

Thermal stability and compatibility of ammonium nitrate explosives on a small and large scale¹

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Abstract

The thermal stability of two types of ammonium-nitrate-based explosives, ammonium nitrate/fuel oil and ammonium nitrate emulsion, were compared with neat ammonium nitrate. The effect on thermal stability of various contaminants was examined by DSC and conventional methods. It was found that salts of weak acids, owing to their basicity, stabilized ammonium nitrate formulations. The ammonium cation, the salt of a weak base, slightly destabilized the ammonium nitrate compositions. Sodium nitrate, where the anion and cation are derived from a strong acid and a strong base respectively, did not appear to affect the thermal stability of ammonium nitrate. Cations of various metals were examined, but only those of chromium, iron and aluminum severely destabilized ammonium nitrate.

INTRODUCTION

Two different mechanisms are operative in the decomposition of ammonium nitrate (AN) over the temperature range 200–380°C [1]. Below 290°C, decomposition is governed by the formation of nitronium ion NO_2^+ from nitric acid [2]. Any source of acidity, such as added nitric acid, increases the rate of AN decomposition dramatically, while bases such as ammonia or water retard the decomposition. Above 290°C, homolysis of nitric acid is the rate-controlling step. The predominant decomposition gas is nitrous oxide, with a small amount of N_2 (13% at 360°C; 22% at 270°C). When AN is thermally decomposed as a component in an AN emulsion or ammonium nitrate/fuel oil (ANFO), it is still the dissociation of AN, forming nitric acid, that triggers decomposition [3]. However, nitric acid, which reacts with ammonia in fuel-free AN to form N_2O , can be diverted into reaction with the hydrocarbon. Ultimately, the hydrocarbon is oxidized to CO_2 .

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Nitric oxide and nitrous acid, resulting from hydrocarbon oxidation, cause an increase in the N_2/N_2O ratio in the product gases. Ammonia from AN dissociation builds up, slowing markedly the decomposition of the fuel-containing AN formulations at low temperatures (below 290°C), but causing little decrease in the decomposition rate at higher temperatures.

Having determined the effect of added hydrocarbon on AN thermal stability, we examined the effect of other additives. Only two have been studied in detail, and both enhance the decomposition of AN. Keenan and co-workers [4] have published a number of papers on the effect of chloride, concluding that chloride is oxidized to chlorine by NO_2^+ and NO^+ and reduced back to chloride by NH_3 and NH_4^+ , thus providing an acceleratory, catalytic cycle. Rosser et al. [5] found that all chromium compounds soluble in liquid AN would catalyze its decomposition. They also suggested an oxidation/reduction cycle involving Cr^{6+} and Cr^{3+} and possibly other oxidation states of chromium.

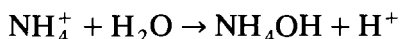
EXPERIMENTAL

Samples were sealed under air in glass capillaries with a total volume of about 40 μ l for isothermal samples (0.5–3 mg) or of about 4 μ l for DSC samples (about 0.5 mg). The AN-based emulsion contained 77 wt.% AN, 16 wt.% water, 5 wt.% mineral oil, and 2 wt.% emulsifier. Additives (5 wt.%) were usually folded into the emulsion, but in a few specified cases the additive was introduced into the AN melt prior to emulsification. ANFO was prepared by grinding together AN and mineral oil (5 wt.% of Sontex 100, about 382 g mol⁻¹) to form a solid slurry. Differential scanning calorimetric scans were conducted at 20°C min⁻¹ from 50 to 450°C on a Perkin-Elmer DSC-4. Thermal stability was evaluated on differential scanning calorimetric samples by noting the temperature at 10% and 30% decomposition and the temperature of the exothermic maximum. The lower the temperature of 10% AN decomposition, the less stable the system was assumed to be. Isothermal samples were heated for 30 min at 270°C, and the percentage of AN remaining was determined by monitoring nitrate or ammonium concentrations by ion chromatography (Dionex 2000 i/SP).

RESULTS AND DISCUSSION

To determine the effect of various anions on the thermal stability of AN, it was necessary that the additives be introduced with inert counter-ions. Our first thought was to use the sodium or ammonium ion to ensure compatibility with AN. Added sodium nitrate was found to have no effect on the rate of ammonium nitrate decomposition; therefore the sodium ion was considered an inert counter-ion. The ammonium ion, however, was not

inert. When AN formulations were spiked with a variety of sodium or ammonium salts (SO_4^{2-} , BF_4^- , $\text{B}_4\text{O}_7^{2-}$, HCO_3^-), sodium-salt-containing AN formulations were slightly more stable than ammonium-salt-containing AN formulations (Table 1). It was concluded that added ammonium cation accelerates the decomposition of AN formulations, although this destabilization may not always be evident if the anion is stabilizing. Although this conclusion is based on only a slight difference in the effect of the ammonium and sodium salts, it is concurrent with the fact that the ammonium ion is a weak base, and the salts of weak bases acidify aqueous solutions:



In acidifying the solution, added NH_4^+ destabilizes AN formulations. Conversely, salts of weak acids should give basic aqueous solutions and stabilize AN. Sulfate, the anion of the weak acid bisulfate, tended to retard AN decomposition. We found a number of sodium salts of weak acids (carbonic, acetic, formic, oxalic and hydrofluoric) that, when added to AN or ANFO, retarded decomposition. The salts of strong acids, which leave aqueous solutions neutral, did not affect the rate of AN decomposition. Salts of weak acids and urea stabilized AN formulations, even in the presence of destabilizing species such as iron salts (Table 1).

Our study of the effect of various cations on AN thermal stability began with the iron salts that might possibly be present in mining operations. The Bureau of Mines reported that pyrite and its weathering product FeSO_4 accelerate the decomposition of AN and ANFO [6]. We examined the effect of a number of iron-containing additives. AN, ANFO, and AN emulsion were mixed with 5 wt.% of various iron-containing salts: $\text{Fe}(\text{NO}_3)_3$, $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , FeS , and FeS_2 (in ore). All accelerated the decomposition of AN, ANFO, and AN emulsion at 270°C (Table 1). To study systematically the effect of cations on AN stability, it was necessary to select appropriate counter-ions. Nitrate, the anion of a strong acid, was chosen as an inert anion; sulfate, as the anion of a weak acid, was expected to have a stabilizing effect; and oxides were examined because they are ubiquitous. The thermal stability of AN with most common metals was assessed by differential scanning calorimetry (DSC) (Table 2). As expected, metal sulfates and oxides tended to be more thermally stable than the nitrates. Most oxides were water insoluble, and those that were soluble were basic. The exception was Cr_2O_3 , and it was the only oxide that had a detrimental effect on AN thermal stability.

If an oxidation/reduction cycle is important in promoting AN decomposition, then metals with multiple oxidation states should be most destabilizing. This was not the case. Cobalt and copper nitrate exhibited no strong destabilizing effect on ammonium nitrate, even though both commonly use two oxidation states ($\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Cu}^+/\text{Cu}^{2+}$). However, aluminum, which has only one oxidation state, Al^{3+} , had a strong destabilizing effect

TABLE 1
Thermal stability of AN formulations – DSC and isothermal data

5 mol.% additive	AN data			ANFO data			AN-emulsion		
	DSC 10% decomp. (°C)	Heat (cal g ⁻¹)	Isothermal (%NO ₃ left)	DSC 10% decomp. (°C)	Heat (cal g ⁻¹)	Isothermal (%NO ₃ left)	DSC 10% decomp. (°C)	Heat (cal g ⁻¹)	Isothermal (%NO ₃ left)
Fe(NO ₃) ₃	258	535	17.3				243	864	30.9
Fe ₂ (SO ₄) ₃	266	482	13.5	234	838	41.6	262	987	22.7
FeSO ₄	269	412	13.9	255	847	26.8	269	966	23.4
FeS	270	474	13.4	264	819	51.2	251	348	46.1
FeS ₂ ore	272	474	22.9	261	964	44.5	275	1236	44.5
Na ₂ S	254	477	26.0				324	651	77.1
Neat	292	350	35.3	294	737	62.0	316	781	73.2
NaNO ₂	297	393	21.4	300	1001	83.5	321	925	60.2
NaNO ₃ (5%)	288	390	33.9	293	684	59.4	318	784	60.9
NaNO ₃ (30%)	287	446	25.1	318	503	74.8	329	680	55.8
NaHSO ₄	294	385	17.7						
Ca(NO ₃) ₂ (5%)	300	364	32.9	304	663	60.8	327	544	69.1
Ca(NO ₃) ₂ (30%)	309	368	45.0	322	398	61.5	337	918	70.4

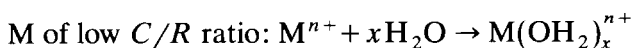
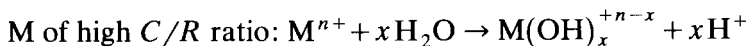
Na ₂ SO ₄	303	330	61.0	355	400	338	623	73.4
(NH ₄) ₂ SO ₄	312	371	60.8			322	920	68.9
NaBF ₄	307	355	58.1	297	695	322	653	31.9
NaBF ₄ in melt						333	812	
NH ₄ BF ₄	325	363	38.6	285	670	242	416	59.4
NaHCO ₃	352	364	72.3	356	705	341	738	51.6
NH ₄ HCO ₃	346	402	66.7	336	773	330	888	53.9
Na ₂ B ₄ O ₇	336	359	87.1	347	656			
(NH ₄) ₂ B ₄ O ₇	346	358	39.4	339	722			
Na ₂ CO ₃	335	358	65.5	317	731	373	575	53.0
NaCH ₃ CO ₂	335	390	95.6	333	630	344	710	52.9
NaCHO ₂	354	410	98.3	347	686	371	650	45.0
NaCHO ₂ in melt						313	758	72.5
Na ₂ C ₂ O ₄	368	346	95.6	355	642	373	559	50.8
NaF	374	354	89.7	364	578	376	692	54.3
Urea	369	436	91.0	337	860	378	897	84.9
FeS + urea	358	367				342	1000	
FeS + Bipy	261	558				226	1292	
FeS ₂ + NaF						324	740	
FeS + NH ₄ HCO ₃	316	342						
FeSO ₄ + urea	357	366	88.5			358	763	82.2

TABLE 2

DSC results for ammonium nitrate + 5 wt.% additives (20°C min⁻¹)

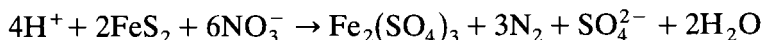
	Nitrate salts					Sulfate salts		Oxides	
	10% decomp. (°C)	Heat (cal g ⁻¹)	No. of runs	pH aqueous soln.	Charge/radius (pm)	10% decomp (°C)	No. of runs	10% decomp (°C)	No. of runs
Cr(III)	251	570	8	5	0.039	263	4	257	3
Fe(III)	258	535	3	2	0.043	274	5	296	11
Fe(II)						271	5	292	3
Al(III)	262	436	8	3	0.044	274	10	295	3
Cu(II)	280	366	3	4	0.023	277	3	317	3
Cu(I)								319	3
Neat AN	289	389	15	6	–	–	–	–	–
Ba(II)	288	355	8	7	0.015	286	7	321	10
Mn(II)	288	414	5	7	0.025	304	5		
Mn(IV)								299	3
Co(II)	293	411	9	6	0.025	282	5	292	3
K(I)	293	375	5	7	0.007	286	5		
Na(I)	294	361	5	7	0.011	302	3		
Pb(II)	294	417	12	7	0.015	313	5	335	6
Pb(IV)								337	8
Mg(II)	296	335	8	7	0.023	301	5	374	3
Zn(II)	298	335	8	6	0.023	302	4	332	8
Cd(II)	299	250	3	7	0.018	313	5	340	8
Ag(I)	305	317	4	6	0.008				
Ni(II)	311	388	9	7	0.024	302	5	339	3
Ca(II)	317	333	3	7	0.018	298	8	325	8

on AN. Because both Cr³⁺ and Al³⁺ had such a strong destabilizing effect, it suggested they have some common property that promotes decomposition. Chromium nitrate, aluminum nitrate, and iron nitrate, all of which strongly promote AN thermal decomposition, have two properties in common: they were the only 3 + oxidation state metal salts examined, and they all have a rather small ionic radius. As a result, each has a relatively high charge-to-radius ratio. Furthermore, in water these three nitrates produce acidic aqueous solutions. Charge-to-radius (*C/R*) ratio may be related to acidity because that ratio determines how many water molecules can surround an ion and how a cation interacts with water:



In thermal hazard assessment, it is unwise to apply kinetics of decomposition obtained at relatively high temperatures on microsystems to life-size systems, where the critical temperature T_c may be substantially lower.

thermocouples or a 600 ml stainless-steel pressurizable (about 600 atm rupture disk) cylinder with one internal thermocouple and a pressure transducer (Fig. 1). If thermal runaway does not occur, the bath temperature is raised to just above the predicted T_c ; if runaway then occurs, the T_c has been successfully bracketed by experiment, confirming the small-scale kinetics. Two cook-off experiments were performed on an AN emulsion spiked with 10 wt.% iron pyrite ore; thermal runaway was observed between 86 and 101°C. The predicted T_c from isothermal 2-mg-scale kinetics was 105°C. Without added ore, the emulsion exhibited thermal runaway at about 150°C; with added ore and 3 wt.% urea, thermal runaway was observed at about 175°C. The results support the microscale isothermal kinetics, and, to the extent that ore lowers the runaway self-heating temperature (T_c) and urea raises it, the DSC data are also supported. However, in contrast to DSC scans which suggest that the ore promotes early decomposition of AN, visual observations of the cook-off residue and other samples thermolyzed at temperatures below 140°C suggest that little AN is consumed in the low temperature exothermic process. The residue from the 110°C cook-off was a brown mud permeated with white AN needles. Apparently, it is primarily a reaction of the ore rather than AN that is involved in the low temperature thermal runaway:



CONCLUSIONS

In the temperature range 200–290°C where AN decomposes by an ionic mechanism, the thermal stability of AN is strongly influenced by added acids or bases. Any species which acidifies the system (HNO_3 , salts of weak bases such as NH_4^+ , metal cations of high charge-to-mass ratio) destabilizes AN, while bases (NH_3 , H_2O , salts of weak acids, most metal oxides) stabilize AN.

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