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THERMAL DECOMPOSITION OF AMMONIUM NITRATE-BASED COMPOSITES *

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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 building-up of ammonia and, thus, in termination of that pathway. Mineral oil appears to be unique among the hydrocarbons in its ability to destabilize ammonium nitrate. The experiments utilized differential scanning calorimetry in combination with conventional isothermal techniques.

INTRODUCTION

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

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

$$HNO_3 + HX \underset{\text{slow}}{\overset{-X}{\rightleftharpoons}} H_2ONO_2^+ \rightarrow NO_2^+ + H_2O$$

$$NO_2^+ + NH_3 \rightarrow NH_3NO_2^+$$

$$NH_3NO_2^+ \rightarrow N_2O + H_3O^+$$

$$NH_4NO_3 \rightleftharpoons N_2O + 2H_2O$$

Scheme I. $HX \equiv NH_4^+, H_3O^+, HNO_3$.

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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 (see Scheme II) [1].

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

$$HNO_3 \xrightarrow{slow} NO_2 + HO^{\bullet}$$

$$HO^{\bullet} + NH_3 \rightarrow {}^{\bullet}NH_2 + H_2O$$

$$NO_2 + {}^{\bullet}NH_2 \rightarrow NH_2NO_2$$

$$NH_2NO_2 \rightarrow N_2O + H_2O$$

Scheme II.

Over the entire temperature range, nitrous oxide is the major gaseous product, and N_2 the by-product. At 230 °C a 25% yield of N_2 was observed, while at 340 °C the N_2 content was 6%. At low temperatures reaction (1) was thought to produce N_2, while at higher temperatures reaction (2) was suggested [1].

$$HNO_2 + NH_3 \rightarrow N_2 + 2H_2O \tag{1}$$

$$NO + {}^{\bullet}NH_2 \rightarrow NH_2NO \rightarrow N_2 + H_2O \tag{2}$$

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

Reaction vessels were formed from 1.5–2 mm wide capillary tubing. For thermolysis studies at constant temperature, capillaries were sealed so that the total volume was about 40 μl. For samples heated in the DSC cell compartment, capillaries were sealed so that the volume was ~ 4 μl. The ammonium nitrate-based emulsion (0.5–3 mg), formulation shown in Table 1, was loaded by syringe. Mineral oil and other hydrocarbons were ground

TABLE 1

Emulsion formulation

	Aqueous	Anhydrous
NH_4NO_3	69.0%	72.3%
$NaNO_3$	8.0%	18.6%
Mineral oil	6.0%	7.1%
PSA emulsifier	2.0%	2.0%
H_2O	15.0%	–

together with ammonium nitrate to form a solid slurry. The mineral oil used was Sontex 100 (Pennzoil, ~ 382 g mol^{-1}). The hydrocarbon was usually added at 5 wt.% 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, eliminated possible reactions with the metal, and permitted relatively easy recovery of sample and decomposition gases. Unless otherwise specified, temperatures were referenced to an indium standard, and the scan rate was 20 °C min^{-1}.

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 Fig. 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^{-1}. 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 and 387 °C). The average total heat of reaction was ~ 730 cal g^{-1}, 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 ~ 690 cal g^{-1}, the first and second exotherms contributing

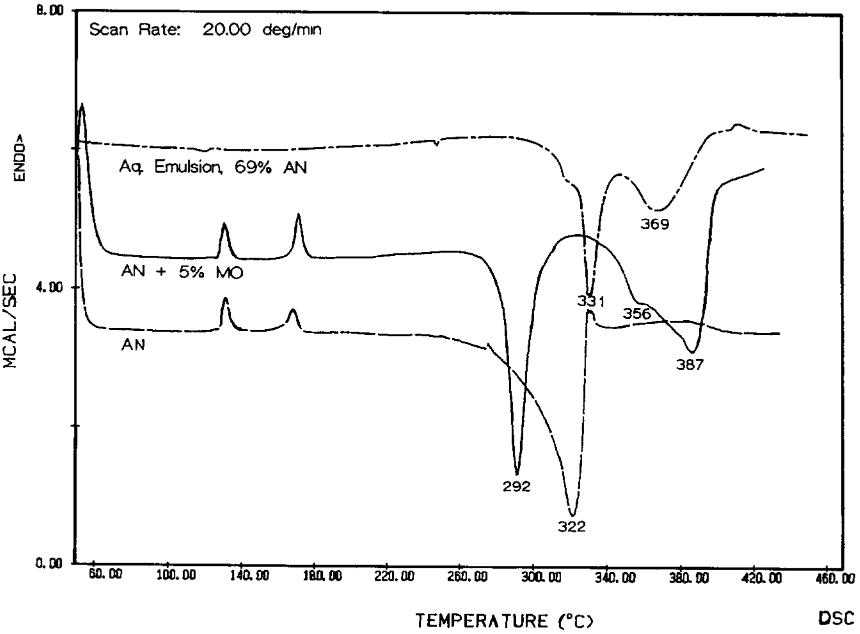

Fig. 1. Thermograms of ammonium nitrate, ammonium nitrate with 5 wt.% mineral oil, and aqueous emulsion, scanned 20 °C $\min^{-1}$.

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 2). Because 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 reactions 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 230–370 °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 and 3).

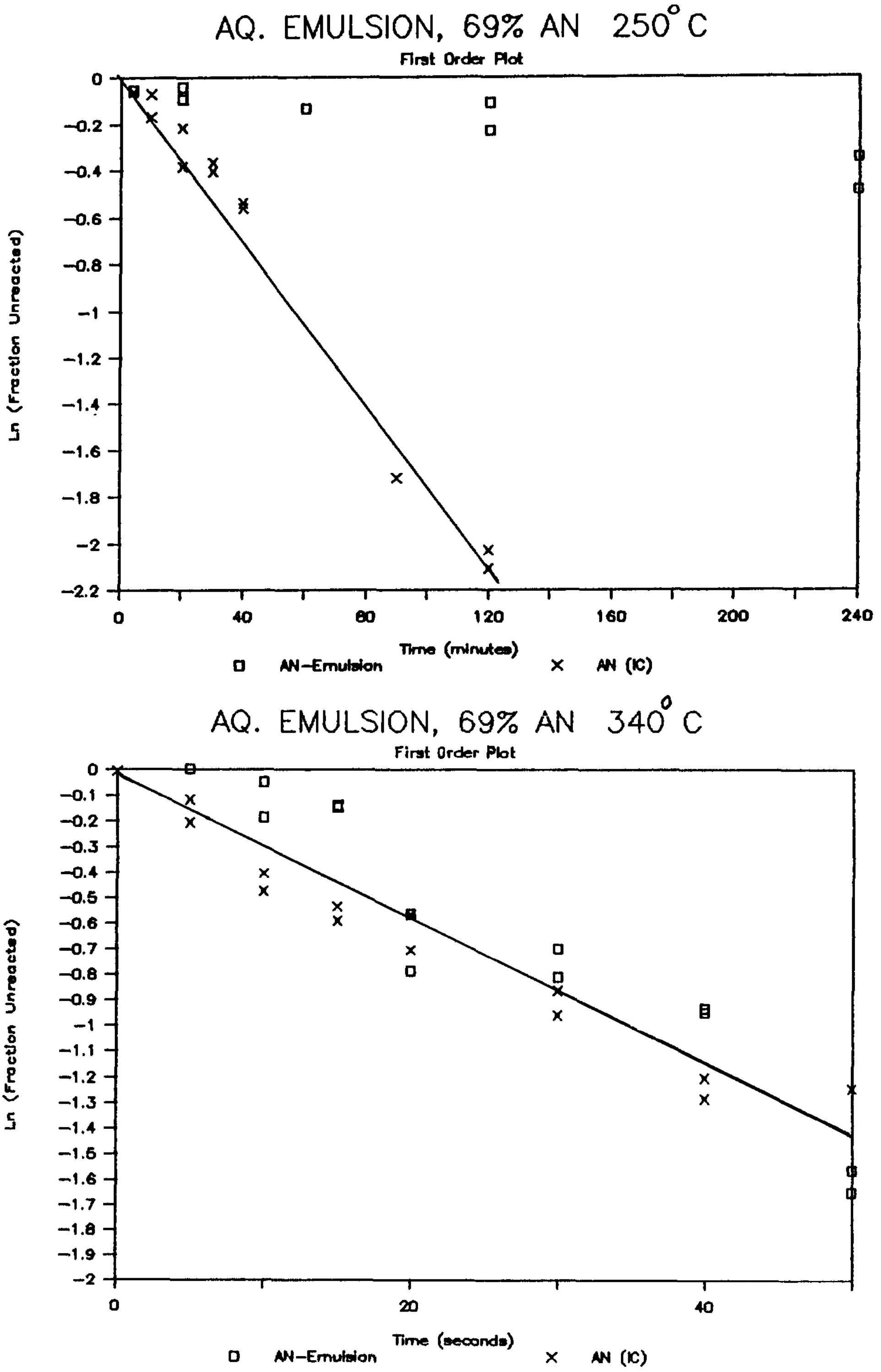

Fig. 2. First-order plots for thermolysis of the aqueous emulsion at 250 and 340 ° C compared with ammonium nitrate decomposition at those temperatures.

TABLE 2

Kinetic parameters calculated by DSC and conventional techniques

Sample [a]	E_{act} (kJ)	E_{act} (kcal)	log A (s^{-1})	Conditions [b]
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 + 10% dodecane	164	39.2	12.36	250–370 °C
AN + 10% mesitylene	165	39.4	12.56	250–370 °C

[a] AN = ammonium nitrate; MO = mineral oil.

[b] A temperature range indicates data from isothermal experiments over that range. The designation DSC and temperature range is a 20 °C min^{-1} scan over that range.

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 Figs. 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 Fig. 1. From the relative position of the first exotherms, it appears 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. As 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

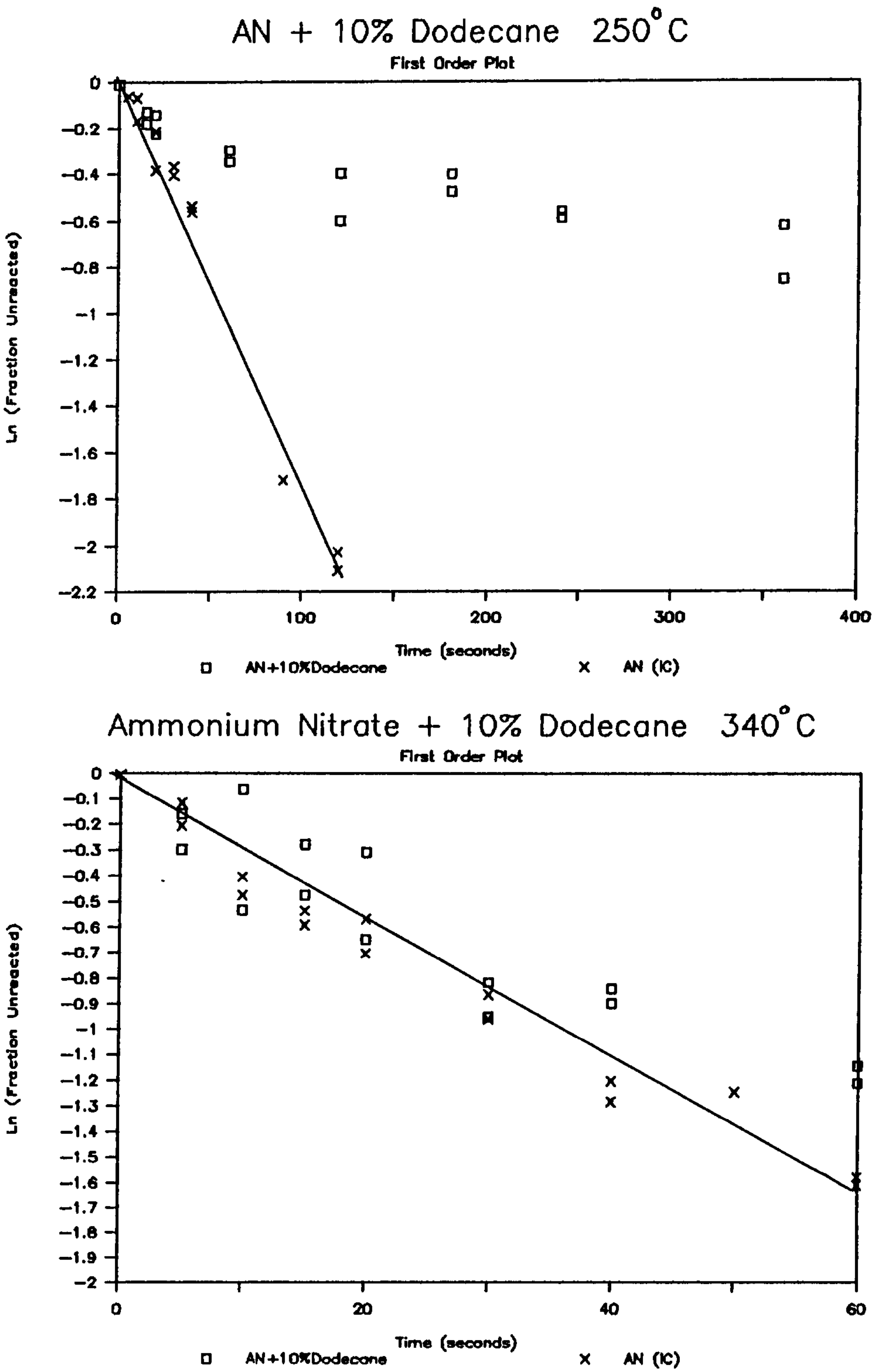

Fig. 3. First-order plots of the thermolysis of a slurry of ammonium nitrate with 10 wt.% *n*-dodecane at 250 and 340 °C compared with ammonium nitrate decomposition at those temperatures.

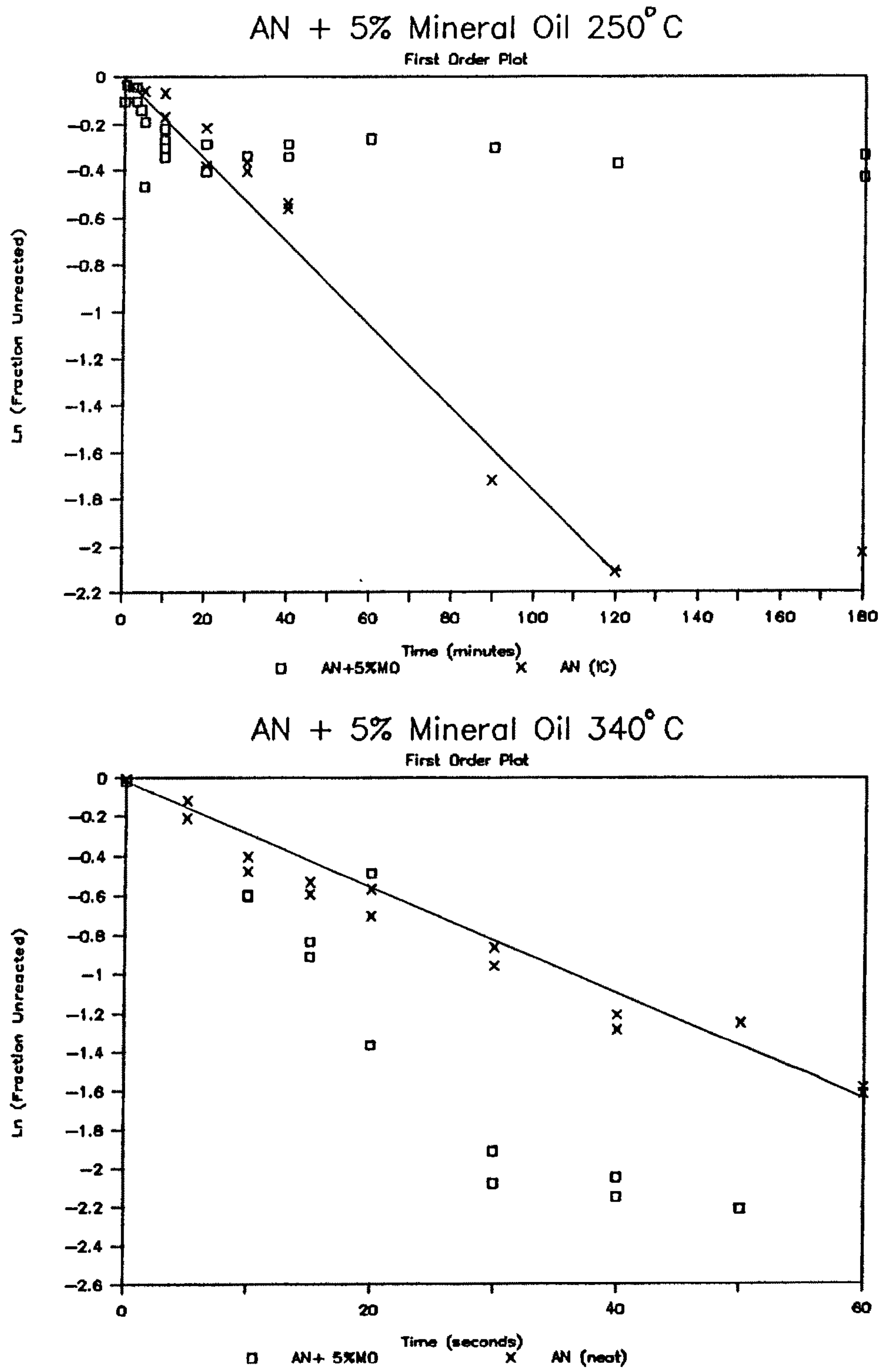

Fig. 4. First-order plots of the thermolysis of a slurry of ammonium nitrate with 5 wt.% mineral oil at 250 and 340 °C compared with ammonium nitrate decomposition at those temperatures.

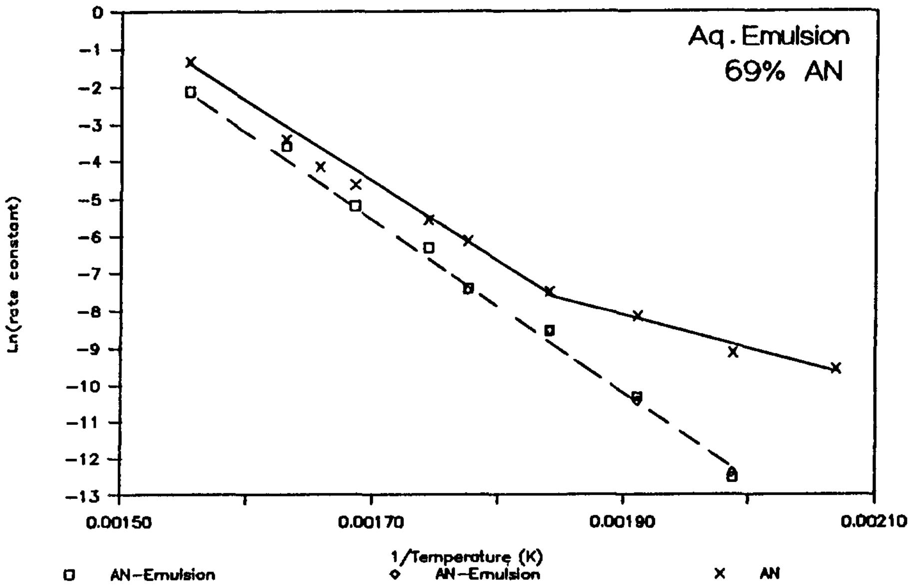

Fig. 5. Arrhenius plot of the thermolysis of the aqueous emulsion (dashed line) and of neat ammonium nitrate (solid line).

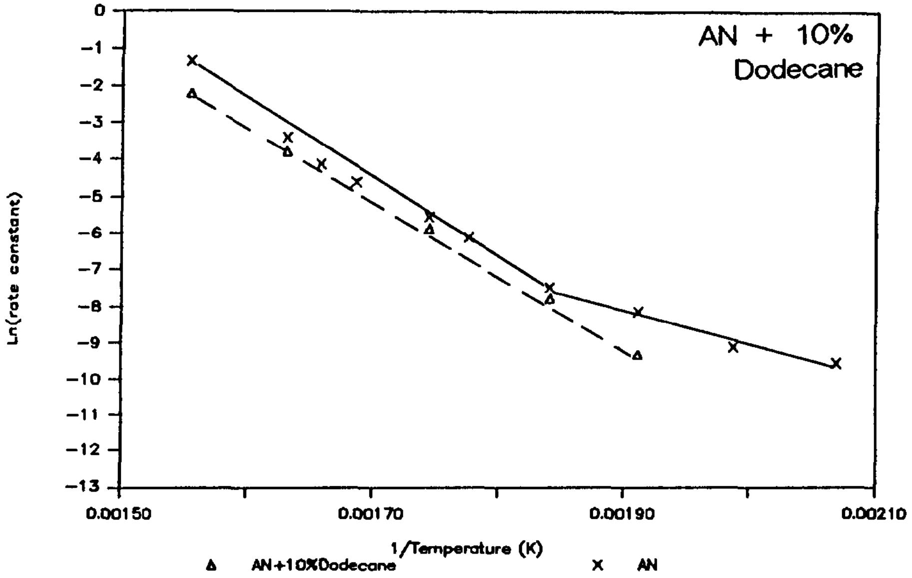

Fig. 6. Arrhenius plot of the thermolysis of a slurry of ammonium nitrate with 10 wt.% *n*-dodecane (dashed line) and of neat ammonium nitrate (solid line).

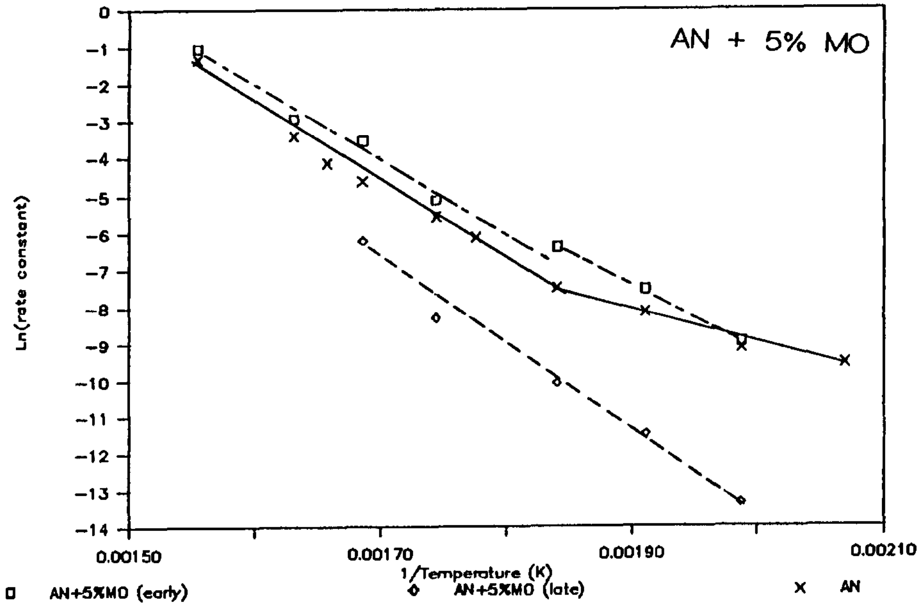

Fig. 7. Arrhenius plot of the thermolysis of a slurry of ammonium nitrate with 5 wt.% mineral oil (dashed lines) and of neat ammonium nitrate (solid line).

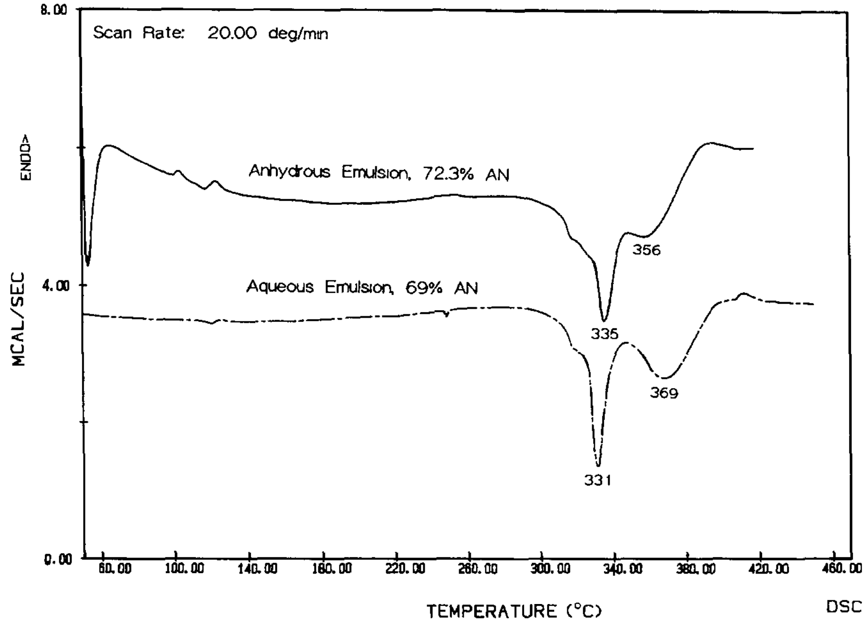

Fig. 8. Thermograms of the aqueous and anhydrous emulsions, scanned 20 °C min^{-1}.

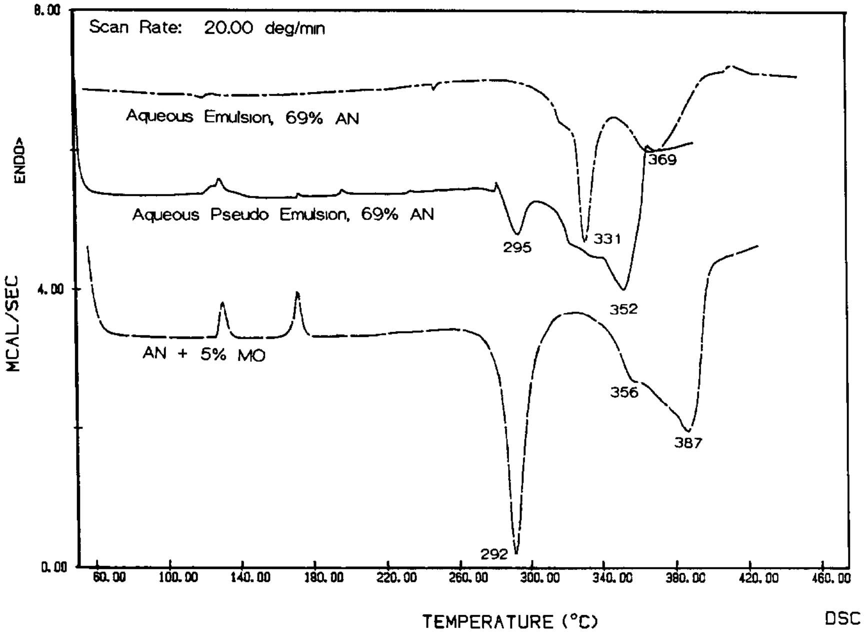

Fig. 9. Thermograms of ammonium nitrate with 5 wt.% mineral oil, an aqueous emulsion, and a pseudo-emulsion, scanned 20 °C min^{-1}.

was prepared (Table 1), 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. Because 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 a higher temperature than it was in neat ammonium nitrate (Table 3). The total heat evolved did not differ dramatically, but the

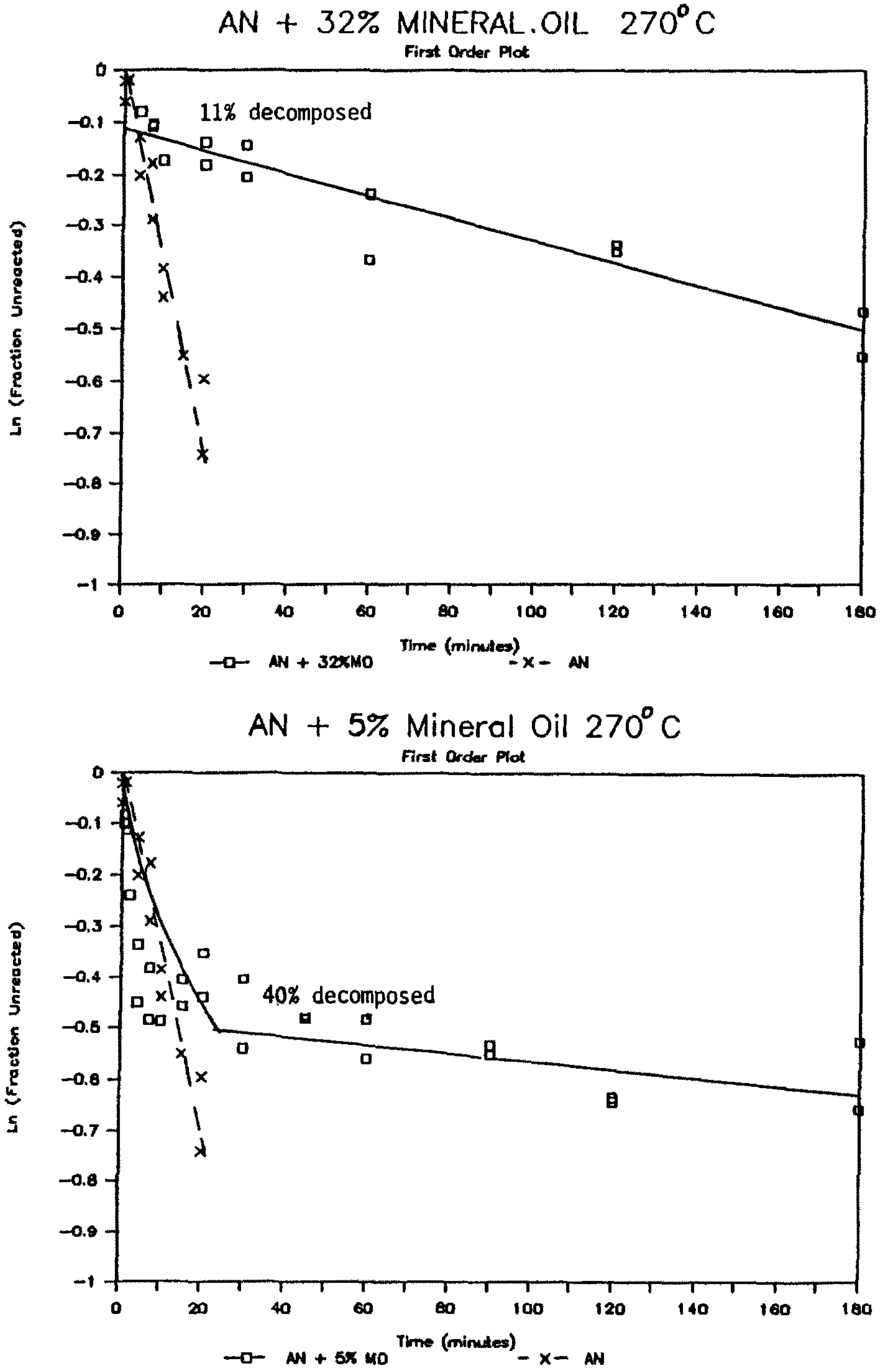

Fig. 10. First-order plots of the thermolysis at 270 ° C of a slurry of ammonium nitrate with 5 wt.% and with 32 wt.% mineral oil. (Ammonium nitrate thermal decomposition indicated by --X--).

TABLE 3

Characterization of DSC thermograms

Formulation [a]	Total (cal g^{-1})	1st exotherm		% nitrate lost
		% heat	max.	
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	560	9	330	not measured
Emulsion (aq)	692	52	331	52

[a] AN = ammonium nitrate; MO = mineral oil; aq = aqueous.

[b] Energy values are in cal (g ammonium nitrate)$^{-1}$.

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. Comparing the DSC and isothermal results, we find that 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 3). 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.

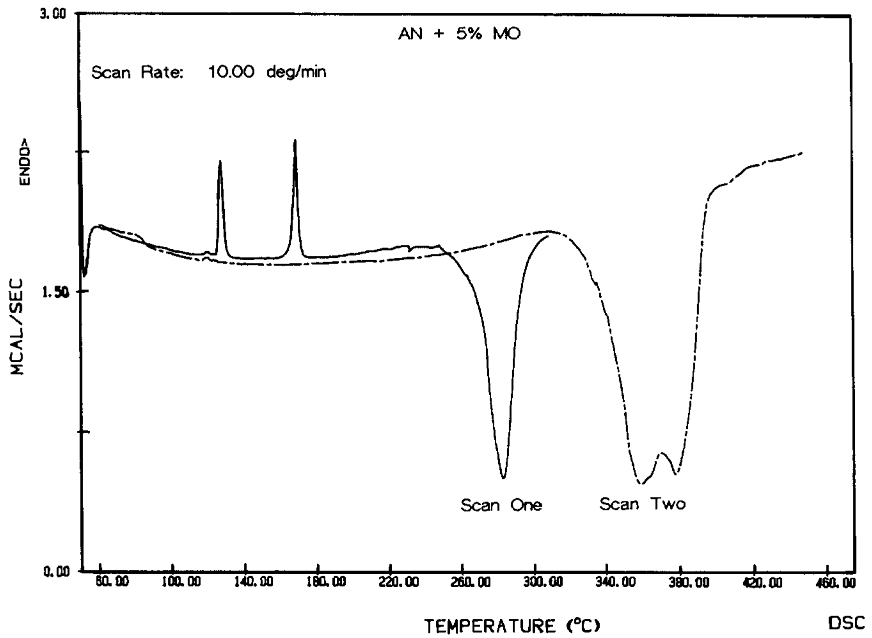

Fig. 11. Thermogram of ammonium nitrate with 5 wt.% mineral oil scanned to 315 °C (Scan One, solid line), cooled, and rescanned (Scan Two, dashed line); scans at 10 °C min^{-1}.

Decomposition gases

The composition of gaseous decomposition products of ammonium nitrate in various hydrocarbons is reported in Table 4. The most notable departures from neat ammonium nitrate decomposition are the production of CO_2 and the marked decrease in nitrous oxide with concomitant increase in N_2. 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 CO_2 production. Gases collected from isothermal thermolysis showed that ammonium nitrate/mineral oil produced much less CO_2 at 340 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 that the formation of CO_2 is a secondary process. Ammonium nitrate begins to decompose with some interaction from the hydrocarbon, as the N_2 to N_2O 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

TABLE 4

Thermolysis gas composition

Formulation [a]	% total heat	Gas Production from DSC Scan (60–460 °C) (%) [b]			
		CO_2	N_2O	N_2	NO
Ammonium nitrate	100	0	78	22	
Aqueous emulsion 69% AN	52 1st	10	35	55	
	48 2nd [c]	27	10	63	
	100	18	23	59	
Ammonium nitrate, 5 wt.% mineral oil	26 1st	11	21	69	
	74 2nd [c]	18	45	36	
	100	16	39	45	
AN + HNO_3	100	0	79	21	
AN + 2% MO	100	11	51	38	
AN + 5% tetradecane	100	10	39	45	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	

[a] AN = ammonium nitrate; MO = mineral oil.

[b] GC with thermal conductivity detector, values to 6%.

[c] For AN/MO calculation based on 26% of sample reacted in first exotherm; for emulsion 52% reaction was assumed.

oil; the ammonium nitrate phase changes and the two exothermic regions were observed. However, the initial exotherm was not at lower temperatures 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 chromatrography 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 s, 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-dimethylbenzonitrile and 2,4-dimethylbenzaldehyde 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 NO_2 which also produced naphthalone [5]. Unfortunately, when ammonium nitrate was heated with straight chain hydrocarbons no

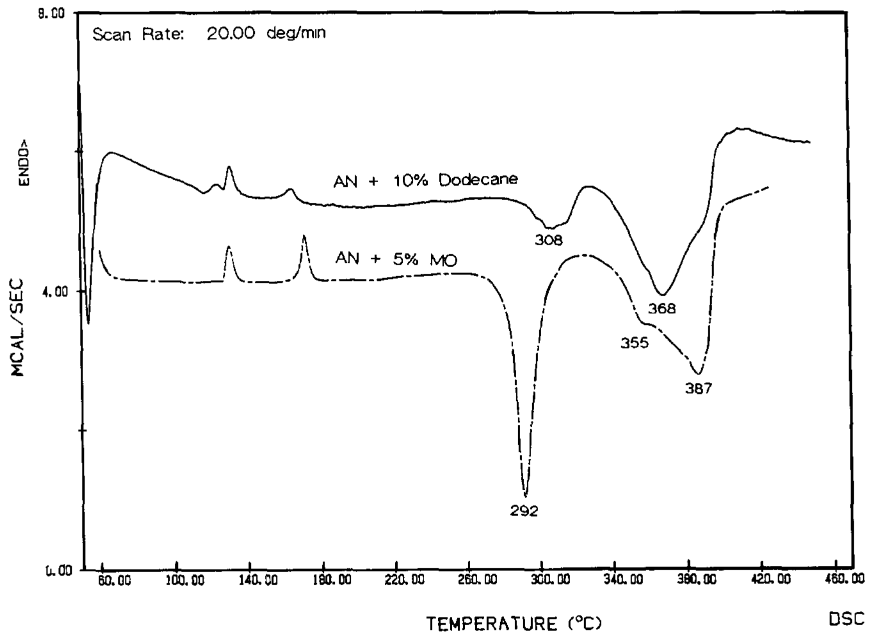

Fig. 12. Thermograms of ammonium nitrate with 5 wt.% mineral oil (dashed line), and ammonium nitrate with 10 wt.% *n*-dodecane (solid line), scanned 20 ° C min^{-1}.

organic products were detectable by GC/MS; black tar and CO_2 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 N_2O 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 NH_3 and HNO_3. Once nitric acid has been formed, it may follow the decomposition route of neat ammonium nitrate (attack on NH_3 to form N_2O), or the nitric acid may attack the hydrocarbon.

Ammonium nitrate decomposition

$$HNO_2 + NH_3 \rightarrow N_2 + 2H_2O \qquad (3)$$

$$NO + {}^{\cdot}NH_2 \rightarrow N_2 + H_2O \quad (4)$$

$$HNO_3 + NH_3 \rightarrow N_2O + 2H_2O \quad (5)$$

Nitrogen oxides equilibria

$$NO + 2HNO_3 \rightleftharpoons 3NO_2 + H_2O \quad (6)$$

$$HNO_3 + HNO_2 \rightleftharpoons 2NO_2 + H_2O \quad (7)$$

The interaction of hydrocarbons with nitric acid (5) has been much studied [6]. The active agent has been shown to be nitrogen dioxide and the reaction to proceed by $H^{\cdot}$ 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 HNO_2 and NO during the oxidation of the hydrocarbon account for the significantly higher N_2 content in the decomposition gas via reactions 3 and 4. The reaction of ammonia with nitric acid (5) to form N_2O proceeds to a lesser extent than in neat ammonium nitrate.

$$RCH_3 + NO_2 \rightarrow RCH_2^{\cdot} + HONO$$

$$RCH_2^{\cdot} + NO_2 \rightarrow RCH_2NO_2$$

$$RCH_2^{\cdot} + HONO \xrightarrow{-NO} RCH_2OH$$

$$RCH_2NO_2 \rightarrow RCH_2ONO \xrightarrow{-NO} RCH_2O^{\cdot} \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH \xrightarrow{[O]} CO_2$$

Scheme III. Hydrocarbons.

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.

The reason for the disappearance of the first exotherm in a rescan of the emulsion or any of the ammonium nitrate/hydrocarbon slurries is apparently the build-up of ammonia. Samples heated under ammonia showed no first exotherm. The shifting of the first exotherm to higher temperature with increased mineral oil indicates that nitric acid is being scavenged more effectively by the hydrocarbon; thus, ammonia builds up more quickly. The disappearance of the two endothermic phase changes in the rescan of the slurries is not clear at this time. It may be that the oxidized hydrocarbon emulsifies the ammonium nitrate, or it may be a pressure effect.

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 N_2O and more CO_2 are produced during this exotherm, indicating that the reaction of the hydrocarbon is important.

CONCLUSION

In general, 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 build-up of ammonia 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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