Research paper

Effect of nitration agent and water on thermal behavior during the nitration of sulfamates

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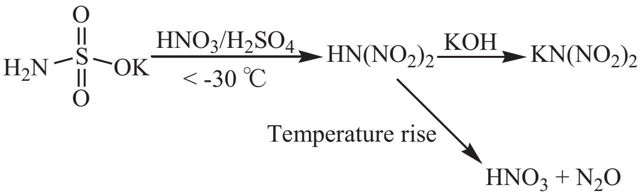
Abstract

Ammonium dinitramide (ADN) has attracted significant interest as a potential oxidizer for next-generation rocket propellants because it is a halogen-free alternative to the widely used ammonium perchlorate. During the synthesis of ADN, N-nitration is required to form the N-$(NO_2)_2$ group, in conjunction with the decomposition of sulfamate. The study reported herein used calorimetry to assess thermal variations during the nitration of both K and NH_4 sulfamates, applying a number of different nitration agents (HNO_3/H_2SO_4, $HNO_3/H_2SO_4+H_2O$, HNO_3/AcOH and HNO_3). It was determined that the heat of decomposition of the sulfamates in HNO_3/H_2SO_4 at 0°C was greater than at 20°C, although the similar trend was not observed in HNO_3/AcOH and HNO_3. The heats of decomposition in HNO_3/AcOH and in HNO_3 were greater than in HNO_3/H_2SO_4 because of how the nitration reagent affects the relative contributions of different pathways to the decomposition process. The heat of decomposition in $HNO_3/H_2SO_4+H_2O$ was less than that in HNO_3/H_2SO_4 because the addition of water inhibits both nitration and decomposition by HNO_3. Under such conditions, however, a second exothermic peak is observed, due to the hydrolysis of potassium sulfamate.

Keywords : ammonium dinitramide, sulfamate, nitration, reaction calorimetry, hydrolysis

1. Introduction

Ammonium perchlorate is widely used as an oxidizer in solid propellants, but has the drawback of releasing significant quantities of HCl during combustion. For this reason, much research has been performed with the aim of finding suitable chlorine-free oxidizers[1)−4)]. Ammonium dinitramide (ADN) is a promising chlorine-free alternative oxidizer for next-generation rocket propellants. ADN may be obtained from either organic or inorganic starting compounds *via* several reaction steps, although the number of steps required when using organic compounds is usually more than that required when starting with inorganic raw materials, because ADN is itself inorganic and so organic raw materials must first be transformed into inorganic compounds. ADN contains an N-$(NO_2)_2$ group, and so N-nitration is required in its synthesis, and several different nitrating agents have been applied, including N_2O_5, NO_2BF_4, and mixed acid solutions[5)−9)]. N-nitration is a key reaction in ADN synthesis and affects the total yield. The actual nitration occurs at the nitrogen included in an amino or isocyanate group, usually at a reaction temperature below 0°C, and strong nitrating agents are often used in a stepwise nitration procedure. The nitration yield varies widely depending on the raw materials, the reaction temperature and the nitrating agent.



Scheme 1 Synthesis of ADN from potassium sulfamate.

Potassium dinitramide (KDN) is an important precursor of ADN in terms of the ease with which ADN is obtained from KDN. In the synthesis of KDN (Scheme 1)[5], the nitration of potassium sulfamate occurs in the presence of HNO_3/H_2SO_4.

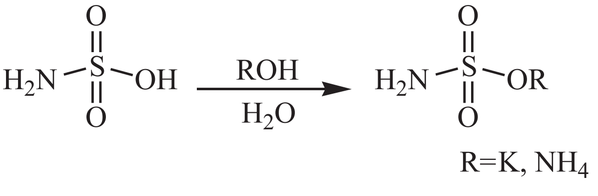
The nitration of potassium sulfamate must be conducted at temperatures below −40°C, because the intermediate product, dinitramidic acid (HDN), is very unstable even at −30°C and readily decomposes to HNO_3 and N_2O at higher temperatures[10)−13)]. Thus, under less-than-ideal nitration conditions, exothermal decomposition and gas formation occur. For this reason, careful control over the reaction temperature and procedure must be maintained to perform the nitration safety. For safety assessment, calorimetry is often used to elucidate the attendant thermal hazards[14),15)]. In a previous study, we found that the heat of decomposition during the nitration reaction varied depending on the particular sulfamate employed and the reaction temperature[16)]. However, higher temperatures were not always associated with increased thermal hazards when using less-than-ideal reaction conditions. Therefore, the present study focused on the thermal behavior during the nitration of sulfamates under undesirable nitration conditions. The effects of the nitration agent and the reaction temperature were investigated by measuring heats of decomposition using a reaction calorimeter. In this study the obtained heats of decomposition included the heats of the nitration reaction. Because nitration and decomposition was occurred simultaneously. In addition, the effects of water, a potential impurity within the nitration system, were also investigated by examining the heats of decomposition.

2. Experimental

2.1 Materials

All sulfamates were prepared by the neutralization of sulfamic acid, as shown in Scheme 2[6)].

During this process, sulfamic acid was dissolved in water at room temperature and the pH was adjusted to 7−8 using both 10 % aq. KOH and 1 % aq. KOH. The mixture was then concentrated using an evaporator to approximately one quarter of its original volume and 2−propanol was used to promote crystallization of the product. The resulting precipitate was isolated by suction filtration, washed with ethanol to remove excess KOH and then recrystallized from a mixed solvent composed of 2−propanol and water. Potassium sulfamate was obtained as a colorless solid. Ammonium sulfamate was obtained as a colorless solid using the same method, except with the addition of NH_4OH to adjust the pH. The sulfamates were characterized by elemental analysis (Vario, EL CHNOS Elemental Analyzer) and Fourier-transform infrared spectrometry (Jasco, FT/IR-420).



$$H_2N-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \xrightarrow[H_2O]{ROH} H_2N-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OR \quad R=K,\ NH_4$$

Scheme 2 Synthesis of sulfamates from sulfuric acid.

Diluted H_2SO_4 solutions were prepared for use in the measurement of heats of decomposition with a reaction calorimeter. H_2SO_4/H_2O mixtures for this purpose were made using mass ratios of 99.9/0.1, 99.5/0.5, 99/1, 98/2, and 97/3.

2.2 Measurement of heats of decomposition

Heats of decomposition were measured using a reaction calorimeter (Omnical, Super CRC) in the isothermal mode, as shown in Figure 1.

During these trials, the apparatus temperature was adjusted to either 20°C or 0°C. A quantity of the desired sulfamate (12 mg) was suspended in a mixture of conc. H_2SO_4(0.2 mL) or acetic acid (0.22 mL) or diluted H_2SO_4 (0.2 mL) in a glass vial and allowed to cool to the set temperature. When solely HNO_3 was used as the nitrating agent, only the sulfamate was placed in the vial. Fuming HNO_3(0.5 mL) was subsequently added dropwise into the vial from a plastic syringe was made from polypropylene positioned above it. An empty vial was used as a reference. At least three measurements were performed at each temperature for each sample. Before measuring the heats of decomposition, the heats of mixing the conc. H_2SO_4, acetic acid or diluted H_2SO_4 with fuming HNO_3 were determined at each temperature and calibration curves were plotted using the heats of mixing and mass data. From these calibration curves, the heats generated by mixing the acids in each experimental trial were obtained. The values obtained by subtracting the heats of mixing from the average measured gross calorific values were used in the data analysis. In the present study, the heats of decomposition include the heats of the nitration reaction.

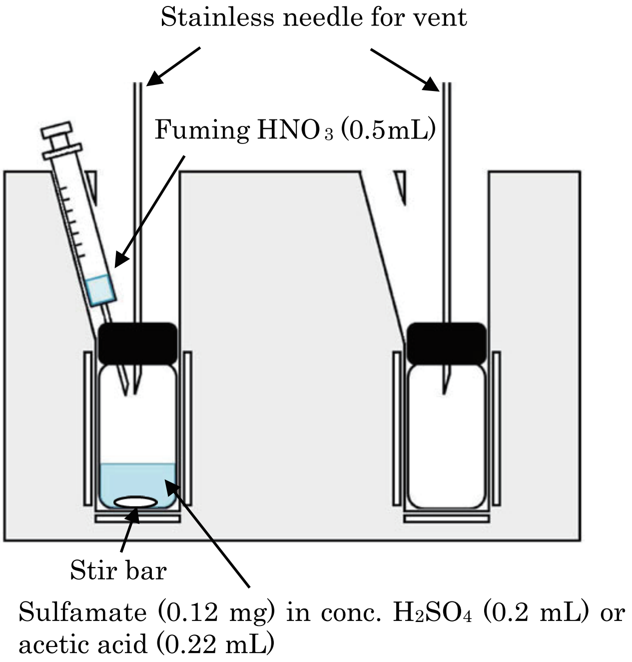


Figure 1 Schematic diagram of Super CRC.

3. Results and discussion

3.1 Measurement of the decomposition heats of sulfamates using various nitrating agents

The thermal data obtained during the decomposition of potassium sulfamate at 20°C in different nitrating agents in the reaction calorimeter are summarized in Figure 2.

A single exothermic peak was observed for each sample and this thermal behavior was observed reproducibly over repeated trials. The same thermal behavior was observed when using ammonium sulfamate and with the same degree of reproducibility. The heat of mixing of HNO_3 and H_2SO_4 was large and was included in Figure 2, thus the heat flow in HNO_3/H_2SO_4 was largest. The heats of decomposition of sulfamates using different nitration agents are shown in Table 1.

From table 1, it is evident that the heats of decomposition in HNO_3/AcOH and in HNO_3 were greater than those obtained in HNO_3/H_2SO_4. Sulfamic acid decomposes to H_2SO_4, H_2O and N_2O upon the addition of HNO_3 17) and therefore, under these same nitration conditions, we propose that the sulfamate decomposes as shown in Scheme 3.

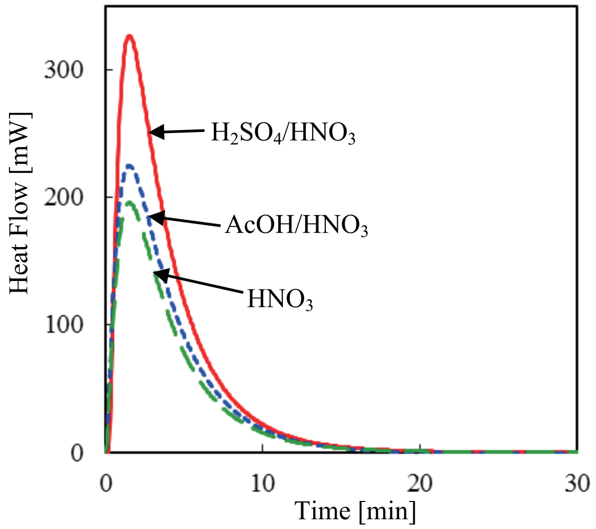
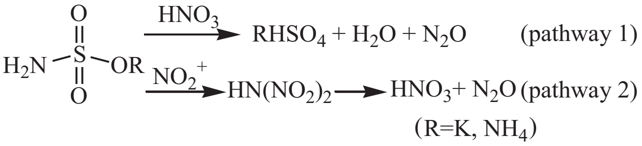


Figure 2 Thermal behavior of decomposition of potassium sulfamate at 20°C.

Table 1 Heat of decomposition of sulfamate in different nitrating agents.

Sulfamate	Heat of decomposition [kJ mol^{-1}]					
	HNO_3/H_2SO_4		$AcOH/HNO_3$		HNO_3	
	20°C	0°C	20°C	0°C	20°C	0°C
KSO_3NH_2	180	240	330	340	340	300
$NH_4SO_3NH_2$	130	190	420	380	320	280

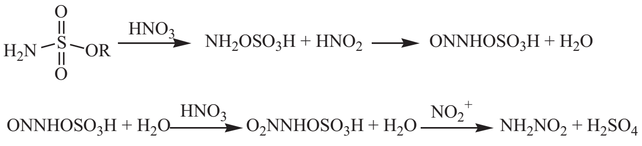


$$H_2N\text{–}SO_2\text{–}OR \xrightarrow{HNO_3} RHSO_4 + H_2O + N_2O \quad \text{(pathway 1)}$$

$$H_2N\text{–}SO_2\text{–}OR \xrightarrow{NO_2^+} HN(NO_2)_2 \longrightarrow HNO_3 + N_2O \quad \text{(pathway 2)}$$

(R=K, NH_4)

Scheme 3 Decomposition route of sulfamate during nitration.



$$H_2N\text{–}SO_2\text{–}OR \xrightarrow{HNO_3} NH_2OSO_3H + HNO_2 \longrightarrow ONNHOSO_3H + H_2O$$

$$ONNHOSO_3H + H_2O \xrightarrow{HNO_3} O_2NNHOSO_3H + H_2O \xrightarrow{NO_2^+} NH_2NO_2 + H_2SO_4$$

Scheme 4 Decomposition of sulfamic acid by HNO_3 via oxidation.

Sulfamate can undergo direct decomposition to $RHSO_4$ ($R = K$, NH_4), H_2O and N_2O in the presence of HNO_3 (pathway 1). Although this mechanism has not been fully elucidated, NH_2NO_2 is likely the intermediate product during the decomposition and decomposes to N_2O and H_2O 18). In addition, the decomposition of sulfamate following oxidation by HNO_3 has been suggested17).

Sulfamate can also decompose to N_2O and HNO_3 after forming HDN (pathway 2). These two decomposition pathways occur simultaneously, although the heat of decomposition associated with pathway 2 is larger than that of pathway 1, because the unstable molecule HDN is generated after nitration and subsequently decomposes.

In H_2SO_4/HNO_3, the reaction temperature affects the contribution of each pathway to the decomposition process. Nitration of sulfamate is enough fast at −30°C. Thus at low temperatures, pathway 2 is likely to occur, whereas pathway 1 has difficultly progressing and has little effect on the reaction outcome. At higher temperatures, both pathways are likely to occur, and so the effect of pathway 1 is significant. Therefore, the heat of decomposition in H_2SO_4/HNO_3 at 0°C was higher than at 20°C. This means that lower temperatures can lead to increased thermal hazards when applying undesirable nitration conditions.

In weaker acids ($AcOH/HNO_3$ and HNO_3),the production of NO_2^+ is lower than in HNO_3/H_2SO_4 as result of limited dehydration of the HNO_3. For this reason the nitration of sulfamates in weak acids is slower than in HNO_3/H_2SO_4. However, weaker acids still have sufficient ability to promote the nitration of sulfamates and therefore the nitration still progresses. Moreover protonation inhibits nitration of sulfamate by repelling because protonation occurs on the nitrogen and nitrogen charges positively. In HNO_3, only sulfamate was in vial before addition of HNO_3, thus protonation was difficult to occur. In $AcOH/HNO_3$, because acetic acid is weak acid, protonation is difficult to progress than HNO_3/H_2SO_4. Therefore, pathway 1 in a weak acid is slower than in HNO_3/H_2SO_4 because pathway 2 in a weak acid occurs faster than in HNO_3/H_2SO_4 and pathway 1 is less important. In pure HNO_3, there is no heat generated by the mixing of acids and thus very little temperature increase occurs on the addition of the HNO_3. As such, the effect of pathway 1 in HNO_3 is less than in the other acids. As a result, the heats of decomposition in the weak acids were greater than those obtained in the HNO_3/H_2SO_4 mixture.

3.2 Measurement of the decomposition heats of sulfamates using diluted H_2SO_4

The heats of decomposition of potassium sulfamate when using diluted H_2SO_4 were also measured, using the same technique and with the results shown in Table 2.

Water inhibits both the nitration of sulfamate and its decomposition by HNO_3, because inhibition of generation of NO_2^+ and decrease of concentration of HNO_3 occur. Therefore, the heats of decomposition in $HNO_3/H_2SO_4+H_2O$ were smaller than those in HNO_3/H_2SO_4. The local maximum heats of decomposition were observed when applying the 99.5/0.5 and 97/3 diluted mixtures at 20°C and when using the 98/2 mixture at 0°C. The thermal behavior during the decomposition of potassium sulfamate in $HNO_3/H_2SO_4+H_2O$ is shown in Figures 3 and 4.

At 20°C, only one peak was observed regardless of the amount of water added. At 0°C, when the amount of water was less than 1 wt%, only one peak was observed, whereas a second peak was seen when more than 2 wt% water was included. This indicates that another decomposition reaction occurred other than the decomposition following nitration and the direct decomposition by HNO_3. The hydrolysis of sulfamic acid is known to occur slowly in the presence of an acid[19), 20)], and the same decomposition can presumably proceed under the conditions associated with the nitration of potassium sulfamate (Scheme 5).

Table 2 Heat of decomposition for potassium sulfamate in $HNO_3/H_2SO_4+H_2O$.

H_2SO_4/H_2O [wt.%]	Heat of decomposition [kJ mol^{-1}]	
	20°C	0°C
100/0	180	240
99.9/0.1	130	180
99.5/0.5	170	150
99/1	160	120
98/2	150	210
97/3	170	190

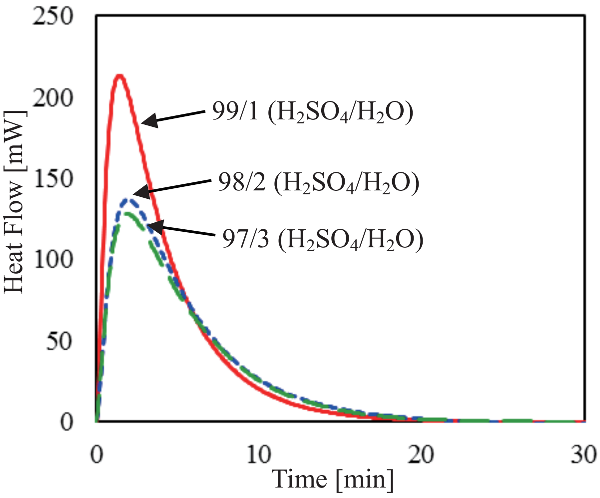


Figure 3 Thermal behavior of decomposition of potassium sulfamate at 20°C in $HNO_3/H_2SO_4+H_2O$.

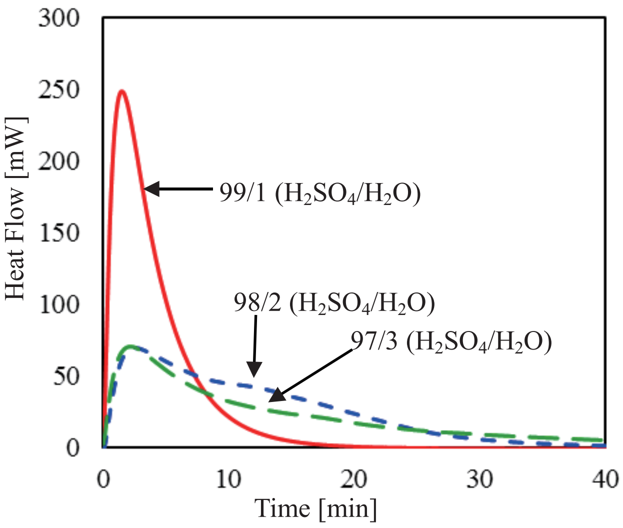
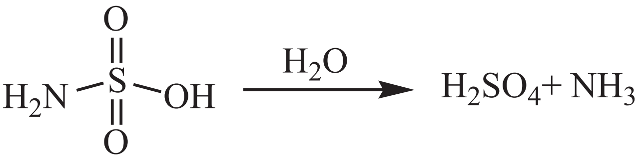


Figure 4 Thermal behavior of decomposition of potassium sulfamate at 0°C in $HNO_3/H_2SO_4+H_2O$.



$$H_2N-S(=O)_2-OH \xrightarrow{H_2O} H_2SO_4 + NH_3$$

Scheme 5 Hydrolysis of potassium sulfamate.

The concentration of water in this reaction system is increased both by the addition of water to the mixture and by the decomposition by HNO_3. Increase of water inhibits the generation of NO_2^+ occurred by protonation of HNO_3 and decreases the concentration of HNO_3. Therefore increase in water inhibits both nitration and decomposition by HNO_3, and increases the hydrolysis of the potassium sulfamate. However hydrolysis is difficult to occur because water is little and decomposition other than hydrolysis is likely to progress from 100/0 to 99/1. The hydrolysis of potassium sulfamate is therefore more likely to occur in 98/2 and 97/3, and so the heat of hydrolysis of potassium sulfamate was observed at 0°C in the 98/2 and 97/3 reaction mixtures. At the same time, however, the addition of water reduces the acidity of the reaction mixture, and therefore the heat of decomposition in the 97/3 solution was lower than that measured in the 98/2 solution. At 20°C, the inhibition effect of water on the nitration and the decomposition by HNO_3 was reduced compared to the effect at 0°C, because higher temperature promoted decomposition other than hydrolysis. For this reason, the observed change in the heat of decomposition at 20°C was smaller than that seen at 0°C and the effect of adding water was not as evident.

4. Conclusion

The heats of decomposition of sulfamates during nitration were investigated using reaction calorimetry. The heat of decomposition at 0°C was greater than that at 20°C in H_2SO_4, although the similar trend was not observed in a weak acid solution, because the dominant decomposition pathway varied with both reaction temperature and nitrating agent. The heat of decomposition in $HNO_3/H_2SO_4+H_2O$ was less than that in HNO_3/H_2SO_4 because the added water inhibited both nitration and decomposition by HNO_3. The effect of the hydrolysis of potassium sulfamate was small at 20°C and thus not clearly observed, however the hydrolysis of potassium sulfamate did have an obvious effect on the thermal behavior and heat of decomposition at 0°C. From the above results, it was determined that both the choice of nitration agent and the presence of water affect the heat of decomposition associated with the nitration of sulfamates.

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