lower temperature than that of neat ammonium nitrate. These hydrocarbons did not destabilize ammonium nitrate in the sense that mineral oil did through its low-temperature decomposition pathway. (Figure 12 compares the thermogram of ammonium nitrate with 10% dodecane to that of the ammonium nitrate/mineral oil slurry.) A scan through the first exotherm, followed by cooling and re-scanning, gave the same result observed with 5% mineral oil--the initial exotherm and the ammonium nitrate phase changes were missing.

Gas chromatography coupled with a mass selective detector (GC/MS) was used to identify the hydrocarbon oxidation products. When toluene was heated with ammonium nitrate at 350° C for 40 seconds benzaldehyde and benzyl alcohol were formed. After heating ammonium nitrate in a 50/50 mix with mesitylene for 10 min at 300°C, 2,4-dimethyl-benzonitrile and 2,4-dimethyl-benzaldehyde were detected in approximately equal yield. A 50/50 mixture of ammonium nitrate and tetralin heated under identical conditions produced naphthalene as the only detected organic product in contrast to its oxidation by NO₂ which also produced naphthalone [5]. The oxidation conditions during ammonium nitrate thermolysis are not rigorous enough to affect this oxidation. Thus, little CO₂ production is seen in the ammonium nitrate/tetralin decompositions. With straight chain hydrocarbons no organic products were detectable by GC/MS; black tar and CO₂ were the decomposition products of the hydrocarbon.

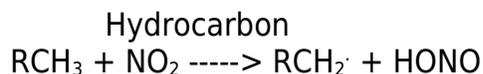
DISCUSSION

Ammonium nitrate slurried with mineral oil, dodecane, tetradecane, and mesitylene exhibited thermograms with at least two exothermic regions. With the exception of ammonium nitrate in mineral oil, the first exotherm appeared at about the same temperature as with neat ammonium nitrate. The first exotherm may occur early in mineral oil because the commercial material is not a straight chain paraffin.

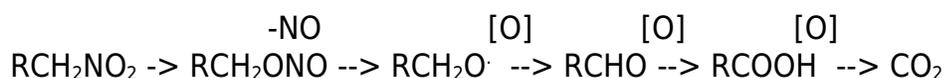
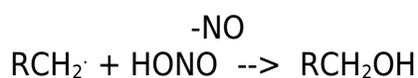
From the fact that N₂O is evolved during the first exotherm and that the onset temperature of the first exotherm is near that of neat ammonium nitrate, it appears that the first exothermic decomposition is triggered by the dissociation of ammonium nitrate into NH₃ and HNO₃. Once nitric acid has been formed, it may follow the decomposition route of neat ammonium nitrate, attack on NH₃ to form N₂O. Or the nitric acid may attack the hydrocarbon.



The interaction of hydrocarbons with nitric acid has been much studied [6]. The active agent has been shown to be nitrogen dioxide and reaction to proceed by H-abstraction. The production of ketones, aldehydes, carbon dioxide, etc. requires further oxidation (Scheme III). It is likely that these stepwise oxidations are responsible for the exotherms above 340°C. The generation of HNO₂ and NO during the oxidation of the hydrocarbon account for the significantly higher N₂ content in the decomposition gas via reactions **1** and **2**. The reaction of ammonia with nitric acid to form N₂O proceeds to a lesser extent than in neat ammonium nitrate.



Scheme III



The reason the first exotherm appears at higher temperatures in the emulsified system than in the ammonium nitrate/mineral oil slurry is not that water is present; the anhydrous emulsion exhibits an exotherm at the same temperature. Ammonium nitrate in the emulsion does not start to dissociate and, thus, decompose until higher temperatures because it is emulsified. Emulsification of the ammonium nitrate is the reason solid-phase changes are not observed in the emulsion thermogram. Apparently, emulsification also inhibits vaporization of ammonium nitrate, and it is this vaporization, forming nitric acid, which initiates the decomposition of ammonium nitrate and hydrocarbon.

For the ammonium nitrate/ hydrocarbon slurries, we speculate that the reason the first exothermic reaction is limited is that the oxidized hydrocarbon emulsifies the ammonium nitrate. Emulsification of ammonium nitrate is the reason a sample heated through the first exotherm and then re-scanned shows neither a low-temperature exotherm nor ammonium nitrate phase changes. The shifting of the first exotherm to higher temperatures with increased mineral oil indicates an earlier emulsification of ammonium nitrate.

The second exotherm involves the major energy release for most of the ammonium nitrate/hydrocarbon systems. It is responsible for the overall slowness of the decomposition of ammonium nitrate in hydrocarbons. As the amount of hydrocarbon in the slurry increases, the importance of this region increases. Less N₂O and more CO₂ are produced during this exotherm, indicating the reaction of the hydrocarbon is important.

CONCLUSION

Generally, ammonium nitrate mixed with hydrocarbons has enhanced thermal

stability. However, ammonium nitrate mixed, rather than emulsified, with mineral oil can decompose along a lower energy pathway than pure ammonium nitrate. The extent of decomposition along that pathway is not large before the decomposition process results in emulsification of the ammonium nitrate and, thus, in termination of that pathway. Mineral oil appears to be unique among hydrocarbons in its ability to initially destabilize ammonium nitrate.

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Table I
Emulsion Formulation
aqueous anhydrous

NH ₄ NO ₃	69.0%	72.3%
NaNO ₃	8.0%	18.6%
Mineral Oil	6.0%	7.1%
PSA emulsifier	2.0%	2.0%
H ₂ O	15.0%	----

Table II
Kinetic Parameters Calculated by DSC & Conventional Techniques

sample	Eact		log A		
	kJ	kcal	sec ⁻¹	conditions*	
AN	95.9	22.9	6.09	230° - 290° C	
	175	41.9	13.50	290° - 370° C	
	122	29.1	8.81	DSC 250° - 450° C	
Emulsion 69% AN	206	49.2	15.96	210° - 370° C	
	179	42.6	14.8	DSC 1st exotherm	
	114	27.5	7.47	DSC 2nd exotherm	
AN + 5% MO	147	35.2	11.38	230° - 370° C early	
	187	44.8	13.67	230° - 320° C late	
	110	26.2	9.11	DSC 1st exotherm	
	180	43.1	12.5	DSC 2nd exotherm	
AN + xs Cyclohexane	192	45.9	14.41	270° - 350° C early	
	197	47.0	14.48	210° - 350° C late	
AN + 10% Dodecane	164	39.2	12.36	250° - 370° C	
AN + 10% Mesitylene	165	39.4	12.56	250° - 370° C	

AN = ammonium nitrate; MO = mineral oil

A temperature range indicates data from isothermal experiments over that range.
The designation DSC and temperature range is a 20°/min scan over that range.

Table III
Characterization of DSC Thermogram

Formulation	Total cal/g	1st exotherm % heat	max.	% nitrate lost
AN neat	320	100	322	100
AN + 5% MO	730	26	292	21
AN + 16% MO	780	15	309	12
AN + 32% MO	630	12	311	11
AN + 90% MO emulsion (aq)	560 692	9 52	330 331	not measured 52

AN = ammonium nitrate; MO = mineral oil; aq = aqueous
Energy values are calories per gram ammonium nitrate.

Table IV: Thermolysis Gas Composition										
	250°C					340°C				
	Time (min)	%CO ₂	%N ₂ O	%N ₂	%CO	Time (sec)	%CO ₂	%N ₂ O	%N ₂	%CO
AN	280	-	75	25		300	-	94	6	
AN +5%	1440	16	20	64	300	7	48	39	6	
Mineral Oil	985	15	26	59	15	4	58	32	4	2
	60	10	30	60						
	20	8	43	49						
	10	5	49	45						
Emulsion (69% AN)	900	20	11	69		300	8	39	53	
	60	11	25	64		15	6	49	45	
	10	16	15	70						
AN + 10% dodecane	900	11	43	43	3	300	1	70	29	
	60	3	66	31		15	-	95	5	
	10	-	86	14						
AN + 10% mesitylene	900	9	60	30	1	300	-	90	10	
	60	1	75	25		15	1	96	4	
	10	1	81	17						
AN + 20% mesitylene	900	17	32	50	1					
	20	3	75	23						
AN + 10% tetralin	900	18	24	58		300	10	54	36	
	60	11	11	82		15	5	65	30	
	10	7	12	81						

AN = ammonium nitrate; MO = mineral oil

Table V: Gases Decomposition Product from DSC

Formulation	% total heat	CO ₂	N ₂ O	N ₂	NO
Ammonium Nitrate	100		0	78	22
Aqueous Emulsion (69% AN)	52 1st	10	35	55	
	48 2nd**	27	10	63	
	100	18	23	59	
Ammonium Nitrate + 5wt% mineral oil	26 1st	11	21	69	
	74 2nd**	18	45	36	
	100	16	39	45	
AN + HNO ₃	100	0	79	21	
AN + 2% mineral oil	100	11	51	38	
AN + 5% tetradecane	100	11	42	39	7
AN + 10% dodecane	100	9	29	52	10
AN + 20% mesitylene	100	20	35	45	
AN/5% MO + HNO ₃	100	20	27	53	
AN + 10% tetralin	100	3	78	19	

*GC with thermal conductivity detector, values to 6%**

For AN/MO calculation based on 26% of sample reacted in first exotherm; for emulsion 52% reaction was assumed. AN = ammonium nitrate; MO = mineral oil

Table VI

T°C	Rate Constants from Conventional Kinetic Techniques					
	neat AN	emulsion AN 69% aq	AN + 5% MO early late		AN + xs cyclohexane early late	
210	7.00E-05	3.00E-07			5.00E-07	
230	1.10E-04	3.70E-06	1.28E-04	1.59E-06		
250	2.86E-04	3.30E-05	5.28E-04	1.04E-05		9.90E-07
270	5.65E-04	1.98E-04	1.70E-03	4.20E-05	1.10E-04	2.64E-05
290	2.22E-03	6.00E-04			6.67E-04	1.44E-04
300	3.88E-03	1.83E-03	6.00E-03	2.50E-04		2.78E-04
310				1.67E-03	6.25E-04	
320	1.00E-02	5.60E-03	2.90E-02	2.00E-03	3.33E-03	1.79E-03
330	1.60E-02			4.00E-03	3.33E-03	
340	3.30E-02	2.80E-02	5.30E-02		1.38E-02	8.00E-03
350				2.75E-02	1.75E-02	
370	2.60E-01	1.20E-01	3.50E-01			

Table VI (cont.)

Isothermal Rate Constants of AN with 10% Organic		
T°C	Mesitylene	Dodecane
250	9.03E-05	8.89E-05
270	5.95E-04	4.20E-04
300	4.50E-03	2.80E-03
340	3.30E-02	2.30E-02
370	1.20E-01	1.10E-01

AN = ammonium nitrate; MO = mineral oil